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**Studies on Novel Coordination Chemistry
of Main Group Elements**

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by

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August, 1999



23 MAY 2000

Declaration

The work described in this thesis was carried out in the University of Durham between October 1998 and August 1999. This work has not been submitted, either completely or in part, for a degree in this or any other University and is the original work of the author except where acknowledged by reference.

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Abstract

Studies on Novel Coordination Chemistry of Main Group Elements

The studies described are mainly concerned with phosphorus coordination chemistry, and coordination chemistry of main group elements with bulky electron-withdrawing ligand. They may be divided into three parts.

Part 1. Identification of new phosphorus species

This project continued the work that had been done in previous student projects, by carrying out a series of reactions of phosphorus(III) halides ($X = \text{Cl, Br, I}$) with thiophosphorus(V) halides ($X = \text{Cl, Br}$) and zinc dust present, to form several new products. Heating was generally used to increase the rate of reaction. The new phosphorus species can be classed into four kinds. A: Mixed valence phosphorus(III)–thiophosphorus(V) halides. B: New dithiophosphorus(V) halides. C: the new triphosphorus(III) halide PI_2PIPI_2 , (the first report of this compound). D: Mixed valence phosphorus(III) – dithiophosphorus(V) halides. ^{31}P NMR studies have been used extensively throughout the project to identify the products.

Part 2. Studies on main group elements compounds containing bulky electron-withdrawing substituents

This project has involved reacting ArLi or $\text{Ar}'\text{Li}$, $\text{Ar}''\text{Li}$ ($\text{Ar} = 2,4,6\text{-(CF}_3)_3\text{C}_6\text{H}_2$; $\text{Ar}' = 2,6\text{-(CF}_3)_2\text{C}_6\text{H}_3$; $\text{Ar}'' = 2,4\text{-(CF}_3)_2\text{C}_6\text{H}_3$) with ECl_3 , ($\text{E} = \text{As or P}$) or $\text{E}'\text{Cl}_4$ ($\text{E}' = \text{Sn, Ge or Si}$) to synthesise new compounds, SiR_2Cl_2 , GeR_2Cl_2 , GeArCl_3 , SnR_2Cl_2 , AsR_2Cl , AsArCl_2 and the previously described PRCl_2 ($\text{R} = \text{Ar, Ar}' \text{ or Ar}''$). All these new compounds have been characterised by elemental analysis and ^{19}F NMR; the molecular structures of SnAr_2Cl_2 , $\text{SnAr}'_2\text{Cl}_2$, $\text{GeAr}''_2\text{Cl}_2$, GeArCl_3 and $\text{SiAr}''_2\text{Cl}_2$ have been elucidated by X-ray diffraction.

Part 3. Attempt to synthesise phosphalkynes with bulky electron-withdrawing substituents

Attempts have been made to synthesise the first phosphalkynes containing a bulky electron-withdrawing ligand; this involves a series of reactions, the first being the preparation of the phosphalkene $\text{RP}=\text{CCl}_2$. A few methods have been tested, but due to limit of time and other factors, the compounds could not be synthesised successfully so far.

Abbreviations:

Ar= 2,4,6-tris(trifluoromethyl)phenyl

Ar'= 2,6-bis(trifluoromethyl)phenyl

Ar''= 2,4-bis(trifluoromethyl)phenyl

DBU= 1,8 diazobicyclo[5.4.0] undec-7-ene

Mes*=2,4,6-tris(t-butyl)phenyl

NMR= nuclear magnetic resonance

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Chapter 1. Introduction

Introduction

The researches are mainly concerned with phosphorus coordination chemistry, and coordination chemistry of main group elements, especially phosphorus, containing bulky electron-withdrawing ligands.

Although most known phosphorus compounds exist in oxidation states P(III) or P(V), mixed valence phosphorus present in one molecule is not found very frequently, particularly in halides. The first mixed valence phosphorus(III)-thiophosphorus(V) halide PI_2PSI_2 was reported in 1963^{1,2}, but so far no further work has been published, probably because they are difficult to prepare and unstable; Even for PI_2PSI_2 however, no ^{31}P NMR data were reported

In 1977 when Dillon and co-workers reacted lithium iodide with PSBr_3 or PSCI_3 to try to prepare the mixed phosphorus thiohalides, they found pairs of doublet signals in the ^{31}P NMR spectra, corresponding to mixed phosphorus(III)-thiophosphorus(V) halides³. Since then in this group a few project students have done some work to try to synthesise new mixed valence phosphorus species^{4,5}.

My project continued the work that had been done in previous projects, by carrying out a series of reactions of PCl_3 , PBr_3 or PI_3 with PSCI_3 or PSBr_3 and zinc dust present, to get a series of products, among them some new phosphorus species, such as mixed valence phosphorus(III)-thiophosphorus(V) halides; new dithiophosphorus (V) halides; the new triphosphorus(III) halide PI_2PIPI_2 and mixed valence phosphorus (III)-dithiophosphorus(V) halides. The detailed research results are described in chapter 2.

Many double-bonded main group element compounds are unstable, in accordance with the "classical double-bond rule", which stipulated that elements possessing a principal quantum number greater than 2 should not be able to form $p\pi-p\pi$ bonds with themselves or with other elements⁶. In 1981 the first stable diphosphene $\text{Mes}^*\text{P}=\text{PMes}^*$ ($\text{Mes}^* = 2, 4, 6\text{-}^t\text{Bu}_3\text{C}_6\text{H}_2$) was synthesised by Yoshifuji⁷. Since then many double-bonded compounds of main group elements with very bulky substituents



to provide kinetic stability have been reported.⁸⁻¹² Very few of these, however contain bulky electron-withdrawing substituents (except two diphosphenes). Because bulky electron-withdrawing ligands Ar and Ar' [Ar=2,4,6-(CF₃)₃C₆H₂; Ar'=2,6-(CF₃)₂C₆H₃] have been exploited to stabilise a variety of unusual main group compounds, including the surprisingly air- and moisture- stable diphosphenes ArP=PAR and Ar'P=PAR', there is considerable current interest in the chemistry of low coordination main group elements containing these ligands.

This project has involved reacting ArLi or Ar'Li, Ar''Li with ECl₃, (E=As, P) or E'Cl₄ (E'= Sn, Ge, Si) to synthesise new compounds SiR₂Cl₂, GeR₂Cl₂, GeArCl₃, SnR₂Cl₂, AsR₂Cl, AsArCl₂ and the previously reported PRCl₂ (R= Ar, Ar' or Ar''). Detailed reaction conditions, characterisation of new compounds and the molecular structures of SnAr₂Cl₂, SnAr'₂Cl₂, SiAr''₂Cl₂, GeAr''₂Cl₂ and GeArCl₃ are presented in chapter 3.

At about the same time as synthesis of the first stable diphosphene, the first stable phosphalkyne ¹BuC≡P was made by Becker¹³. The inorganic and organic chemistry of phosphalkynes has been extensively developed in recently years, phosphalkynes becoming very useful synthetic precursors for incorporating a phosphorus atom into a heterocyclic ring system¹⁴⁻¹⁸. Usually the substituent R in RC≡P is an electron-donating aryl or alkyl group; we would like to try to synthesise the first phosphalkynes containing highly electron-withdrawing Ar or Ar', which should in theory reduce the electron density in the C≡P triple bond, affecting the bonding of the phosphalkynes and the reactions thereof.

Attempts have been made to synthesise the first phosphalkynes containing bulky electron-withdrawing ligands Ar and Ar', involving a series of reactions. A few methods have been tested, but due to limit of time and other factors, the compounds could not be synthesised successfully so far. The experiments are described in chapter 4.

References

1. M. Baudler, G. Fricke and K. Fichtner, *Z. Anorg. Allg. Chem.*, 327,124 (1964).
2. A. H. Cowley and S. T. Cohen, *Inorg. Chem.*, 3, 7807 (1964).
3. K. B. Dillon, M. G. Craveirinha Dillon and T. C. Waddington, unpublished results.
4. M. Coles, project report: *Aspects of the Coordination Chemistry of Phosphorus* (1992).
5. P. Gemmell, project report: *Aspects of Phosphorus Coordination Chemistry* (1994).
6. P. Jutzi, *Angew. Chem.*, 87, 269 (1975).
7. M. Yoshifuji, I. Shima, N. Inamoto, K. Hirotsu and T. Higuchi, *J. Am. Chem. Soc.*, 103, 4587 (1981).
8. R. West, M. J. Fink and J. Michl, *Science*, 214, 1343 (1981).
9. J. Satge, *Adv. Organomet. Chem.*, 21, 241 (1982).
10. J. Escudie, C. Couret and J. Satge, *J. Am. Chem. Soc.*, 107, 3378, 8280 (1985); 109, 386 (1987).
11. J. Escudie, C. Couret and J. Satge, *Phosphorus Sulfur*, 377 (1987).
12. B. Twamley, C. D. Sofield, M. M. Olmstead and P. P. Power, *J. Am. Chem. Soc.*, 121, 3357 (1999).
13. G. Becker, G. Gesser and W. Uhl, *Z. Naturforsch, B* 36, 16 (1981).
14. M. Regitz, T. Allspach, W. Rosch and U. Vogelbacher, *J. Organomet. Chem.*, 306, 39 (1986).
15. K. B. Dillon, F. Mathey and J. F. Nixon, *Phosphorus: The Carbon Copy*. John Wiley & Sons, Chichester (1998).
16. J. C. T. R. Burckett-St. Laurent, P. B. Hitchcock, H. W. Kroto and J. F. Nixon, *J. Chem. Soc., Chem. Commun.*, 1141 (1981).
17. S. I. Al-Resayes, S. I. Klein, H. W. Kroto, M. F. Meidine and J. F. Nixon, *J. Chem. Soc., Chem. Commun.*, 930 (1983).
18. S. I. Al-Resayes, P. B. Hitchcock, M. F. Meidine and J. F. Nixon, *J. Chem. Soc., Chem. Commun.*, 1080 (1984).

Chapter 2. Identification of New Phosphorus Species

Introduction

1. History of mixed halides and mixed valence phosphorus species

Structural reorganization based on exchange of halide ligands attached to phosphorus atoms is a common phenomenon in phosphorus chemistry. The exchange reactions between phosphorus(III) halides or phosphoryl(V) halides to produce mixed species may be conveniently followed by ^{31}P NMR spectroscopy. The first work on mixed monophosphorus(III) halides¹ (PCl_3 , PBr_3 , PCl_2Br and PClBr_2), mixed monophosphoryl(V) halides² (POCl_3 , POBr_3 , POCl_2Br and POClBr_2), and mixed monothio-phosphoryl (V) halides (PSCl_3 , PSBr_3 , PSCl_2Br and PSClBr_2) had been done by Groenweghe and co-workers in 1959.

Dillon and co-workers in 1974 reported the identification of the mixed phosphorus (III) halides³ (PCl_3 , PBr_3 , PI_3 , PCl_2Br , PCl_2I , PClBr_2 , PClI_2 , PBr_2I and PBrI_2) by ^{31}P NMR spectroscopy. The ^{31}P NMR spectrum is shown below.

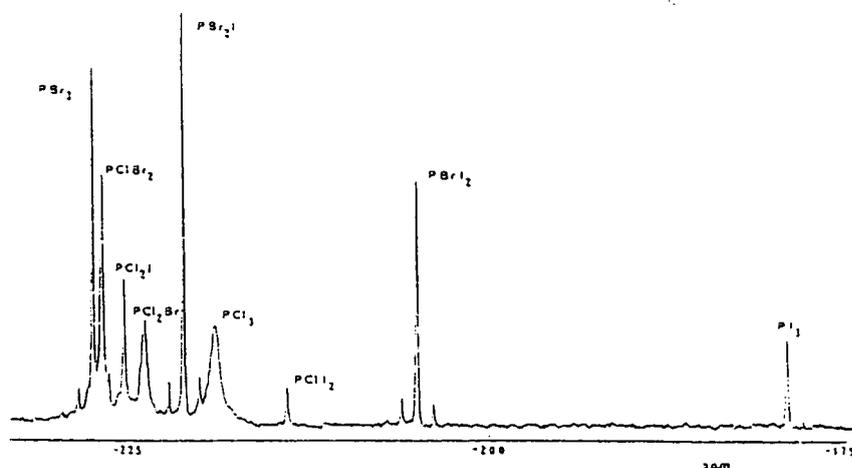


Fig. 1

^{31}P NMR Spectrum of a PCl_3 - PBr_3 - PI_3 mixture

In 1977 they also published work about mixed thiophosphoryl(V) halides by ^{31}P NMR spectroscopy. Excess solid lithium iodide when reacted with PSCl_3 or PSBr_3 in 1,2-dichloroethane, very slowly produced the mixed thiophosphoryl halides PSCl_2I , PSClI_2 , PSI_2Br and PSIBr_2 ; in particular the PSCl_2I , PSClI_2 and PSI_2Br signals only

appeared after two weeks of reaction⁴. PSI_3 was not observed, although its suspected chemical shift was extrapolated from the results.

The mixed diphosphorus (III) halides (PBr_2PBr_2 , PI_2PI_2 , PClIPClI , PBrIPBrI , PCl_2PClI , PBr_2PBrI , PI_2PBrI and PI_2PClI) were also reported by them in 1981.⁵ Unfortunately, however they did not observe the expected pairs of doublets for unsymmetrical species, two singlet resonances being detected.

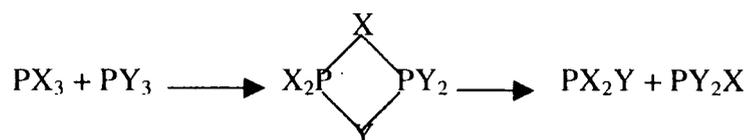
In 1994, Tattershall and Kendall⁶ published work on diphosphorus(III) halides, in which spin-spin coupling was detected. NMR data of mixed monophosphorus(III) halides, most mixed diphosphorus(III) halides and monothiophosphoryl(V) halides (except PSI_3) and monophosphoryl(V) halides (except POI_3) are shown in table 1. (Shifts from references 1-6).

Table 1. NMR Data for $\text{PX}_n\text{Y}_{3-n}$, $\text{PEX}_n\text{Y}_{2-n}$ (E = O or S) and $\text{P}_2\text{X}_n\text{Y}_{4-n}$ (ppm)

	X=Cl, Y=Br	X=Br, Y=I	X=I, Y=Cl
PX_3	219.8	228.5	174.5
PX_2Y	225.0	221.5	227.9
PXY_2	228.0	203.8	213.7
PX_2PX_2	154.1,	149.8	105.5
PX_2PY_2	154.2, 143.6.	149.8, 96.6	
PX_2PXY	154.5 149.7	148.8 125.0	100.6 147.8
PXY^2PXY	150.3	130.6	139.4
PXY^2PY_2	150.1 144.3	132.2 103.8	141.2 103.8
POX_3	2.2	-101.3	
POX_2Y	-29.8	-64.4	
PSX_3	30.1	-110	
PSX_2Y	-14.5	-215	-310
PSXY_2	-61.5	-115	-260

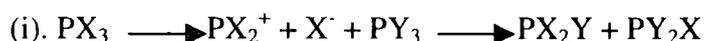
The reaction mechanism for simple halide exchange has not so far been described. Some possible suggestions for halide exchange are:

a. Coordination reaction mechanism.



A lone pair of electrons from a halogen in each of the two exchanging halides forms a weak covalent bond to the neighbouring phosphorus centre, giving a bridged complex. When the species separate, halide exchange has probably occurred. This is probably the main mechanism in halide exchange reactions of phosphorus halide species.

b. Ionic reaction mechanism.



This reaction mechanism does not require the presence of an added anion, but is unlikely, because PX_2^+ is not known as a stable species.



This reaction mechanism is probable when anion sources are present, e. g. if Et_4NBr or LiI is added to a phosphorus halide^{4,7,8}.

c. Radical reaction mechanism



This reaction mechanism may exist in some conditions, such as under the influence of U. V. light or heating.

Mixed valence phosphorus(III)-phosphorus(V) species are not common, especially for halide species; the first mixed valence phosphorus(III)-phosphorus(V) halide compound PI_2PSI_2 was reported in 1963,^{9,10} but probably because it is difficult to

prepare and unstable, so far no further work has been reported and there are no NMR data for it. Mixed valence phosphorus species with mixed halides have never been reported.

2. The previous work of this group

In 1977 when Dillon and co-workers reacted lithium iodide with PSBr_3 and PSCl_3 , and obtained the mixed monothiophosphoryl halides, they found pairs of doublet signals in the ^{31}P NMR spectra corresponding to mixed valence phosphorus(III)-phosphorus(V) thiohalides.¹¹

From 1991 onwards two project students, T.G. Hibbert and M. Coles¹², attempted to extend this in their projects. Coles reacted excess solid lithium iodide with phosphoryl(V) halides POCl_3 , POBr_3 and thiophosphoryl (V) halides PSCl_3 , PSBr_3 . He found POCl_3 and POBr_3 showed less activity than PSCl_3 or PSBr_3 , while POBr_3 and PSBr_3 were more reactive than POCl_3 and PSCl_3 respectively. This is easy to rationalise, since the Br-P bond is weaker than the Cl-P bond and more easily broken, so phosphorus bromides show more activity. Thiophosphoryl (V) halides are more reactive than their oxo analogues, due to sulphur d-orbitals; the phosphorus donates its electrons to these to some extent, reducing the amount of electron density left for bonding to the other ligands and making the compound more reactive.

However, due to limit of time and other reasons, he only obtained some mixed mono-phosphorus halides, most spectra not showing any evidence of coupling. Then he reacted thiophosphoryl(V) halides PSCl_3 or PSBr_3 with phosphorus(III) halides PCl_3 or PBr_3 in the presence of Mg or Zn, in the belief that loss of X_2 could lead to formation of PSX_2PX_2 and the corresponding coupled spectrum could result.

He only observed a weak reaction between $\text{PSBr}_3 + \text{PBr}_3$ in the presence of Zn, because of lack of time, while in the other reactions only starting signals could be seen. But even for this species, the new signals were too small to be identified. Reaction happened preferentially with Zn over Mg, because zinc was added in the form of dust, whereas the magnesium was added in the form of turnings; the zinc therefore has a much larger surface area for reaction.

Meanwhile Hibbert in the reaction of PSCl_3 , PSBr_3 , POCl_3 , or POBr_3 with PI_3 and added excess lithium iodide, found some phosphorus(III)-phosphorus(V) thiohalide coupling. But, because his research project report is not available, the detailed results are not very clear. He seems to have found some coupling signals in reactions of $\text{PSX}_3 + \text{PI}_3$ ($\text{X}=\text{Cl}, \text{Br}$).

In 1994, Gemmell¹³ continued this work via a series of reactions, such as: a. $\text{PSCl}_3 + \text{PCl}_3$ (Zn); b. $\text{PSBr}_3 + \text{PBr}_3$ (Zn); c. $\text{PSBr}_3 + \text{PCl}_3$ (Zn); d. $\text{PSCl}_3 + \text{PBr}_3$ (Zn); e. $\text{PSCl}_3 + \text{PI}_3$ (Zn); f. $\text{PSBr}_3 + \text{PI}_3$ (Zn). But he found that only reaction d and f produced clear coupling signals corresponding to the mixed valence phosphorus thiohalides. In other reactions he only found the singlet signals corresponding to starting material and mixed monophosphorus halides. Even an old sample: $\text{PSBr}_3 + \text{PCl}_3$ (Zn), made during the previous project and about 12 months old, mixed with some new PSBr_3 , yielded only weak signals corresponding to the mixed valence species. Reaction e and a mixture of $\text{PSCl}_3 + \text{PBr}_3$ (LiI + Zn) also gave evidence for mixed valence products, but these could not to be clearly identified.

In the reaction of $\text{PSBr}_3 + \text{PI}_3$, however, not only were there the expected doublets for P-P coupling, but some triplets could also be seen in the spectra. They are in the P(III) region of the spectrum and seemed to be from P_3 units. The rationalisation of this is that two P(V) molecules have reacted with the same P(III) molecule. This sort of species would produce a triplet in the P(III) region and a doublet in the P(V) region of roughly twice the size. These triplets had not been seen previously, but by comparing the chemical shifts of the signals to other known species and matching the two sets of coupling constants, their sources could be fairly accurately identified. They have since been confirmed by our work. The ^{31}P NMR data are shown below and may be compared with our results (described later).

Species	δ (ppm)	J(Hz)
A. Singlets		
PBr ₃	228.4	
PBr ₂ I	223.1	
PBrI ₂	207.6	
PSBr ₂ PSBr ₂	-28.4	
PSBr ₃	-108.2	
PSBr ₂ I	-208.9	
PSBrI ₂	-302.9	
B. Doublets		
PBr ₂ PSBr ₂	175.3, -20.6	86.4
PBrI ₂ PSBr ₂	155.3, -12.0	85.4 ± 0.1
PI ₂ PSBr ₂	136.6, -9.7	86.7 ± 0.1
C. Triplets and Doublets		
PBr(PSBr ₂) ₂	125.0, -22.3	113.4 ± 0.4
PI(PSBr ₂) ₂	102.1, -18.4	103.0 ± 1.4
PSBr(PBr ₂) ₂	97.9, 38.8	73.0 ± 6.2

II. Mixed valence Phosphorus(III)-Phosphorus(V) halides

This project was to continue the work that had been done in previous projects, carry out a series of reactions on phosphorus(III) halides with thiophosphorus(V) halides and achieve full identification of new mixed valence species.

1. The General Procedure

The basic reaction involves the mixture of a thiophosphoryl(V) halide with a phosphoryl(III) halide; excess zinc dust is added to the mixture to act as a halogen extractor, allowing two molecules to combine together.

All reactants and products are highly air- and moisture- sensitive, so all manipulations, including sample preparation, were carried out in an inert atmosphere of dry nitrogen or a glove box. Chemicals of the best available commercial grade were used, in general without further purification, except solvents.

The reactions were stirred and heated for a few days, then samples were taken for analysis. The solutions were retained, and monitored at intervals by ^{31}P NMR spectroscopy. Stirring and heating were the main differences with previous experiments; these were to increase the rate of reaction, so that any slower reactions would be more advanced and the intensity of relevant peaks would be increased.

The study of phosphorus in solution is easily followed by ^{31}P NMR spectroscopy, because ^{31}P is a magnetically active nucleus with spin quantum number $I=1/2$. This isotope is 100% abundant, and has a receptivity of 6.64×10^{-2} (i.e. 6.64% of that of ^1H). All the samples (except reaction 6) described here were without added solvent, although CDCl_3 was added for NMR to provide the deuterium lock. All experiments were done on the 200 or 400 MHz Bruker Fourier- Transform spectrometers, at 80.96 and 161.91 MHz respectively. An external reference of 85% H_3PO_4 was used; shifts to higher frequency were taken as positive. The coupling constants were calculated by multiplying the difference between the apparent chemical shifts in multiplets by the operating frequency.

The species we were hoping to see involve the coupling of P(III)-P(V). This would lead to the formation of two sets of doublets with the same coupling constant, one in the P(III) region ($\delta > 70$ ppm) and one in the P(V) region ($\delta < 70$ ppm).

Along with the desired P(III)-P(V) combination, some P(III)-P(III), and P(V)-P(V) compounds could be found. They would give singlets in the spectra for two equivalent nuclei bound together, and pairs of doublets for different nuclei. Of course, signals from the mixed monophosphorus halides were clearly seen in every spectrum.

In total over fifty ^{31}P spectra were taken, although for many of them, being recorded within a few days or a couple of weeks of each other, there was no great change, but for some spectra we still could observe some changes. The chemical shifts were not constant from spectrum to spectrum, although the differences were quite small, no more than 1-2 ppm, because of solvents and temperature and other factors. They can nevertheless be compared with each other without difficulty, because the coupling constants were identical.

2. Reaction of $\text{PSCl}_3 + \text{Zn}$

This is the simplest reaction, with no halide exchange possible. The only possible course was for two PSCl_3 molecules to react with Zn and each lose a chlorine atom to form $\text{PSCl}_2\text{PSCl}_2$. In a small flask PSCl_3 and Zn dust were placed under nitrogen protection, then the reaction was kept at 70°C for three days; when a sample was taken for NMR, a very weak signal at 50 ppm was found, possibly corresponding to $\text{PSCl}_2\text{PSCl}_2$. After ten days, the ^{31}P NMR spectrum was repeated, but only the starting material signal could be seen and the small signal had disappeared. It could have been just a noise peak. This confirmed that the P-Cl bond is quite strong, and it is very difficult to lose a chlorine atom for combination with another molecule.

3. Reaction of $\text{PSCl}_3 + \text{PCl}_3 + \text{Zn}$

This is the simple reaction of a phosphoryl(III) halide with a thiophosphoryl(V) halide, with no halide exchange, the possible reaction products being $\text{PCl}_2\text{PSCl}_2$,

$\text{PSCl}_2\text{PSCl}_2$ and PCl_2PCl_2 . Under nitrogen protection Zn dust, PSCl_3 and PCl_3 were placed in a flask, then the reaction was kept at 70°C for three days and a sample was taken for NMR, which revealed a small signal at 191ppm, possibly arising from an impurity. After ten days, the ^{31}P NMR was tested again, and as well as the 191ppm signal, a new signal at 3 ppm appeared corresponding to POCl_3 , so phosphorus chlorides are very reluctant to react with zinc dust.

4. Reaction of $\text{PSBr}_3 + \text{PBr}_3 + \text{Zn}$

This reaction only involves different possible bromine phosphorus combinations, P(III)-P(V), P(III)-P(III) and P(V)-P(V), but no halide exchange and is very similar to reaction 3. Because the thiophosphoryl bromide was no longer commercially available, it had to be prepared in situ. Phosphorus tribromide was reacted with sulphur at 120°C for 20 hours, and 70-80% of the PBr_3 changed into PSBr_3 as shown by ^{31}P NMR. Then some zinc and PBr_3 were added and reaction was continued at 110°C for three days. When a sample was taken for NMR testing, only the starting material signals were found. After one week, the ^{31}P NMR was repeated and this time coupling signals appeared. Due to this reaction not being sealed properly, some partial oxidation product signals appeared in the 0-50ppm region. These signals never appeared in other spectra and could safely be ignored. The NMR chemical shifts are shown below.

Species	δ (ppm)	J(Hz)
A. Singlets		
PBr_3	228.9	
PSBr_3	-111.0	
B. Doublets		
$\underline{\text{P}}\text{Br}_2\text{PSBr}_2$	176.5, -20.5	87.0 ± 0.6

SURVEY PHOSPHORUS PARAMETERS

Run on Jun 30 99
Solvent: CDCl3
Ambient temperature
File: /data/m29906/30112634.fid

PULSE SEQUENCE: s2pu1
Pulse 57.6 degrees
Acq. time 1.280 sec
Width 50000.0 Hz
512 repetitions
OBSERVE P31, 80.9575987 MHz
DECUPLE H1, 199.9916053 MHz
Power 37 db
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 131072
Total accumulation time 10 minutes

220.595

1. Spectrum of Reaction of $\text{PSCl}_3 + \text{PCl}_3 + \text{Zn}$

31.727

350 300 250 200 150 100 50 0 -50 -100 -150 -200 ppm

SURVEY PHOSPHORUS PARAMETERS

Pulse Sequence: szpu1

Run on Jun 30 99

Solvent: CDCl3

Ambient temperature

File: /data/m29906/30110840

2 Spectrum of Reaction of PSBr₃ + PBr₃ + Zn

PULSE SEQUENCE: szpu1

Pulse 57.6 degrees

Acq. time 1.260 sec

Width 50000.0 Hz

64 repetitions

OBSERVE P31, 80.9575987 MHz

DECOUPLE H1, 199.9915053 MHz

Power 37 dB

Continuously on

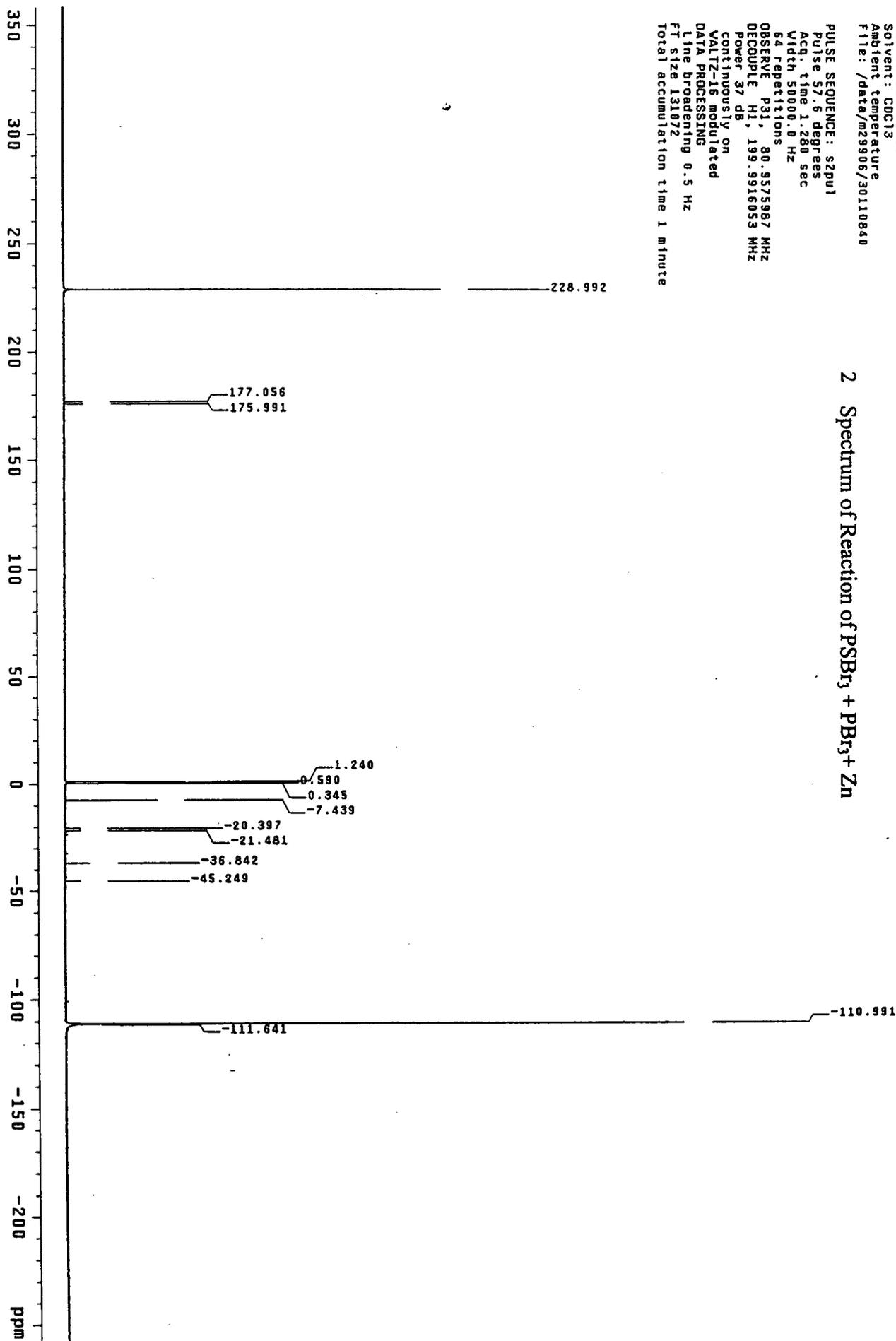
WALTZ-16 modulated

DATA PROCESSING

Line broadening 0.5 Hz

FT size 131072

Total accumulation time 1 minute



5. Reaction of $\text{PSCl}_3 + \text{PBr}_3 + \text{Zn}$

This reaction, involving halide exchange, and different possible phosphorus combinations, P(III)-P(V), P(III)-P(III) and P(V)-P(V), forms a complex system. PSCl_3 , PBr_3 and Zn dust were placed into a small flask under nitrogen protection, then the reaction was kept at 80°C for three days; a sample was taken for NMR, but only showed the starting material signals and mixed phosphorus halide signals. After two weeks, the ^{31}P NMR was tested again and this time most of the expected signals appeared. After another two weeks, the signals were basically the same, although rather weak.

In the P(III) region of the ^{31}P NMR spectra, between 176-182 ppm five doublets appeared; these may be assigned to either PBrCl- or PBr_2- ; 176-179 ppm is the PBr_2- region, while 180-182 ppm corresponds to the PBrCl- region. In the P(V) region, there are two doublets between 55-60 ppm due to PSCl_2- , two doublets between 18-21 ppm corresponding to PSBrCl- , and one doublet at -21.3 ppm corresponding to PSBr_2- . So the P(III)-P(V) combination products are PBrClPSCl_2 , PBrClPSBrCl , $\text{PBr}_2\text{PSCl}_2$, $\text{PBr}_2\text{PSBrCl}$ and $\text{PBr}_2\text{PSBr}_2$. Because the starting materials are PSCl_3 and PBr_3 , the most likely product is $\text{PBr}_2\text{PSCl}_2$, then further possible products are PBrClPSCl_2 and $\text{PBr}_2\text{PSBrCl}$. These doublets can easily be identified according to intensity. As for the doublets at 150 ppm and 130 ppm, these are in the diphosphorus(III) halide region; because the starting materials are PSCl_3 and PBr_3 , the likely products are PBr_2PBr_2 , PBr_2PBrCl and PBrClPBrCl ; other less likely products are PBr_2PCl_2 , PBrClPCl_2 and PCl_2PCl_2 . According to the literature, the PBr_2- group (in PBr_2PBr_2 or PBr_2PBrCl) has a shift of around 144 ppm⁶. Our value of 130 ppm is quite different, but in this region it seems the only possible explanation. However the PBrCl- (in PBrClPBr_2 and PBrClPBrCl) NMR chemical shifts of 150.3 and 150.1 ppm respectively are very close to our values of 150.5 and 149.8 ppm. The coupling constants are also quite close; our value is 234.9 Hz, while the literature was 223.5 Hz, so we believe our assignment is correct. The small doublet at -125 ppm could not be observed again later, so has not been assigned. The small signals in the 190- 200

ppm region could also not be assigned as yet. The NMR chemical shifts are shown below.

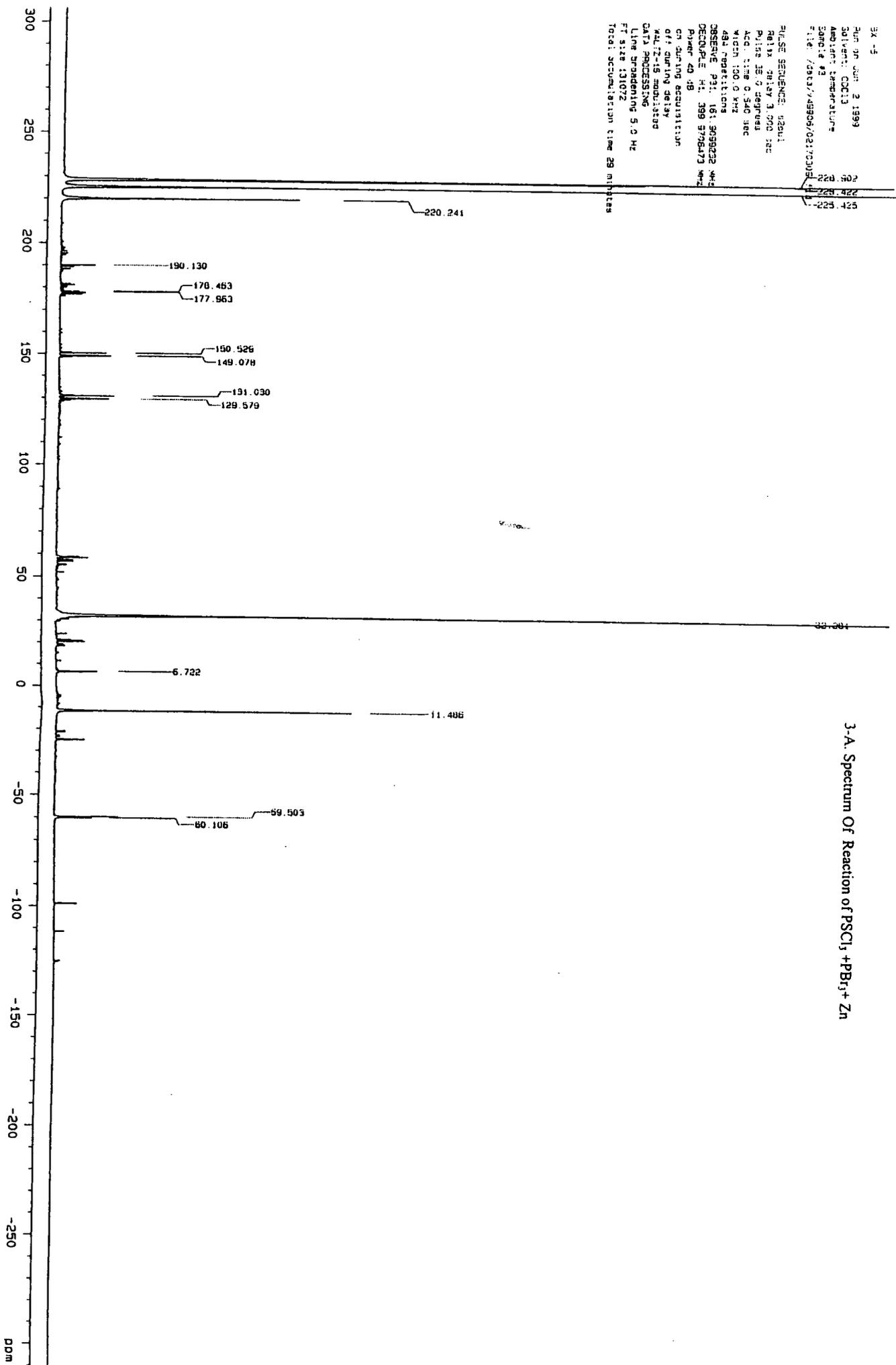
Species	δ (ppm)	J(Hz)
A. Singlets		
PBr ₃	228.9	
PBr ₂ Cl	228.4	
PBrCl ₂	225.4	
PCl ₃	220.2	
PBrClPBrCl	150.5	
PBr ₂ PBr ₂	129.6	
PSCl ₃	32.3	
PSBrCl ₂	-11.5	
PSBr ₂ Cl	-59.5	
PSBr ₃	-111.5	
(POCl ₃)	6.7	
(POBrCl ₂)	-24.8	
(POBr ₂ Cl)	-60.1	
(POBr ₃)	-98.6	
B. Doublets		
PBrClPSClBr	181.5, 19.0	82.4
PBrClPSCl ₂	180.5, 57.3	83.9
PBr ₂ PSCl ₂	178.2, 58.9	80.9 ± 0.1
PBr ₂ PSBrCl	177.4, 20.6	83.2 ± 0.7
PBr ₂ PSBr ₂	176.5, -21.3	85.3
PBrClPBr ₂	149.8, 130.6	234.9

3A-5

Run on Jun 2 1993
Solvent: CDCl3
Acquire Temperature:
Sample #2
File: /data/49909/02170308

PULSE SEQUENCE: zgpg30
Relax 28.547 3.750 sec
Pulse 28.0 degrees
Acq. time 0.340 sec
Width 100.0 kHz
481 repetitions
OBSERVE P1: 181.309222 kHz
DECOUPLE H1: 399.5706173 kHz
P1over 49.48
on during acquisition
off during delay
MAG 2.15 modulation
CAT3 PROCESSING
Line broadening 5.0 Hz
SI size 131072
Total accumulation time 29 minutes

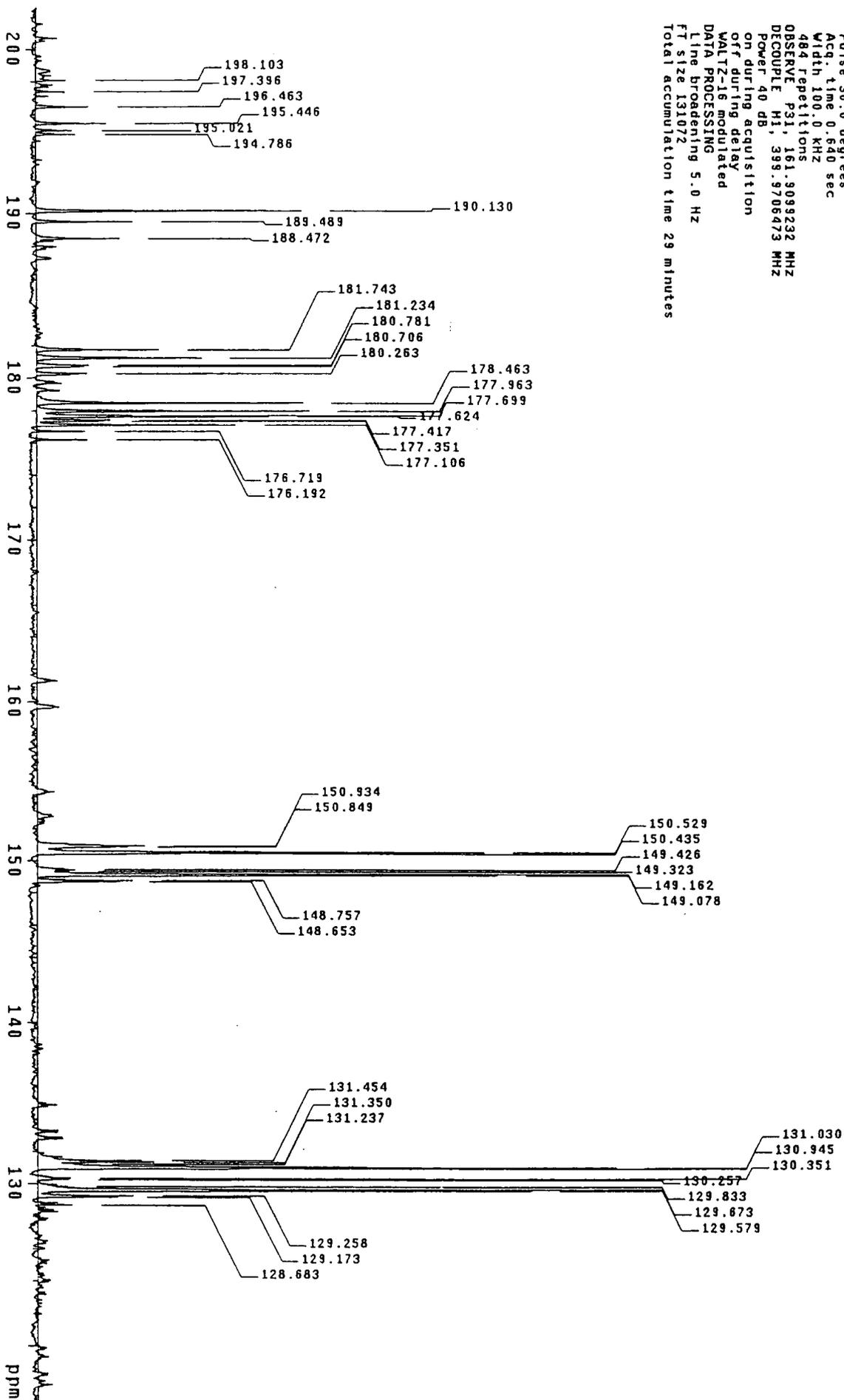
3-A. Spectrum Of Reaction of PSCl₂ +PBr₂+ Zn



Pulse Sequence: s2pu1
 Run on Jun 2 1999
 Solvent: CDCl3
 Ambient temperature
 File: /data/vv49906/02170309

PULSE SEQUENCE: s2pu1
 Relax. delay 3.000 sec
 Pulse: 36.0 degrees
 Acq. time 0.690 sec
 Width 100.0 KHz
 484 repetitions
 OBSERVE P31, 161.9099232 MHz
 DECOUPLE H1, 399.9706473 MHz
 Power 40 dB
 on during acquisition
 off during delay
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 5.0 Hz
 FT size 131072
 Total accumulation time 29 minutes

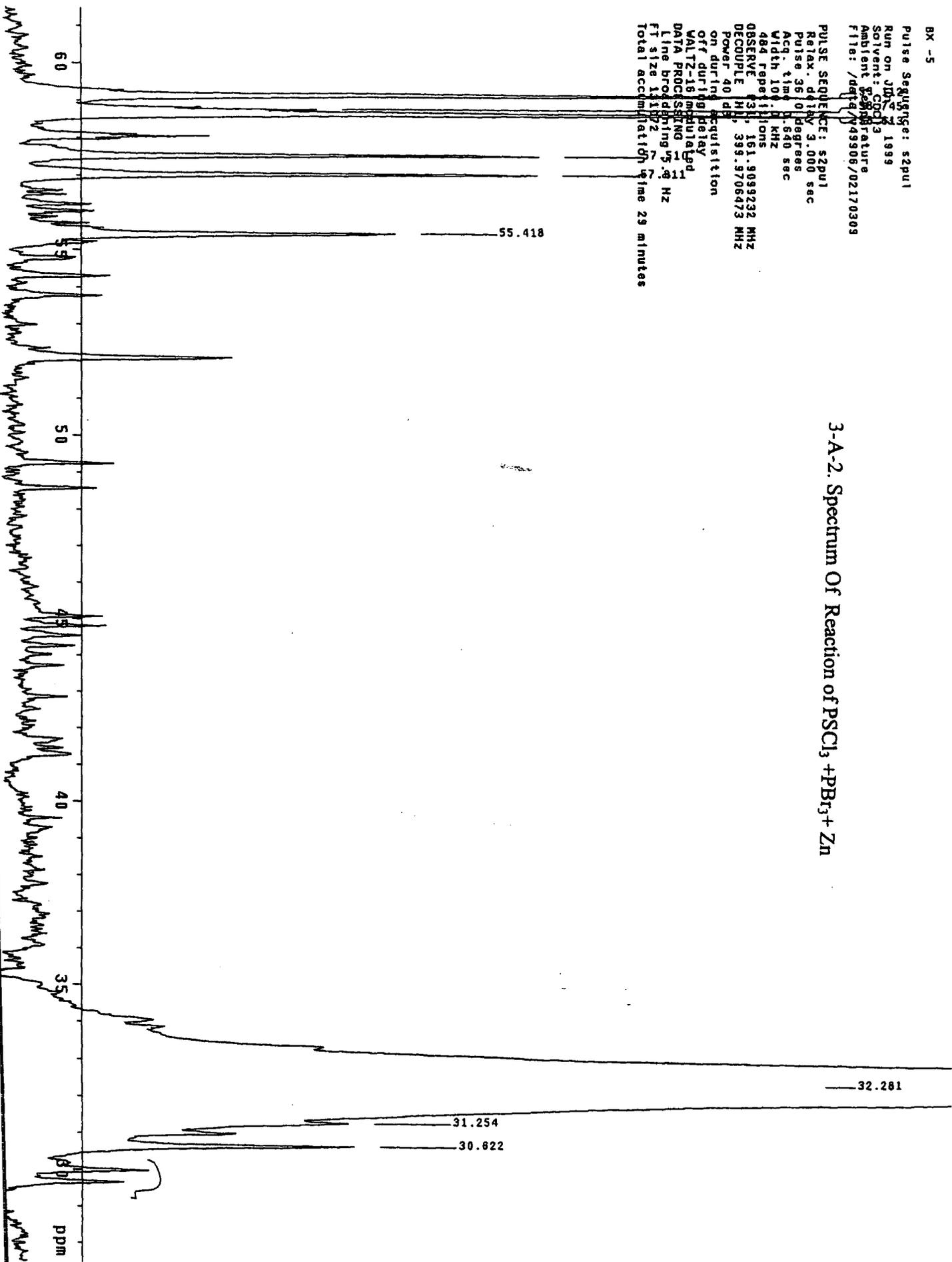
3-A-1. Spectrum Of Reaction of $\text{PSCl}_3 + \text{PBr}_3 + \text{Zn}$



Pulse Sequence: s2pu1
Run on JNM-2 1999
Solvent: CDCl3
Ambient Temperature
File: /data/499906/02170309

PULSE SEQUENCE: s2pu1
Relax. delay: 3.000 sec
Pulse: 98.01 degrees
Acq. time: 1.640 sec
Width: 10.000 MHz
484 repetitions
OBSERVE F3: 161.909292 MHz
DECOUPLE H1: 399.9706473 MHz
Power 40 dB
off during acquisition
WALTZ-16 modulation
DATA PROCESSING
Line broadening: 5.0 Hz
FT size: 131072
Total accumulation time: 29 minutes

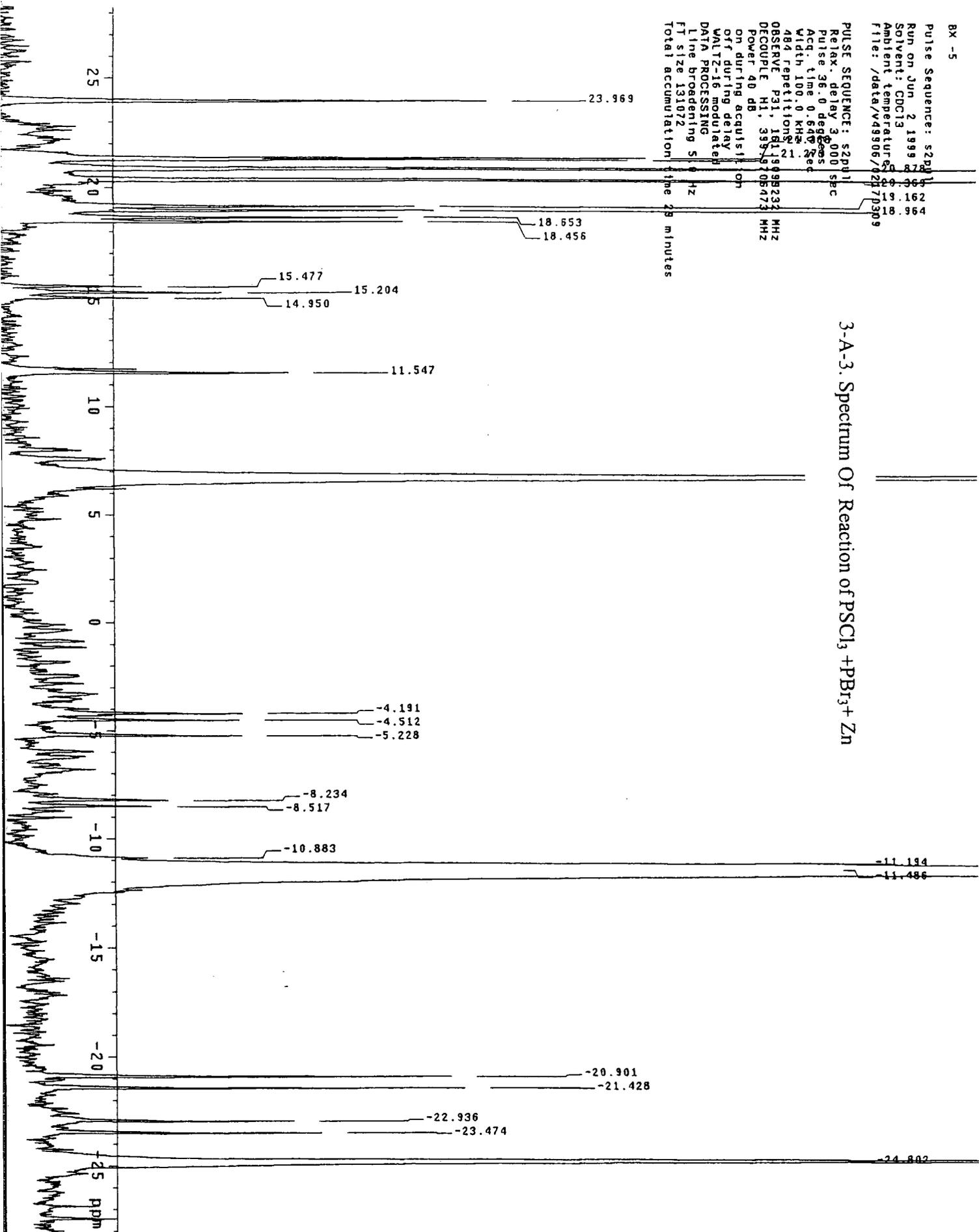
3-A-2. Spectrum Of Reaction of $PCl_3 + PBr_3 + Zn$



Pulse Sequence: s2p11
Run on Jun 2 1998 10:06:16
Solvent: CDCl3
Ambient temperature: 25.18
File: /data/v49906/0217p309

PULSE SEQUENCE: s2p11
Relax. delay 3.000 sec
Pulse 36.0 degrees
Acq. time 0.640 sec
Width 100.0 kHz
404 repetitions
OBSERVE P1, 181.19088233 MHz
DECUPLE M1, 559.2108473 MHz
Power 40 dB
on during acquisition
off during delay
WALTZ-16 modulated
DATA PROCESSING
line broadening 5.0 Hz
FT size 131072
Total accumulation time 28 minutes

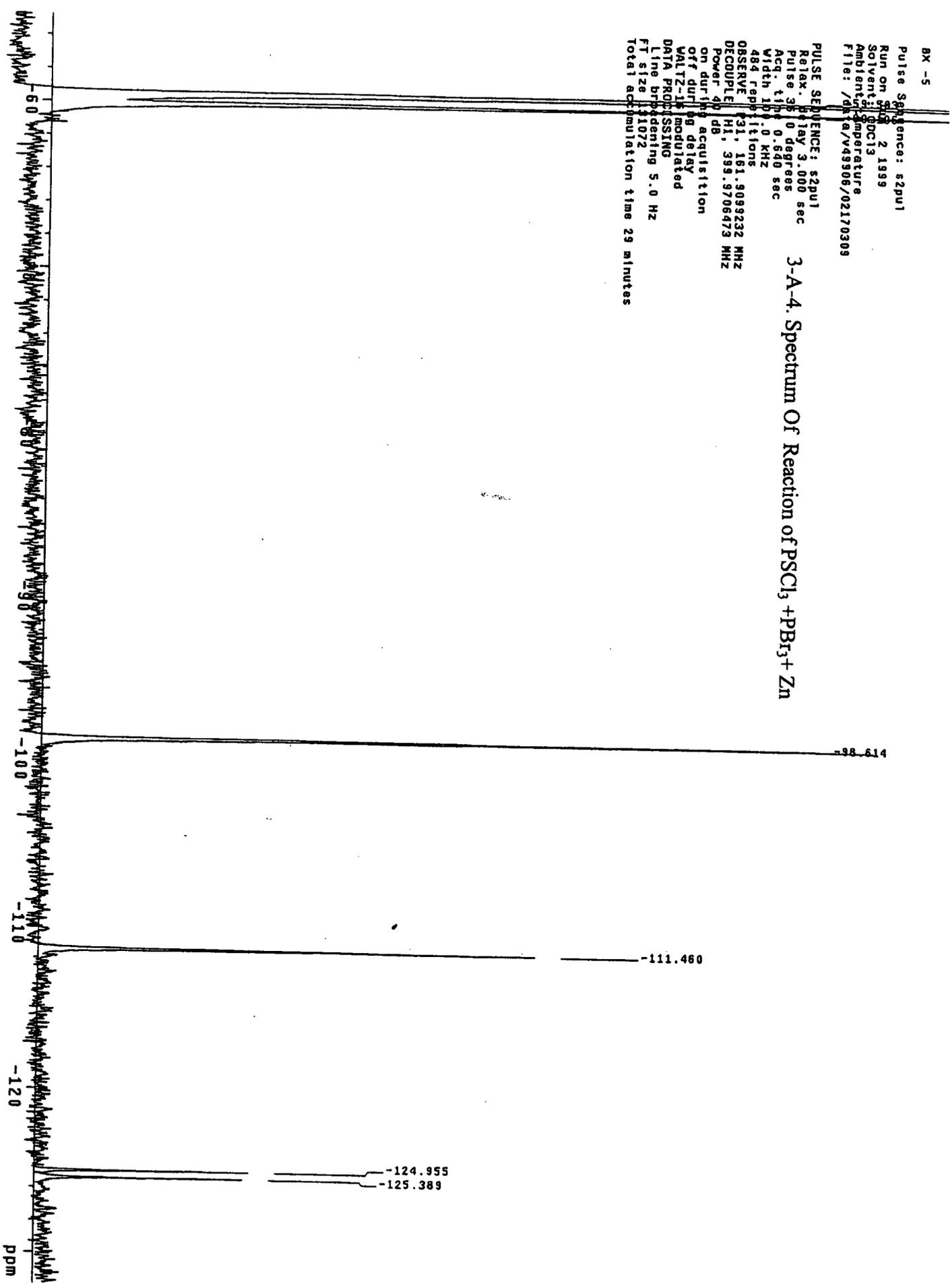
3-A-3. Spectrum Of Reaction of PSCl₃ + PBr₃ + Zn



Pulse Sequence: s2pu1
Run on 2 1989
Solvent: CDCl3
Ambient temperature
File: /data/v49906/02170309

PULSE SEQUENCE: s2pu1
Relax. delay 3.000 sec
Pulse prg 0 degrees
Acq. time 0.640 sec
Width 109.0 kHz
484 repetitions
OBSERVE F31, 161.909232 MHz
DECOUPLE H1, 399.3706473 MHz
Power 40 dB
on during acquisition
off during delay
WALTZ-16 modulated
DATA PROCESSING
Line broadening 5.0 Hz
FT size 131072
Total accumulation time 29 minutes

3-A-4. Spectrum Of Reaction of PSCl3 + PBr3 + Zn



6. Reaction of $\text{PSCl}_3 + \text{PI}_3 + \text{Zn}$

This reaction also involves halide exchange, and different possible phosphorus combinations, P(III)-P(V), P(III)-P(III) and P(V)-P(V), very similar to reaction 5. In the dry glove box PI_3 was added into a small flask, then under nitrogen protection PSCl_3 , Zn dust and solvent CH_2Cl_2 were added, and the reaction mixture was refluxed for 7 hours. When a sample was taken for NMR analysis, only the starting material signals and mixed phosphorus halide signals were found. After stirring over the weekend the ^{31}P NMR was recorded again, but the spectra looked similar. The solution was kept for 6 weeks and the ^{31}P NMR was examined again; this time the expected signals appeared.

In the ^{31}P NMR spectrum many doublet signals appeared; the doublets in the P(III) region appeared in three ranges. The doublet at 188 ppm corresponds to PCl_2 - of P(III)-P(V), the doublets between 155-160 ppm are from PCl - of P(III)-P(V), while the doublets between 130-138 ppm may be assigned to PI_2 - of P(III)-P(V). In the P(V) region, the doublets appeared in four areas, one between 60-69 ppm for the PSCl_2 - of P(III)-P(V) species, doublets between -54 and -60 ppm corresponding to PSCl - of P(III)-P(V), while the doublet at -185 ppm arises from PSI_2 - of P(III)-P(V); however, the doublet at -88 ppm may correspond to PSCl of a P(V)-P(V) combination. So the P(III)-P(V) combination products were $\text{PCl}_2\text{PSCl}_2$, PClIPSCl_2 , PClIPSCl , PI_2PSCl_2 , PI_2PSCl and PI_2PSI_2 . Because the starting materials are PI_3 and PSCl_3 , the most likely P(III)-P(V) product is PI_2PSCl_2 , the subsequent probable products are PClIPSCl_2 and PI_2PSCl , while further possible products are $\text{PCl}_2\text{PSCl}_2$, PClIPSCl and PI_2PSI_2 . It is not difficult to assign the P(III)-P(V) combination products from the relative signal intensity. As for P(V)-P(V) combinations, the probable products are $\text{PSCl}_2\text{PSCl}_2$ and PSClIPSCl_2 . $\text{PSCl}_2\text{PSCl}_2$ in the ^{31}P NMR spectrum should give rise to a singlet, which has been assigned to the 53.2 ppm signal. Hence the doublet corresponding to PSCl_2 of PSCl_2PSCl should be more negative than 53.2 ppm. A small doublet at 29 ppm was found, with the coupling constant exactly the same as that of the doublet at -88 ppm, so the pair of doublets may be assigned to PSClIPSCl_2 .

As for the signals seen at 150 ppm and 102 ppm after 6 weeks, they probably correspond to PClPI_2 . Interestingly, the signal at 102 ppm was replaced by a triplet and a new doublet appeared at 98 ppm after a further two weeks. Another two weeks later, the signals became weaker and the triplet and doublet disappeared. The signal at 150 ppm was replaced by a clear singlet at 149 ppm, corresponding to PClPCl . This is because PI_2PCl is not stable, and reacts with PI_3 to produce the new compound PI_2PIPI_2 , so the new pair of resonances appears at 102.3 ppm and 98.2 ppm. PI_2PIPI_2 is also unstable, however, and continues to decompose, so the pair of signals is lost again. This is the first time that the new phosphorus halide P_3I_5 has been identified in solution. The NMR chemical shifts are shown below.

Species	δ (ppm)	J(Hz)
A. Singlets		
PCl_2I	228.5	
PCl_3	220.3	
PCl_2	213.9	
PI_3	175.9	
PClPCl	149.4	
$\text{PSCl}_2\text{PSCl}_2$	53.2	
PSCl_3	33.1	
PSCl_2I	-111.9	
PSCl_2	-267.4	
B. Doublets		
$\text{PCl}_2\text{PSCl}_2$	188.3, 54.6	85.5
PClPSCl_2	159.7, 66.8	80.8 ± 0.2
PClPSCl	155.6, -56.3	84.8 ± 0.8
PClPI_2	151.1, 102.8	broad signal
PI_2PSCl_2	136.9, 68.3	80.9 ± 0.1
PSClPI_2	133.5, -55.1	87.8 ± 2.2
PI_2PSI_2	129.2, -185.7	108.1 ± 5.9

$\text{PSCl}_2\text{PSCl}_2$	28.9, -88.1	59.6
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C: Triplets and doublets

$\text{PI}(\text{PSCl}_2)_2$	105.5, 61.5	92.2 ± 0.8
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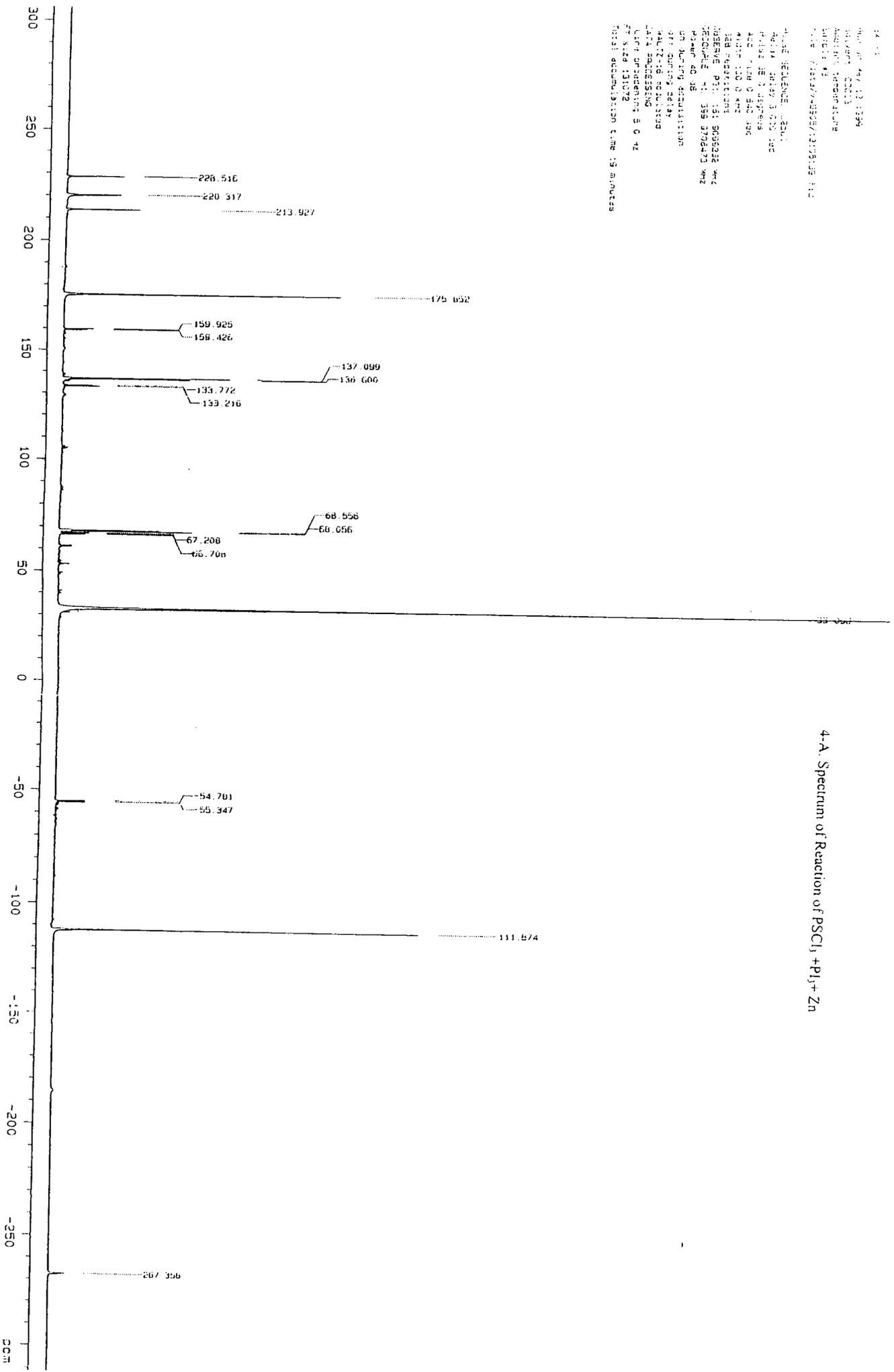
$\text{PI}(\text{PI}_2)_2$	102.3, 98.2	50.4
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$\text{PI}(\text{PSCl}_2)_2$	87.5, -58.5	88.2 ± 0.4
------------------------------	-------------	----------------

14-11
 Run on 4/11/72 1399
 Sample 00013
 ANALYST INFORMATION
 NAME: M. J.
 FILE: 71817/4322/1399139 112

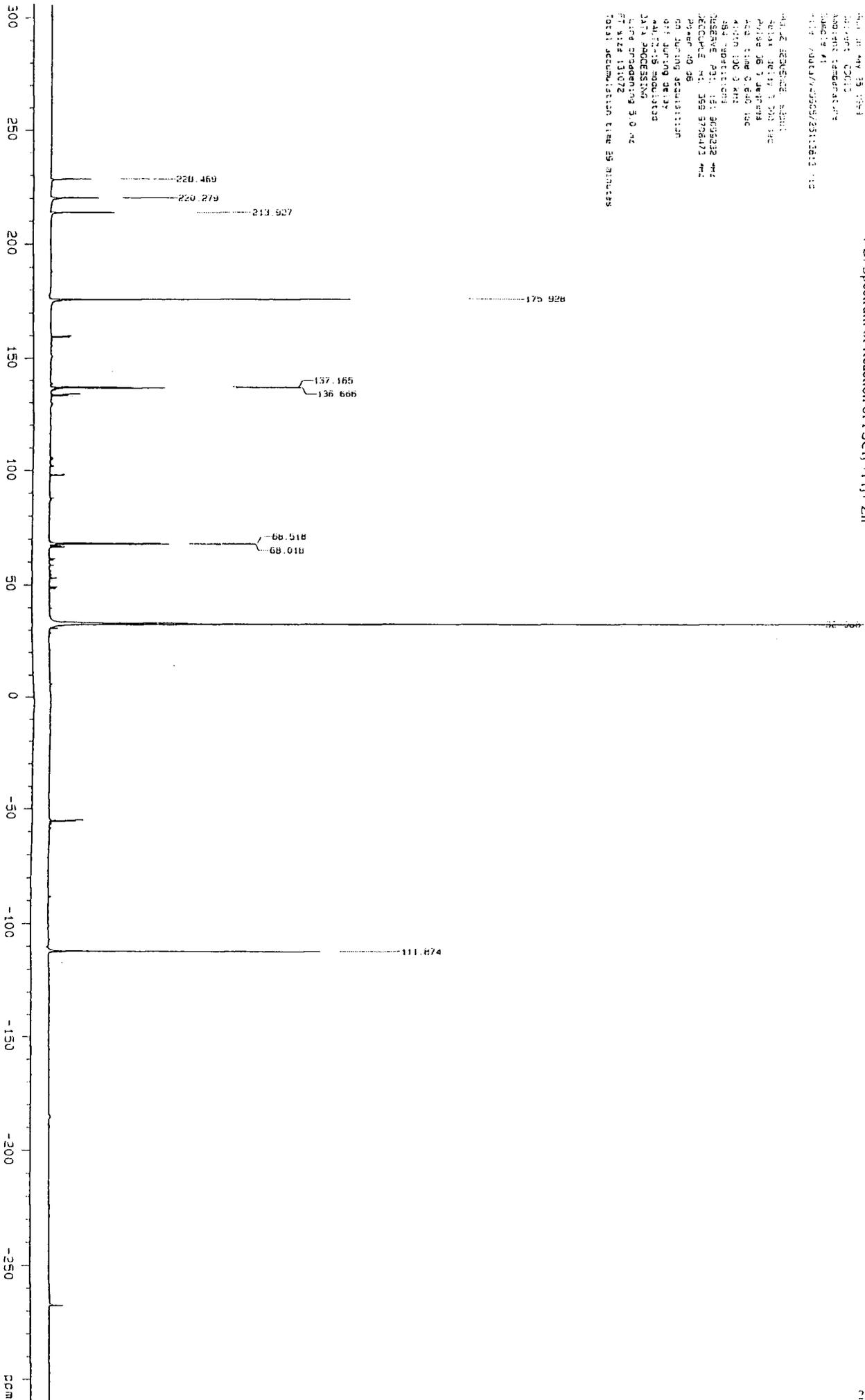
THESE RESULTS ARE:
 FROM 100% OF THE
 FILLS AND RESIDUES
 AND FROM 0.5% OF
 4100 100.0 KHZ
 3000 100.0 KHZ
 3000 100.0 KHZ
 OBSERVE P1: 151 906532 W42
 RECORD: 41 358 376473 W42
 POWER: 40.00
 ON PULSES: 1000000
 OFF PULSES: 1000000
 PULSE WIDTH: 10.00000
 DATA PROCESSING
 LEFT OFFSET: 5.0 42
 FT SIZE: 13102
 Total accumulation time: 15 minutes

4-A. Spectrum of Reaction of $\text{PSCl}_2 + \text{PI}_3 + \text{Zn}$



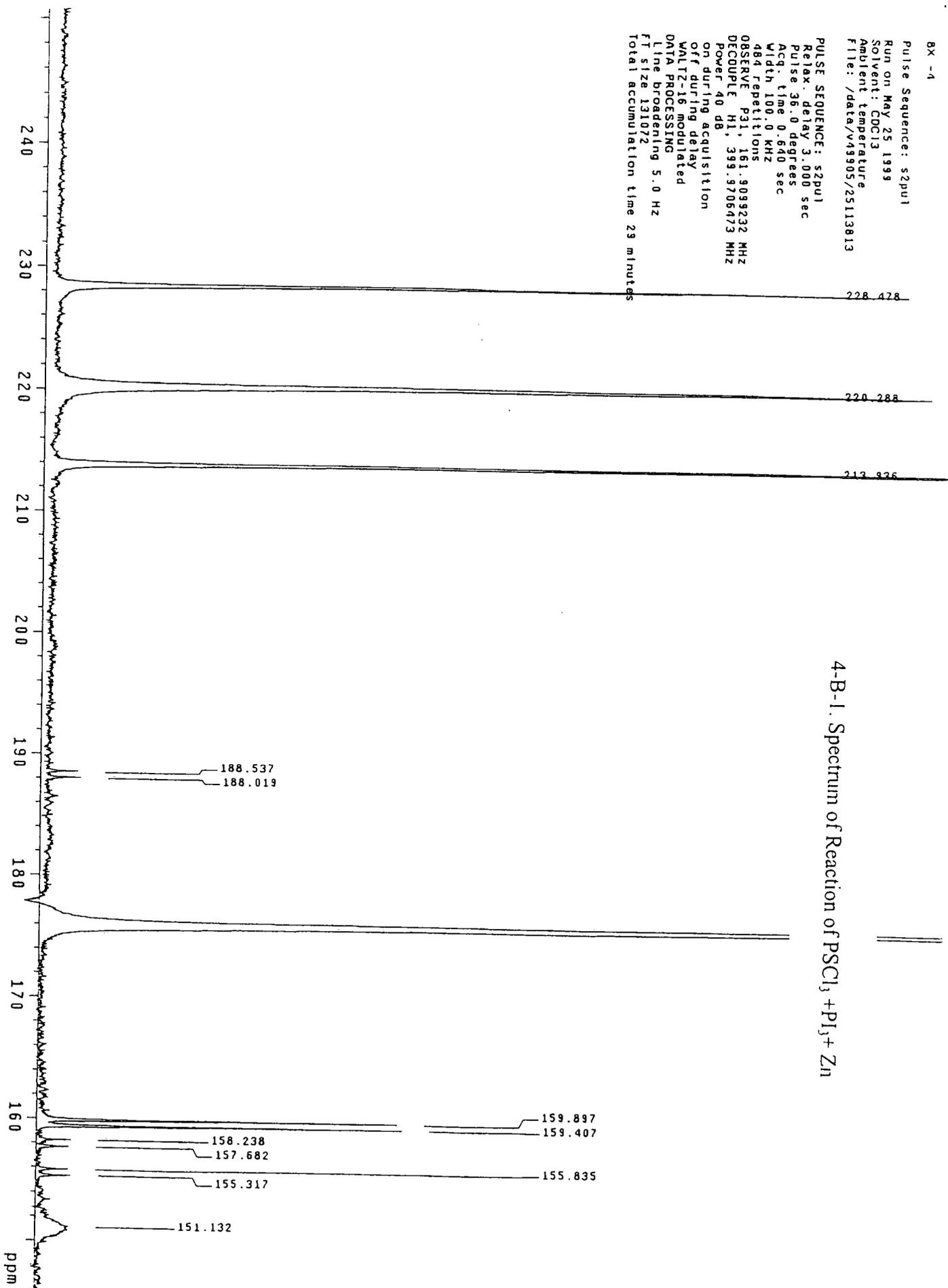
4-B Spectrum of Reaction of $PCl_5 + PI_3 + Zn$

24.11
 Date: 04/23/84
 Operator: CCH
 Sample Name: 4-B
 Sample #1
 File: /DATA/2082/25112613.12
 NAME: 208225112613
 Pulse: 10.000 MHz
 Pulse: 16.700 MHz
 Acc Time: 0.640 Sec
 Kinetic: 100.0 kHz
 984 Scans
 Reserve: 231.121 809232 442
 Module: 11.389 378473 442
 Power: 40 dB
 on during acquisition
 off during delay
 44.7215 modulation
 3.171 processing
 Lock: 3.000 Hz
 FT Size: 131072
 Total accumulation time: 39 minutes



Pulse Sequence: s2pu1
Run on: May 25 1999
Solvent: CCl₄
Ambient temperature
File: /data/v49905/25113813

PULSE SEQUENCE: s2pu1
Relax. delay: 3.000 sec
Pulse: 36.0 degrees
Acq. time: 0.640 sec
Width: 100.0 KHz
484 repetitions
OBSERVE P31, 161.9089232 MHz
DECOUPLE H1, 399.9706473 MHz
Power: 40 dB
on during acquisition
off during delay
WALTZ-16 modulated
DATA PROCESSING
line broadening 5.0 Hz
FT size 131072
Total accumulation time 23 minutes



4-B-1. Spectrum of Reaction of PSCl₃+PI₃+ Zn

BX - 4

Pulse Sequence: s2pu1

Run on May 29 1999

Solvent: CDCl3

Ambient temperature

File: /data/199905/25113813

PULSE SEQUENCE: s2pu1

Relax. delay 3.000 sec

Pulse 36.0 degrees

Acq. time 0.1840 sec

Width 100.000 MHz

484 repetitions

OBSERVE P1 161.9099232 MHZ

DECOUPLE P2 299.9706473 MHZ

Power 40 db

on during acquisition

off during delay

WALTZ-16 modulated

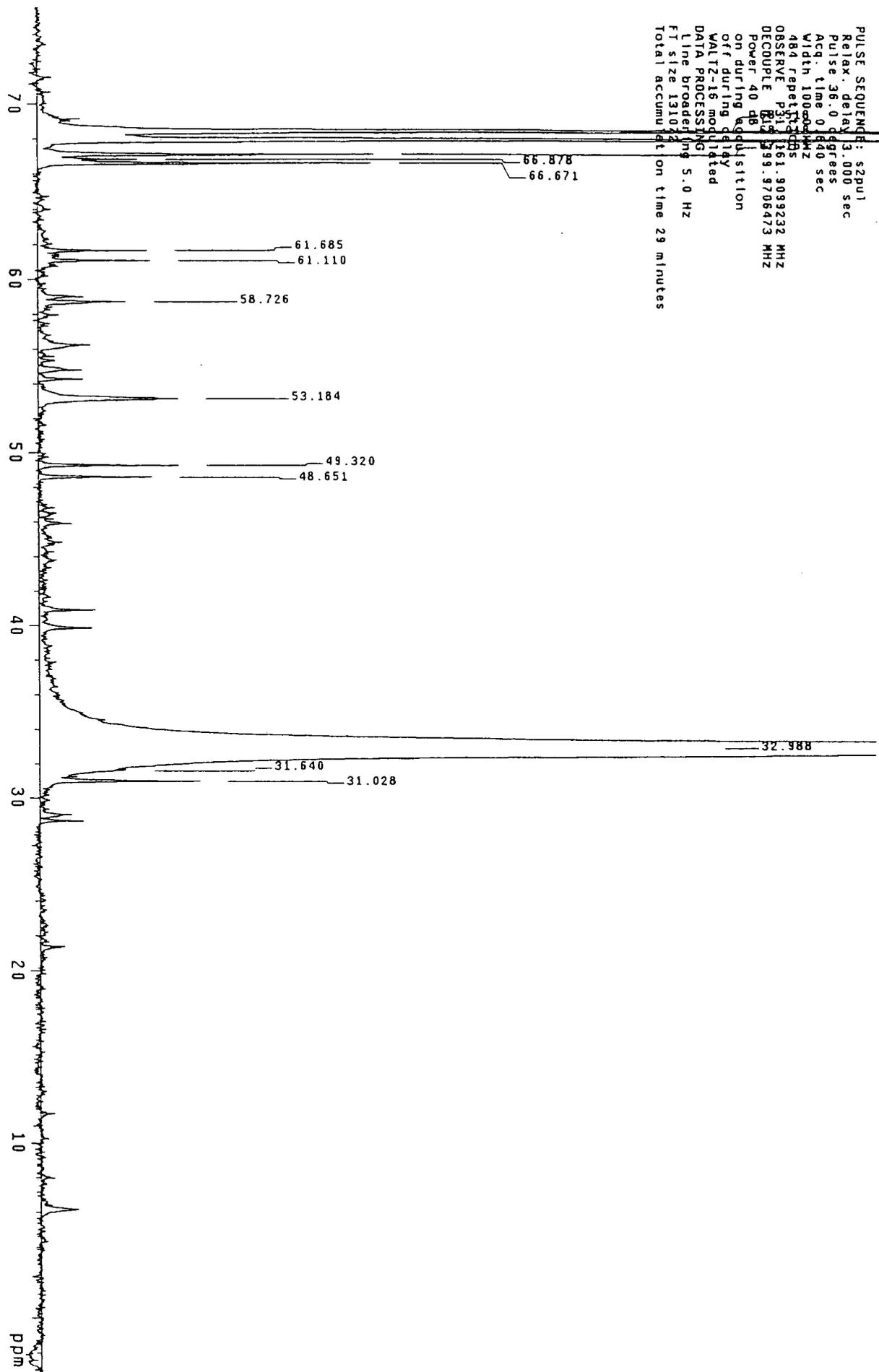
DATA PROCESSING

line broadening 5.0 Hz

FT size 131072

Total accumulation time 29 minutes

4-B-3. Spectrum of Reaction of PSCl₃ + PI₃ + Zn

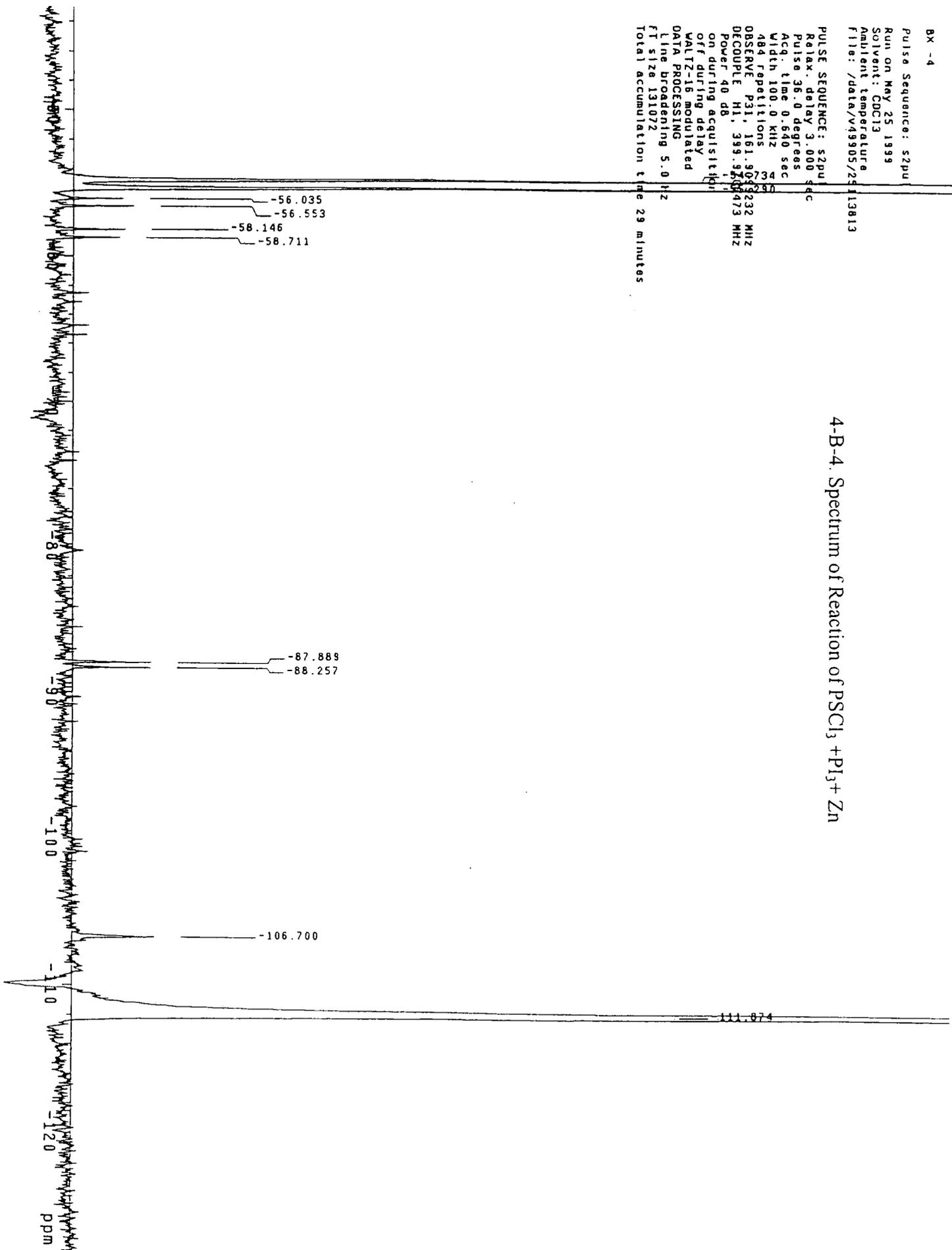


BX - 4

Pulse Sequence: s2pu
Run on May 25 1999
Solvent: CDCl3
Ambient temperature
file: /data/vv49905/2513813

PULSE SEQUENCE: s2pu
Relax. delay 3.000 sec
Pulse 36.0 degrees
Acq. time 0.640 sec
Width 100.0 kHz
484 Repetitions
OBSERVE P31, 161.9043232 MHz
DECOUPLE H1, 399.970473 MHz
Power 40 dB
on during acquisition
off during delay
WALTZ-16 modulated
DATA PROCESSING
Line broadening 5.0 Hz
FT size 131072
Total accumulation time 29 minutes

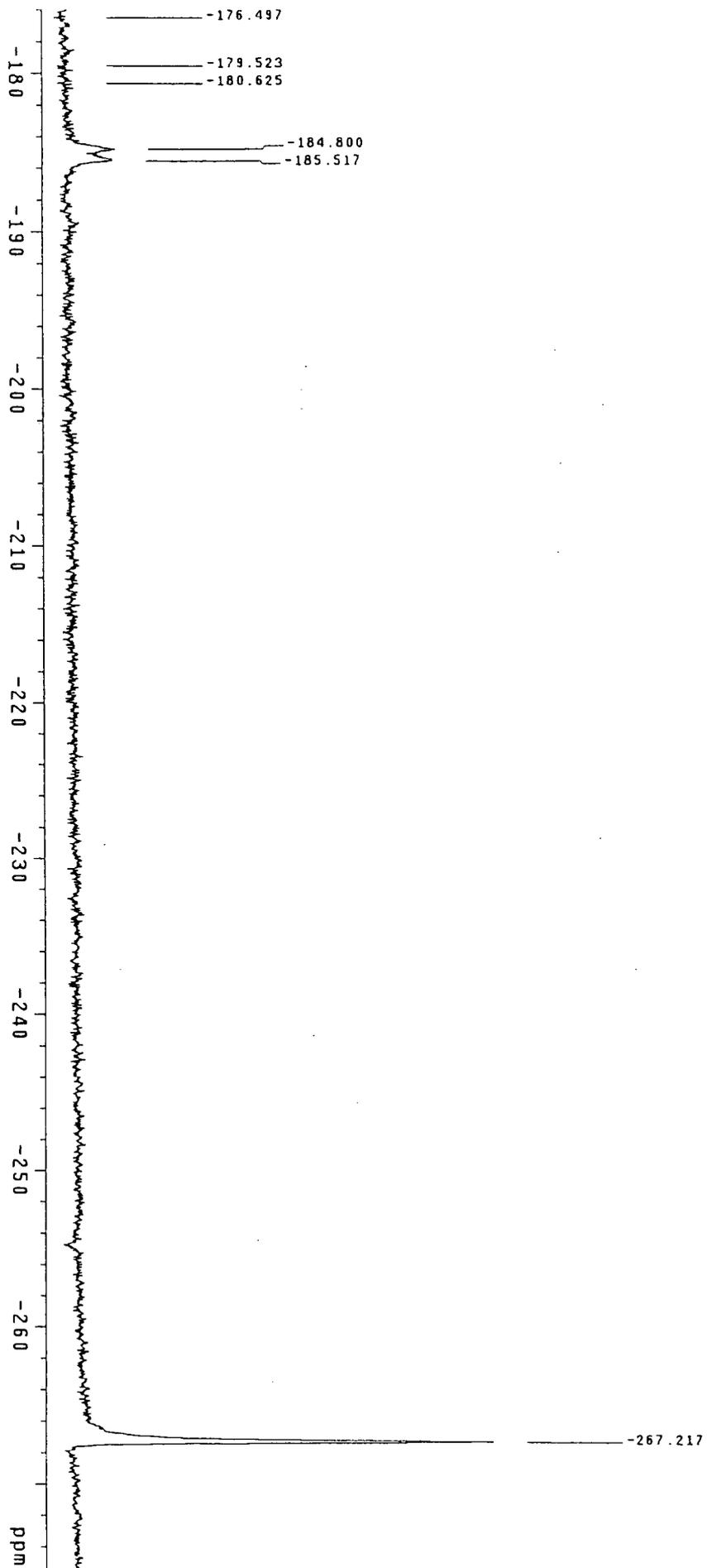
4-B-4. Spectrum of Reaction of $\text{PSCl}_3 + \text{PI}_3 + \text{Zn}$



Pulse Sequence: s2pu1
Run on May 25 1999
Solvent: CDCl3
Ambient temperature
File: /data/v49905/25113813

PULSE SEQUENCE: s2pu1
Relax. delay 3.000 sec
Pulse 36.0 degrees
Acq. time 0.640 sec
Width 100.0 KHz
4dd repetitions
OBSERVE P31, 161.9099232 MHz
DECUPLE H1, 399.9706473 MHz
Power 40 dB
on during acquisition
off during delay
WALTZ-16 modulated
DATA PROCESSING
Line broadening 5.0 Hz
FT size 131072
Total accumulation time 29 minutes

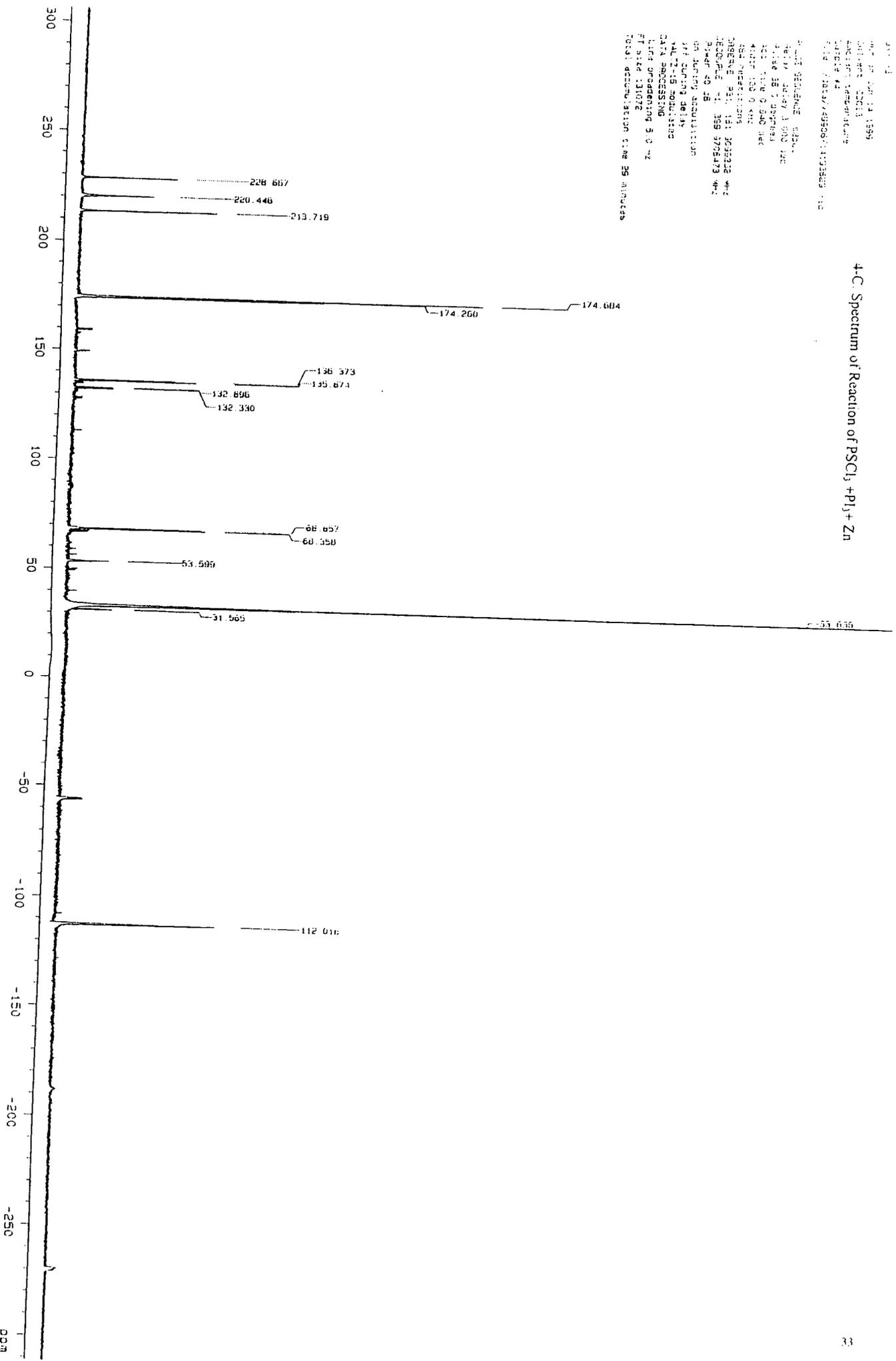
4-B-5. Spectrum of Reaction of $\text{PSCl}_3 + \text{PI}_3 + \text{Zn}$



DATE: 01/14/1999
 INSTRUMENT: JEOL
 SAMPLE: PSCl2 + PI3 + Zn
 FILE: 00004749508.F (103829)

4-C Spectrum of Reaction of PSCl₂ + PI₃ + Zn

UNIT: SEQUENCE: 0001
 REACTION: 0007 1 000 000
 F1: 100 35 1 (ppm/s)
 F2: 100 0 000 (Hz)
 F3: 100 0 000 (Hz)
 F4: 100 0 000 (Hz)
 F5: 100 0 000 (Hz)
 CHANNEL: 0001 101 000000
 RECORDS: 1 359 070473 (Hz)
 P1: 0.00 28
 ON: during acquisition
 OFF: during delay
 NAL: 18 (ppm/s)
 DATA PROCESSING
 LINE: 00000000 5 0 0 0
 F1 size: 131072
 Total accumulation time: 29 minutes



7. Reaction of $\text{PSBr}_3 + \text{PBr}_3 + \text{PI}_3 + \text{Zn}$

This is a most complex reaction, but similar to reaction 5 involving halide exchange, and different possible phosphorus combination, P(III)-P(V), P(III)-P(III) and P(V)-P(V). Due to the PSBr_3 not being commercially available, the first step was to prepare thiophosphoryl tribromide. PBr_3 was directly reacted with sulphur (no solvent) at 135°C for 8 hours, when 60-70% PBr_3 changed into PSBr_3 . Then some zinc dust was added and reaction continued at 115°C overnight. A sample was taken for NMR, but showed only the starting material signals. Then some PI_3 was added and the reaction kept at 104°C overnight. A sample was taken for NMR again, and some expected signals were observed, but quite weak. More PI_3 was added and reaction continued at 108°C for 6 hours; this time the spectra looked stronger, but some signals were still weak. After two weeks the ^{31}P NMR was re-examined, and this time most signals appeared. After another 3 weeks, the NMR was re-examined again (run for 30 minutes). The intensity of the ^{31}P NMR spectra appeared to be similar, but more signals appeared, such as a multiplet (triplet + triplet) at 102 ppm, a doublet at 98 ppm, a new signal at 145 ppm and a triplet near 125 ppm

In the P(III) region for P(III)-P(V) mixed valence species, doublets clearly appeared in three places. The signals between 174-177 ppm correspond to PBr_2^- , the doublets between 152 and 156 ppm may be assigned to PBrI^- , and the pairs of doublets between 131 and 135 ppm to PI_2^- . In the P(V) region, the doublets appeared at two places; between -9 and -21 ppm is due to PSBr_2^- , while between -98 and -113 ppm corresponds to PSBrI^- . So P(III)-P(V) combination products are $\text{PBr}_2\text{PSBr}_2$, PI_2PSBr_2 , PBrIPSBr_2 , PBr_2PSBrI , PBrIPSBrI and PI_2PSBrI . Since the starting materials are PBr_3 , PI_3 and PSBr_3 , the most likely products are $\text{PBr}_2\text{PSBr}_2$, PI_2PSBr_2 and PBrIPSBr_2 , and the other possible products are PBr_2PSBrI , PBrIPSBrI and PI_2PSBrI . It is not difficult according to intensity to assign each doublet of a P(III)-P(V) combination, and this was confirmed by the J values.

There are a few signals corresponding to a P(III)-P(III) combination. Since the starting materials are PBr_3 and PI_3 , possible products are PBr_2PBr_2 , PBr_2PI_2 , PBr_2PBrI , PBrIPI_2 and PBrIPBrI (PI_2PI_2 is unstable). But assignment of these signals was

difficult, partly because the signals are quite weak, and some signals probably overlap. For example, the signals near 145 ppm corresponding to PBr_2^- of PBr_2PBr_2 and PBr_2PBrI are very close, and it is difficult to separate them; then the 125 ppm triplet corresponding to PBr^- of $\text{PBr}(\text{PSBr}_2)_2$ perhaps overlaps with the doublet of PBrIPBr_2 ; near 130 ppm the doublet of PI_2PSBrI may overlap with PBrIPI_2 , and at 102 ppm a triplet from $\text{PI}(\text{PI}_2)_2$ can overlap with the triplet of $\text{PI}(\text{PSBr}_2)_2$, giving a multiplet appearance. An effort has been made to assign every signal.

As shown by the triplet signal at 102.0 ppm and the doublet at 98.1 ppm, described in section 5, corresponding to PI_2PIPI_2 , which comes from PI_2PCII reacting with PI_3 , PI_2PBrI may also react with PI_3 to form PI_2PIPI_2 . From the spectra here these signals were again observed, but the signals subsequently disappeared again after 4 weeks, confirming the previous assignment.

The assignment of the doublet near 98 ppm differs from that of Gemmell, who suggested that it arose from $(\text{PBr}_2)_2\text{PSBr}$. This value looks incorrect for a PBr_2 group, however, and the more accurate value of the coupling constant in the present work is in good agreement with that obtained for P_3I_5 in section 5. The triplet signals at 102 ppm from $\text{PI}(\text{PI}_2)_2$ and $\text{PI}(\text{PSBr}_2)_2$ by coincidence overlap together, the centre line from both triplets forming one line, so that five lines are seen, instead of six, with J values of 50.4 and 100.7 Hz respectively, calculated from the apparent shifts of the four other lines. The small signals around 50-60 ppm, as Gemmell suggested, probably arise from partial oxidation of monothiophosphoryl halides. Comparing with his data, we find many more signals, like those from P(III)-P(V) combination products Br_2PSBrI , PBrIPBrI , PI_2PSBrI , the new P3 Unit PI_2PIPI_2 , the diphosphorus halides PBr_2PBr_2 , PBr_2PBrI , PBrIPBrI and PBrIPI_2 and P(V)-P(V) combination products $\text{PSBr}_2\text{PSBr}_2$ and PSBrIPBrI . The only problem is the doublet at -112.3 ppm which appears to correspond with PSBrIPBr_2 , but unfortunately another doublet could not be found to match. Samples were then taken every two weeks; the first spectrum looked exactly the same, the second spectrum looked similar, but a lot weaker, while the third spectrum looked much weaker and some signals had been lost, such as the multiplet at 102 ppm and the doublet at 98 ppm. The NMR data are shown below.

Species	δ (ppm)	J(Hz)
A. Singlets		
PBr ₃	228.9	
PBr ₂ I	221.8	
PBrI ₂	203.8	
PI ₃	175.4	
PBr ₂ PBr ₂	145.5	
PSBr ₂ PSBr ₂	-31.2	
PSBr ₃	-110.5	
PSBrI ₂ PSBrI	-128.1	
PSBr ₂ I	-219.7	
B. Doublets		
PBr ₂ PSBr ₂	176.5, -20.5	85.4
PBr ₂ PSBrI	174.6, -103.0	94.5
PBrI ₂ PSBr ₂	154.8, -11.8	84.0
PBrI ₂ PSBrI	152.6, -101.4	89.2 ± 0.8
PBr ₂ PBrI	145.2, 125.5	broad signal
PI ₂ PSBr ₂	134.2, -9.6	85.4 ± 0.1
PI ₂ PSBrI	131.8, -99.1	96.9 ± 0.7
C. Triplets and Doublets		
PBr(PSBr ₂) ₂	126.1, -22.3	111.8 ± 0.3
PI(PSBr ₂) ₂	102.0, -18.2	100.7
PI(PI ₂) ₂	102.0, 98.1	50.4

III. Summary

1. The P-I bond is the weakest bond in each of the systems and so is the most likely to be broken and form new bonds, both in exchange with other halides and in

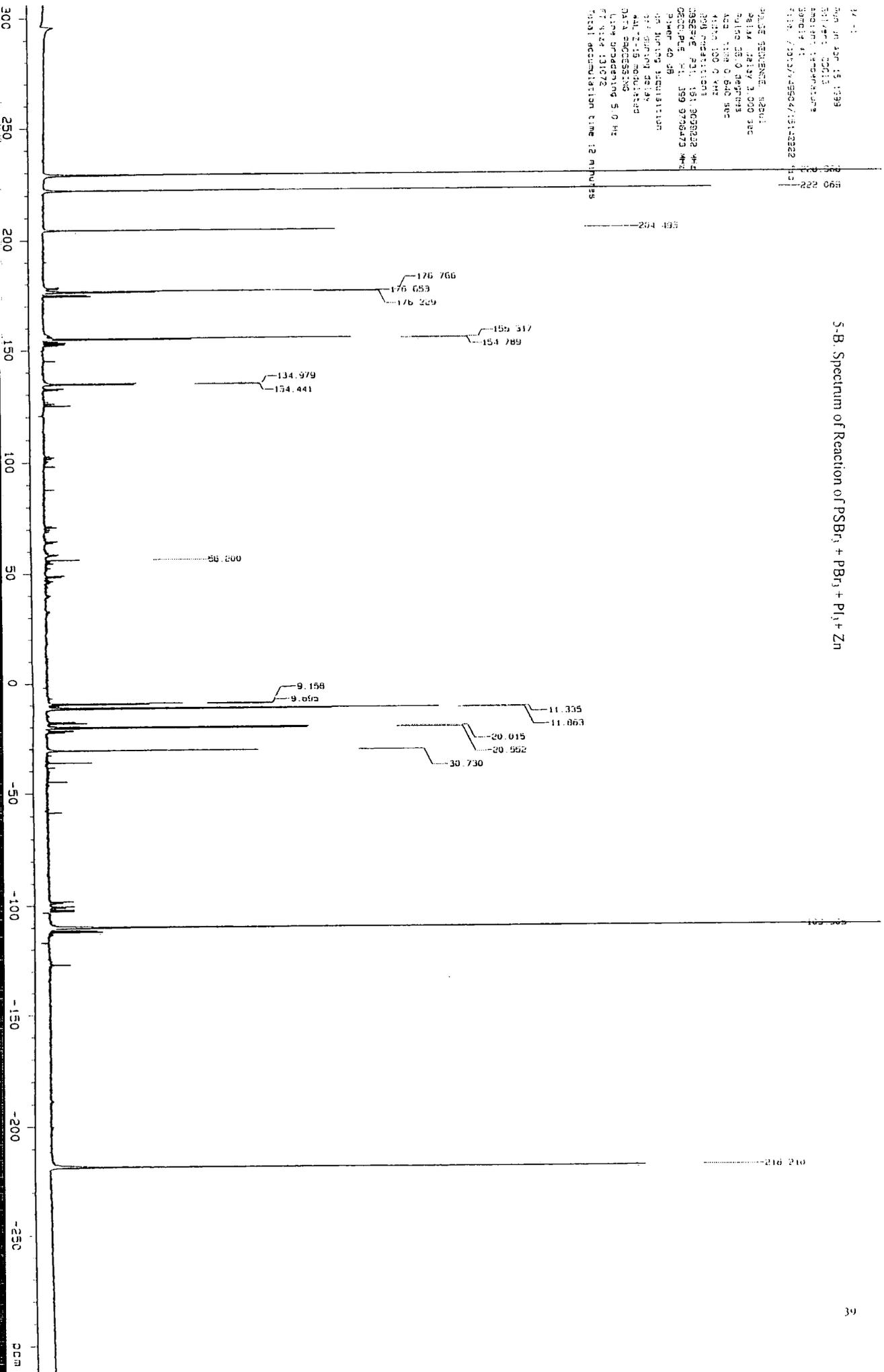
coupling phosphorus to phosphorus; The P-Br bond is next, and the P-Cl bond is the strongest bond, very difficult to react with zinc dust, even at 70 °C for three days.

2. Halide exchange is a common phenomenon in phosphorus chemistry. Thiophosphoryl(V) halides were more stable than phosphorus(III) compounds and the substitution takes place preferentially on P(III), as can be seen in all spectra.
3. The strong P-Cl bond may be activated by the breaking of P-Br or P-I bonds; PSCl_3 and PCl_3 will normally not react together, but they will react if PBr_3 or PI_3 is present.
4. Formation of the mixed valence P(III)-P(V) compounds is quite feasible, although some of the reactions are slow.

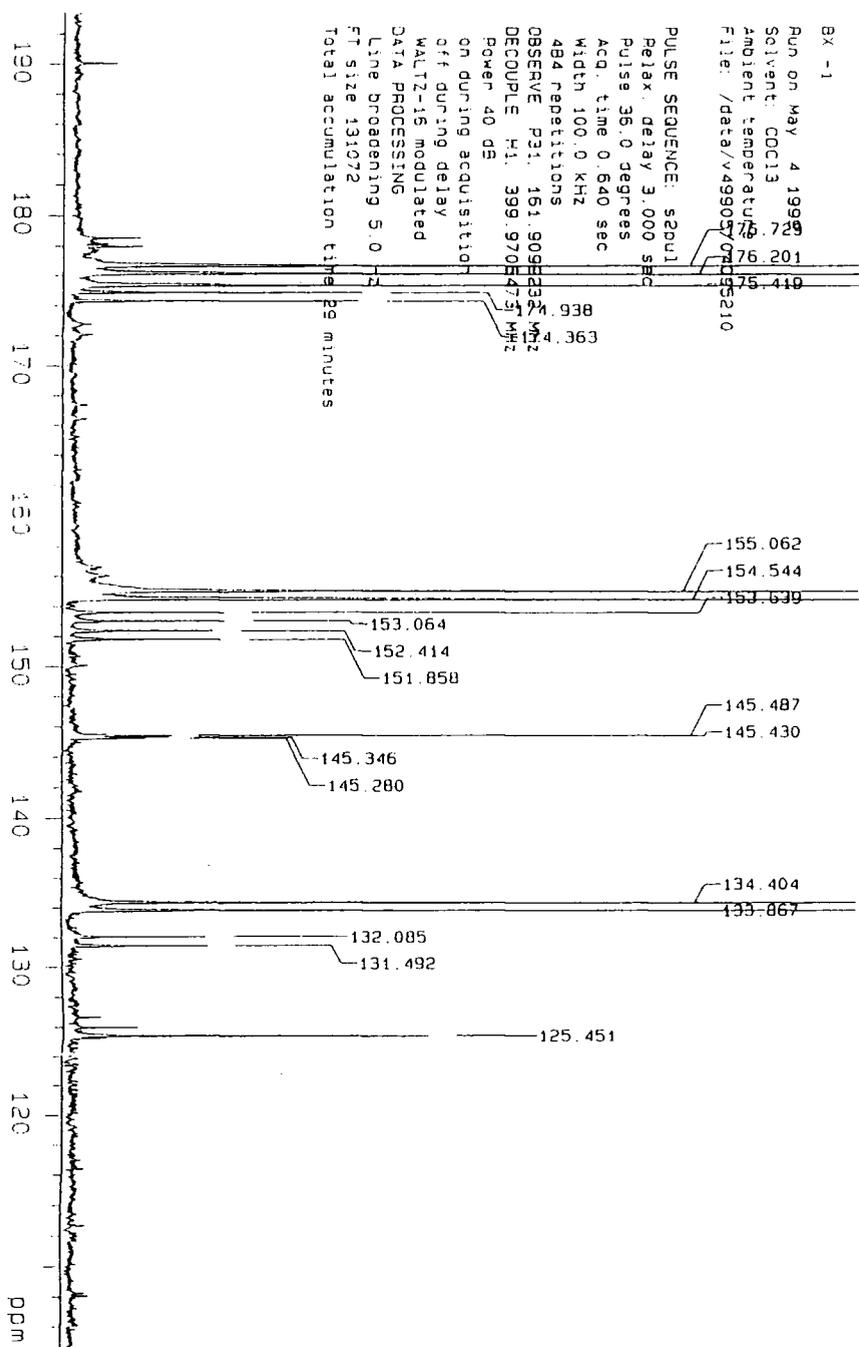
5-B. Spectrum of Reaction of PSBr₃ + PB₃ + PI₁ + Zn

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 Run on Apr 15 1969
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 Sample Temperature
 Sample #1
 File: /2013/4564/151-2222 15.2

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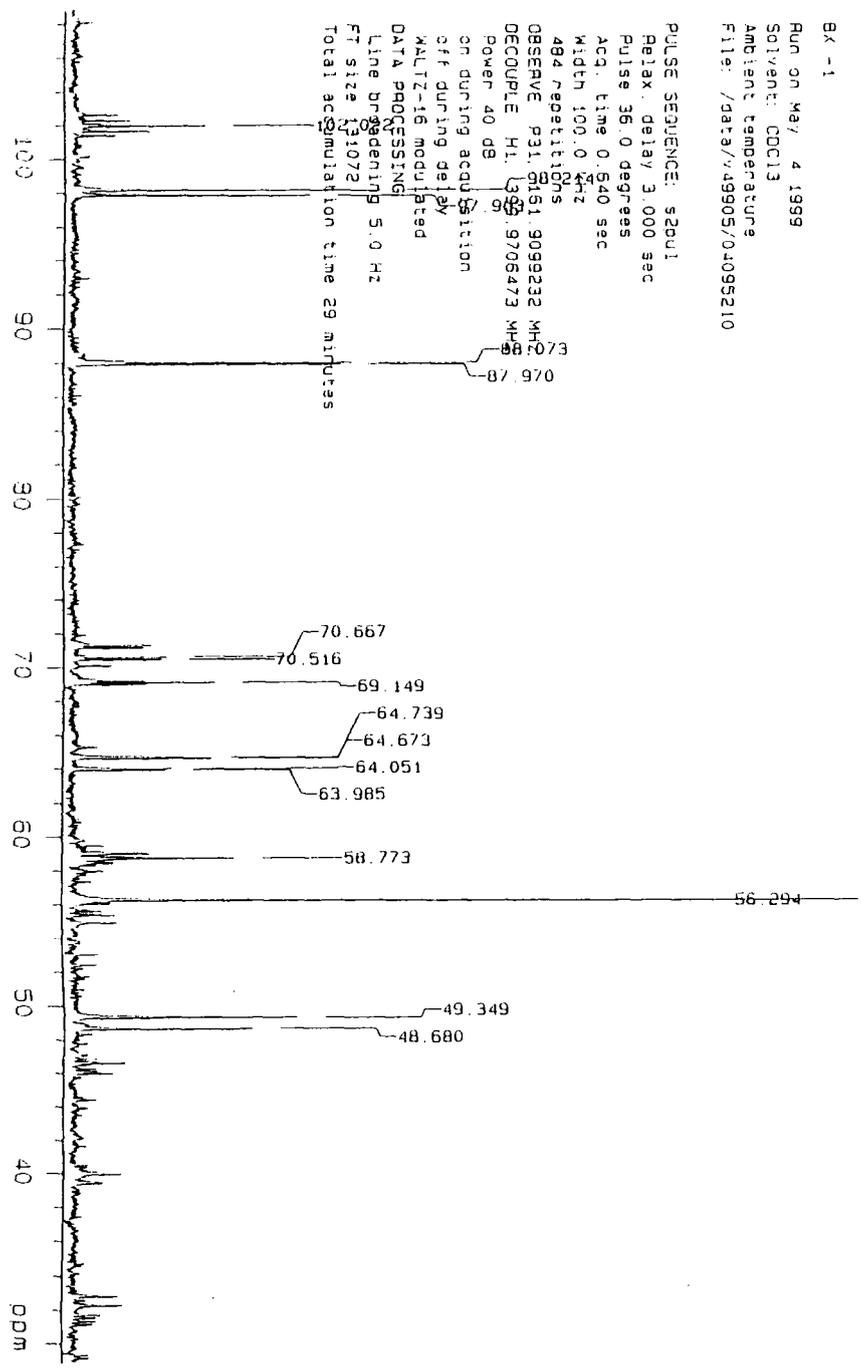
5-C-1 Spectrum of Reaction of $\text{PSBr}_3 + \text{PBr}_3 + \text{PI}_3 + \text{Zn}$



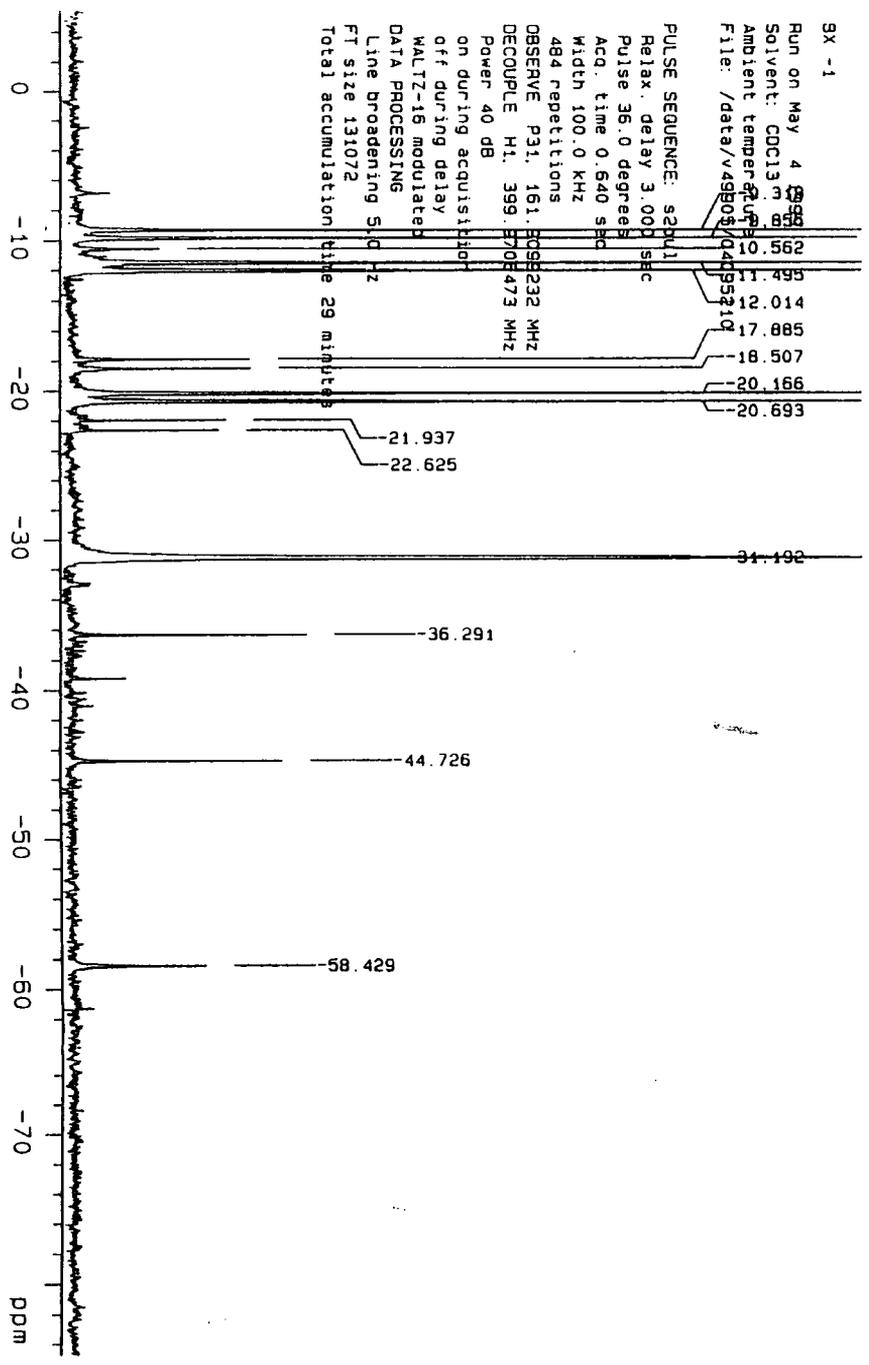
5-C-2. Spectrum of Reaction of $PSBr_2 + PBr_3 + PI_2 + Zn$

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 File: /data/v49905/04095210

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 Pulse 36.0 degrees
 Acq. time 0.640 sec
 Width 100.0 kHz
 484 repetitions
 OBSERVE P31.8151.909232 MHz
 DECOUPLE H1.328.9706473 MHz
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 on during acquisition
 off during delay
 MALTZ-16 modulated
 DATA PROCESSING
 Line broadening 5.0 Hz
 FT size 31072
 Total acquisition time 29 minutes



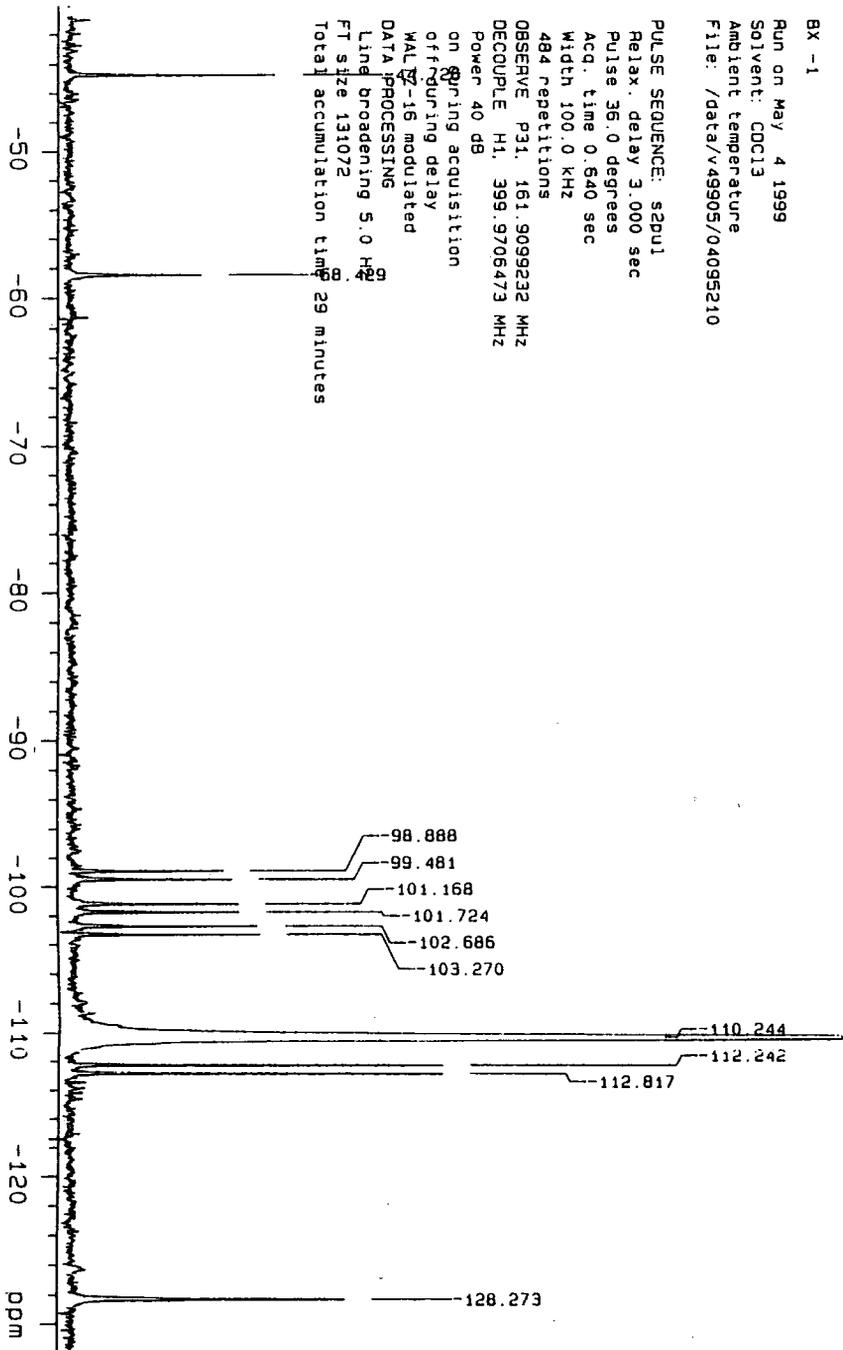
5-C-3. Spectrum of Reaction of $\text{PSBr}_3 + \text{PBr}_3 + \text{PI}_3 + \text{Zn}$



5-C-4. Spectrum of Reaction of PSBr₃ + PBr₃ + P₄ + Zn

BX -1
Run on May 4 1999
Solvent: CCl₃
Ambient temperature
File: /data/v49905/04095210

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Pulse 36.0 degrees
Acq. time 0.640 sec
Width 100.0 KHz
484 repetitions
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DECOUPLE H1. 399.9706473 MHz
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off during delay
MAL 15-15 modulated
DATA PROCESSING
Line broadening 5.0 Hz
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Total accumulation time 29 minutes

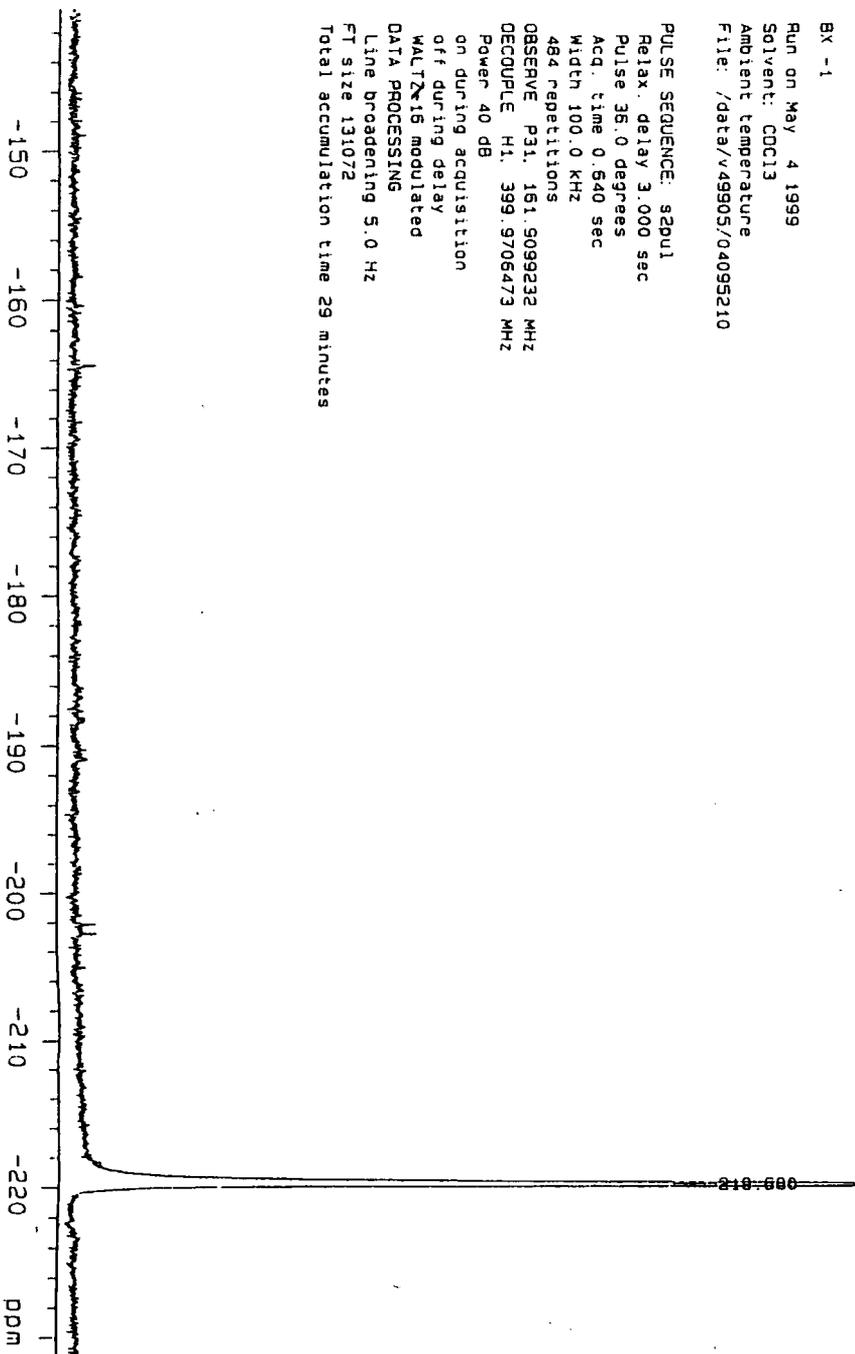


5-C-5. Spectrum of Reaction of PSBr₃ + PBr₃ + P₂S₅ + Zn

BX - 1

Run on May 4 1999
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Ambient temperature
File: /data/v49905/04095210

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Pulse 36.0 degrees
Acq. time 0.640 sec
Width 100.0 KHz
484 repetitions
OBSERVE P31. 161.9099232 MHz
DECUPLE H1. 399.9706473 MHz
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WALTZ16 modulated
DATA PROCESSING
Line broadening 5.0 Hz
FT size 131072
Total accumulation time 29 minutes



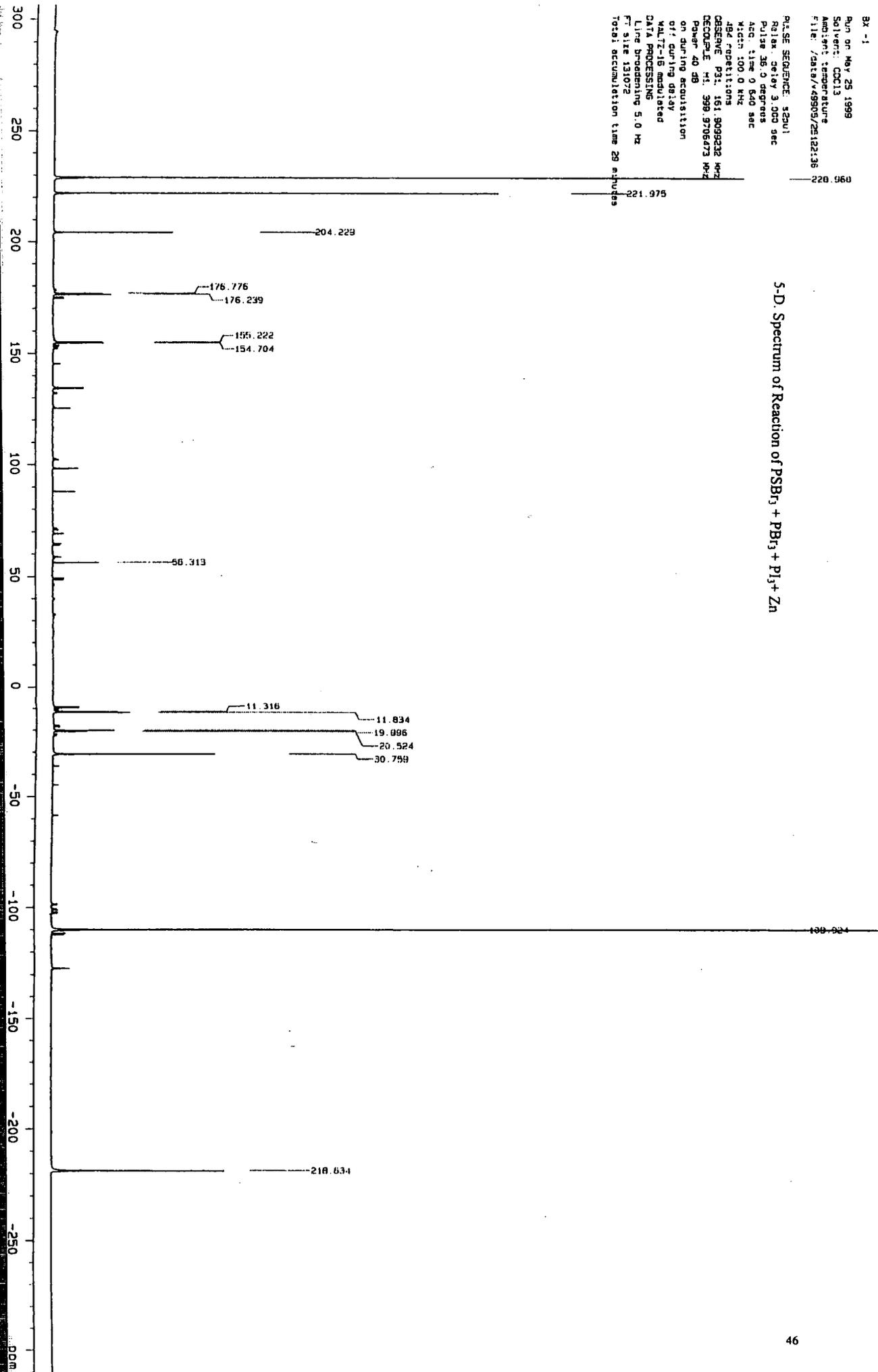
BX -1

Run on May 25 1999
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Amount: temperature
file: /data/45909/25122136

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Pulse: 36.0 degrees
Acq: time 0.640 sec
Width: 100.0 kHz
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SFO: 101.625 MHz
AQ: 0.195 sec
RG: 655.357
SFO: 101.625 MHz
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RG: 655.357
SFO: 101.625 MHz
AQ: 0.195 sec

DECOUPLE: M1: 399.970673 MHz
Power: 40.00 dB
on during acquisition
off during display
MULTI-16 multiscan
DATA PROCESSING
Line broadening 5.0 Hz
F1 size 131072
Total accumulation time 29 minutes

5-D: Spectrum of Reaction of PSBr₃ + PBr₃ + PI₃ + Zn



References.

1. E. Fluck, J. R. Van Wazer and L. C. D. Groenweghe, *J. Am. Chem. Soc.*, **81**, 6363 (1959).
2. L. C. D. Groenweghe and J. H. Payne, *J. Am. Chem. Soc.*, **81**, 6359 (1959).
3. K. B. Dillon, T. C. Waddington and D. Younger, *Inorg. Nucl. Chem. Letters*, **10**, 777 (1974).
4. K. B. Dillon, M. G. Craveirinha Dillon and T. C. Waddington, *Inorg. Nucl. Chem. Letters*, **13**, 349 (1977).
5. K. B. Dillon, A. W. G. Platt and T. C. Waddington, *Inorg. Nucl. Chem. Letters*, **17**, 201 (1981).
6. B. W. Tattershall and N. L. Kendall, *Polyhedron*, **13**, 1517 (1994).
7. K. B. Dillon, A. W. Platt, A. Schmidpeter, F. Zwaschka and W. S. Sheldrick, *Z. Anorg. Allg. Chem.*, **94**, 4762 (1990).
8. K. B. Dillon and T. C. Waddington, *Chem. Commun.*, 1317 (1969).
9. M. Baudler, G. Fricke and K. Fichtner, *Z. Anorg. Allg. Chem.*, **327**, 124 (1964).
10. A. H. Cowley and S. T. Cohen, *Inorg. Chem.*, **3**, 7807 (1964).
11. K. B. Dillon, M. G. Craveirinha Dillon and T. C. Waddington, unpublished results.
12. M. Coles, project report: *Aspects of the Coordination Chemistry of Phosphorus* (1992).
13. P. Gemmell, project report: *Aspects of Phosphorus Coordination Chemistry* (1994).

**Chapter 3. Studies on Main Group elements compounds Containing
Bulky Electron-Withdrawing Substituents**

I. Introduction

The history of the multiple bonds of heavier main elements of group 14 and 15 may have started in 1877, when Kohler and Michaelis¹ reacted PhPH_2 and PhPCl_2 and obtained what they believed to be "phosphobenzene", $\text{PhP}=\text{PhP}$. Although a double bond between the phosphorus atoms was implied, subsequent physical studies revealed that "phosphobenzene" in fact is a σ -bonded cyclopolyphosphine $(\text{PhP})_n$ ($n=5,6$)². This was further confirmed in 1964 by X-ray crystallography.³ Likewise, compounds that were thought to contain arsenic-arsenic⁴ and silicon-silicon⁵ double bonds have since been shown to possess cyclic oligomeric structures.

Little experimental effort was expended in this field for the next half-century. Possibly, synthetic chemists were discouraged by these early results and by the emergence of the "classical double-bond rule," which stipulated that elements possessing a principal quantum number greater than 2 should not be able to form π - π bonds with themselves or with other elements⁶.

In the late 1960's methodologies began to be developed for the generation and subsequent trapping of a significant variety of transient molecules with implied double bonding between heavier group 14 or group 15 atoms.^{7,8} In 1981 Yoshifuji and co-workers⁹ reported the first diphosphenes $\text{Mes}^*\text{P}=\text{PMes}^*$ ($\text{Mes}^*=\text{C}_6\text{H}_2\text{-}2,4,6\text{-}^t\text{Bu}_3$), representing a significant landmark in the study of multiple bonding in the heavier main group elements. Following this, the first disilene $\text{Mes}_2\text{Si}=\text{SiMes}_2$ ($\text{Mes}=\text{mesityl}$) was obtained by West, Fink and Michl¹⁰; in 1982 Satge reported the first heteronuclear double bonds in germaphosphene $[\text{Me}_2\text{Ge}=\text{PPh}]$ and stannaphosphene $[\text{Me}_2\text{Sn}=\text{PPh}]$ ¹¹; in 1983, the first heteronuclear phospharsene $[(\text{Me}_3\text{Si})_3\text{C-As}=\text{P-C}(\text{SiMe}_3)_3]$ and homonuclear diarsene $[(\text{Me}_3\text{Si})_3\text{-C-As}=\text{As-C}(\text{SiMe}_3)_3]$ were generated¹². From 1985 several stable germaphosphenes and stannaphosphenes have been made^{13,14}. In totally approximately 20 structural data sets of organodiphosphenes have been published, together with several metalladiphosphenes, in which the organic group at phosphorus is replaced by a transition metal moiety.¹⁵

II. Synthetic Routes

There are quite a few methods for preparing double-bond dipnictenes of heavier main group element, and 5 routes can be distinguished.

1. Thermolysis¹⁶

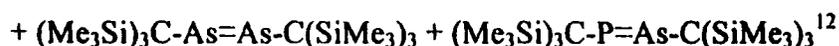
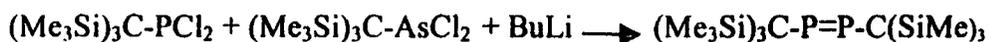


2. Photochemical Elimination¹⁰



3. Dehalogenation of R_nEX_2

This is a widely employed route, where R_nEX_2 reacts with a halide-abstracting agent such as elemental magnesium, potassium or an alkyllithium.



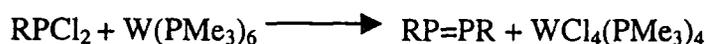
This method has so far only proved synthetically useful for the formation of symmetrical double bonds between main group 14 or 15 elements, due to difficulties in separating the pure components, and seldom can be used to synthesise unsymmetrical double bond compounds.²¹⁻²³

4. Dehydrohalogenation of RnEX-HE'Rm

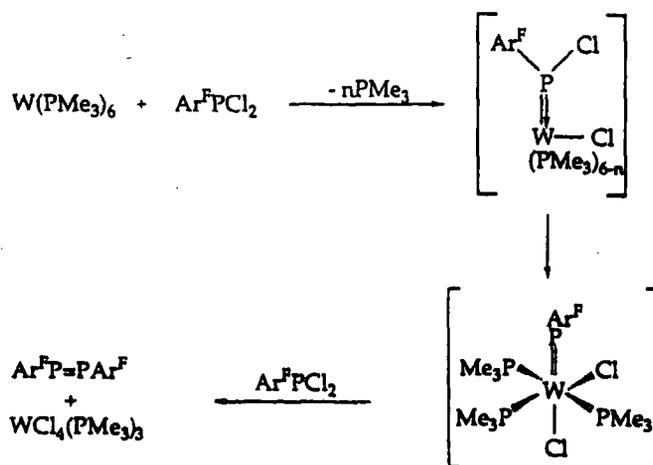
This is a widely used method to synthesise symmetrical and unsymmetrical double bond compounds between heavier main group elements.



5. Transition metal catalysed metathesis of double bonds^{24,25}



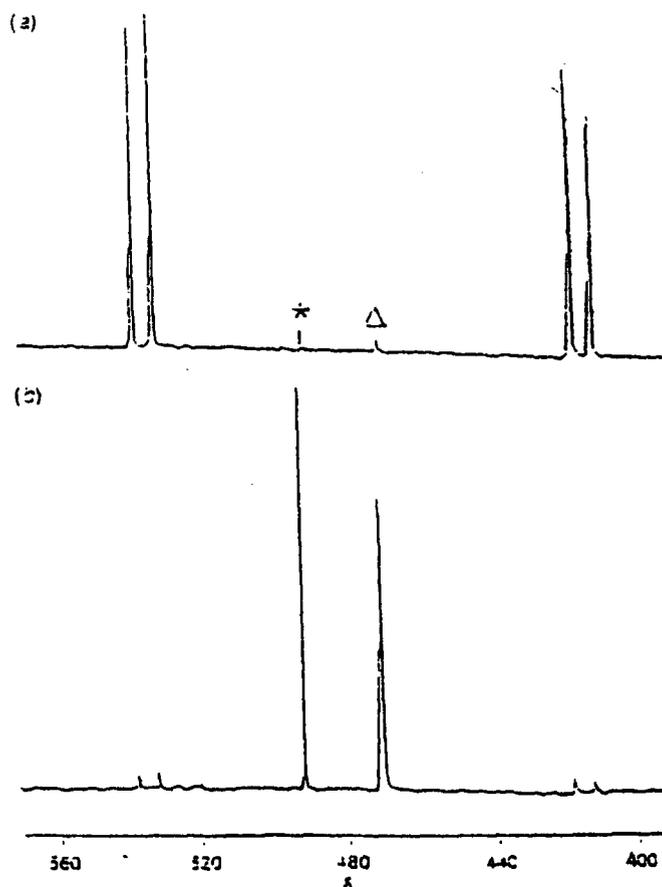
Dillon, Gibson and Sequeira used the highly reducing nature and labile coordination sphere of the zerovalent tungsten complex, $\text{W(PMe}_3)_6$,²⁶ as an efficient chloride ion abstractor; they found dichlorophosphines reacted with $\text{W(PMe}_3)_6$ in benzene at room temperature smoothly over several hours to give the diphosphene RP=PR [$\text{R} = 2,4,6$ -tris(*t*-butyl)phenyl, 2,4,6-tris(trifluoromethyl)phenyl, 2,6-bis(trifluoromethyl)phenyl] in virtually quantitative yield. The possible mechanism for formation of the symmetrical diphosphene is as follows.



The key intermediate proposed in this mechanism is the tungsten-phosphinidene complex. Although a few have been structurally characterised,²⁷⁻³⁰ doubly bonded transition metal phosphorus complexes are relatively rare.

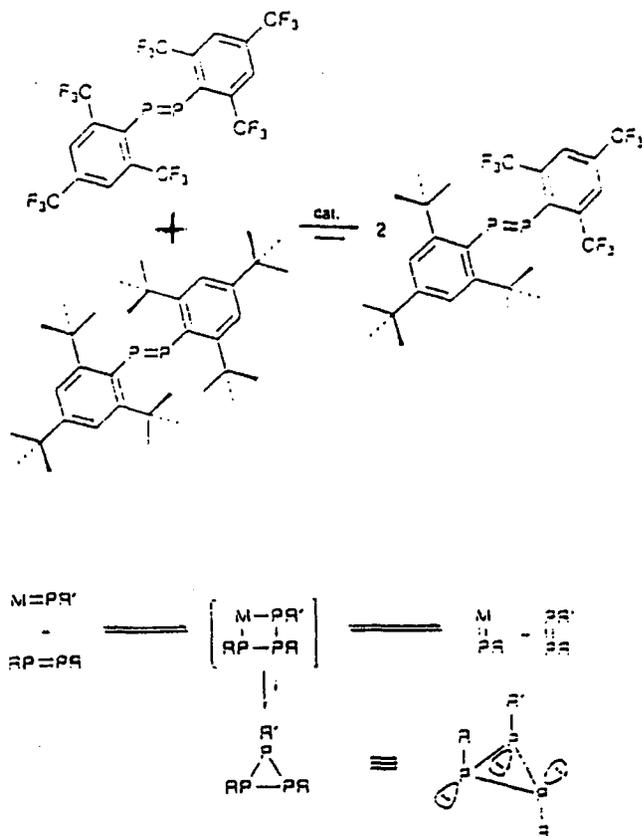
Somewhat surprisingly, when different dichlorophosphines ArPCl_2 and Ar^*PCl_2 [$\text{Ar}^* = 2,4,6\text{-tris}(\text{t-butyl})\text{phenyl}$, $\text{Ar} = 2,4,6\text{-tris}(\text{trifluoromethyl})\text{phenyl}$] reacted with $\text{W}(\text{PMe}_3)_6$, only the unsymmetrical diphosphene $\text{ArP}=\text{PAr}^*$ was produced in good yield (95%). During formation it could be seen that the symmetrical diphosphene $\text{ArP}=\text{PAr}$ formed first, which then converted to the unsymmetrical diphosphene $\text{ArP}=\text{PAr}^*$ with the Ar^*PCl_2 over a few hours.

However, more surprisingly, upon removal of the reaction solvent, the solid symmetrical diphosphenes were precipitated with the unsymmetrical signal almost lost from the ^{31}P spectrum, as shown below.



This indicates the presence of a species in solution that is able of catalysing the exchange of the diphosphene PR end-groups. The exchange does not occur in the absence of the tungsten species, since stirring a mixture of the two symmetrical

diphosphenes in benzene solution at room temperature formed none of the unsymmetrical diphosphene under these conditions. However, when a trace amount of a solution of a $W(PMe_3)_6/ArPCl_2$ mixture was added to the symmetrical diphosphenes $ArP=PAr$ and $Ar^*P=PAr^*$, they changed into the unsymmetrical diphosphene $ArP=PAr^*$. The possible mechanism for the reaction could be PR end-group exchange that involves a phosphinidene intermediate, as shown follow.



In order to isolate the unsymmetrical diphosphene, it is first necessary to destroy the catalyst. A convenient method involves treating the solution mixture with benzaldehyde, a procedure analogous to that used to kill well-defined alkylidene olefin metathesis catalysts .

This is the only route so far using different dichlorophosphines to prepare unsymmetrical diphosphenes, It is planned to do further research by this means, using different kind of R_nEC_2 ($E = P, As, n=1, E = Sn, Ge, n=2$) to try to synthesise symmetrical and unsymmetrical double bond compounds.

III. Coordination Chemistry

Because RE=E'R' compounds (E and E' are group 15 elements) possess a double bond and two unshared electron pairs, both σ and π coordination are possible to transition metals, and there is a significant number of coordination modes. For the diphosphene (as the representative) at least seven modes of coordination have been encountered to date.^{31, 32} They are shown on the next page, followed by some examples.

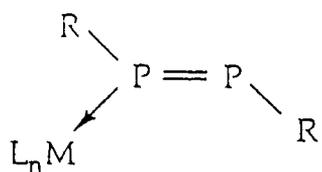
In compounds of type A the diphosphene acts as an η^1 ligand toward the metal centre. Theoretical calculations on the model compound $[\text{Cr}(\eta^1\text{-P}_2\text{H}_2)(\text{CO})_5]$ revealed that a realistic description of the ligand metal interaction involves delocalised σ -donation from the HOMO of the ligand and π -back donation of a filled metal orbital into the empty LUMO (the π^* orbital) of the ligand. The extent of the back donation is quite large and comprises 0.30 electrons.³³

The second type of coordination B comprises an η^2 -interaction of the P=P system with the metal atom. As in olefin complexes, donation from the filled π -orbital to an empty metal orbital transfers electron density from the ligand to the metal. π -back donation operates between filled metal orbitals and the LUMO (π^*) orbital of the diphosphene.

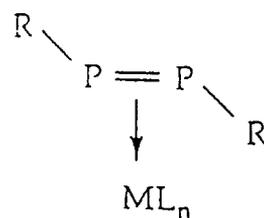
In the coordination modes C-E, a diphosphene bridges two independent metal complex fragments. In C this is achieved by two η^1 interaction, whereas in types D and E coordination is a combination of η^1 and η^2 modes.

In type F the diphosphene is incorporated into a butterfly molecule, whereas G is a representative of a cluster compound with a diphosphene building block. Other types of complexes with such a bonding situation are conceivable.

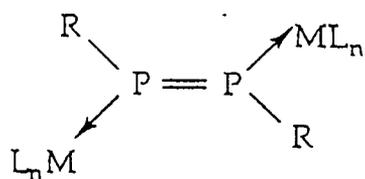
There are two main synthetic pathways which lead to diphosphene complexation. Firstly, a diphosphene ligand can be added to a coordinatively unsaturated complex or



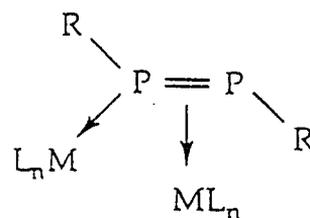
A (η^1)



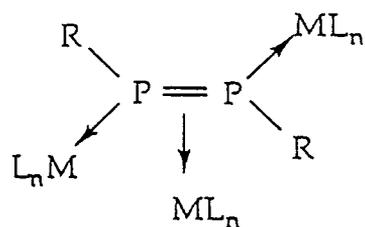
B (η^2)



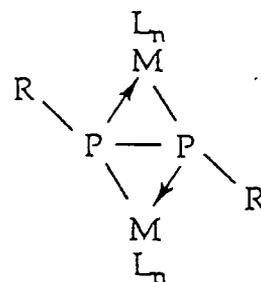
C (η^1, η^1)



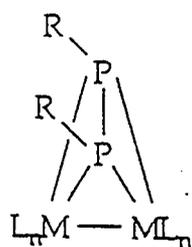
D (η^1, η^2)



E (η^1, η^1, η^2)



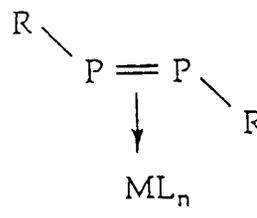
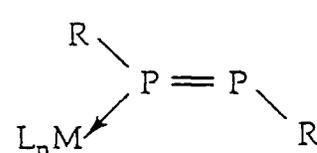
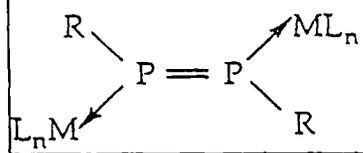
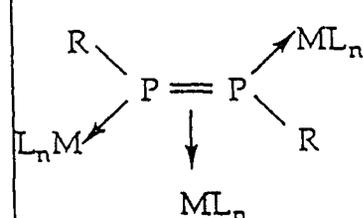
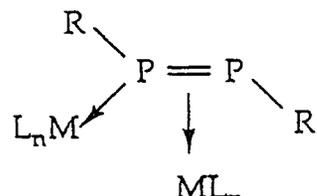
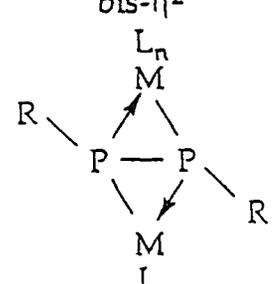
F ($\mu_2(\eta^2, \eta^2)$)



G ($\mu_2(\eta^2, \eta^2)(M-M)$)

Co-ordination Modes of Diphosphene Ligands

The co-ordination modes of diphosphenes.

	ML_n	R	ref
η^2 	$Mo(\eta^5-C_5H_5)_2$ $Pt(PPh_3)_2$ $Ni(PEt_3)_2$ $Pd(dppe)$ $Ni[R'_4P_2(CH_2)_2]$ $Ni(nBu_3)_2$ $Ni(PMe_3)_2, Ni(PEt_3)_2$ $TaCp_2H$	H C_6F_5 $SiMe_3$ C_6H_5 Me, tBu , Ph Supermes, $tBuN(H)$ $SiMe_3, CMe_3, Ph, Me$ Ph	34 34 34 34 35 36 37 38
η^1 	$Cr(CO)_5$ $Mo(CO)_5$ $W(CO)_5$ $Ni(CO)_3$ $Fe(CO)_4$	Supermes, mes, $(Me_3Si)_2CH$ Supermes, mes Supermes, mes Supermes, RNH Supermes	39 40 39 39 41 41
bis- η^1 	$Fe(CO)_4$ $V(\eta^5-C_5H_5)(CO)_3$ $Cr(CO)_5$	$(Me_3Si)_2CH, Me_3Si_2N,$ mes mes Ph	42 43 44
bis- $\eta^1\eta^2$ 	$Cr(CO)_5$ $W(CO)_5$	Ph, tBu, nBu Ph	44 46 45
$\eta^1\eta^2$ 	$Fe(CO)_4$	OSupermes, Ph, $Me_2C_2PN_2$	40 47 48
bis- η^2 	$Mo(CO)_2(\eta^5-C_5H_5)$ $1/2Fe_2(CO)_6$	Ph, $(Me_3Si)_2CH$ tBu	49 50 51

may replace labile ligands in suitable coordination compounds. Secondly, the diphosphene ligand may be constructed from easily available and stable precursors in the coordination sphere of an organometallic complex. This method implies that the stability of the free diphosphene is not a prerequisite for its existence as a ligand in stable complexes.

IV. Synthesis of new main group element compounds with bulky electron-withdrawing substituents

1. Bulky and electron-withdrawing Ligands

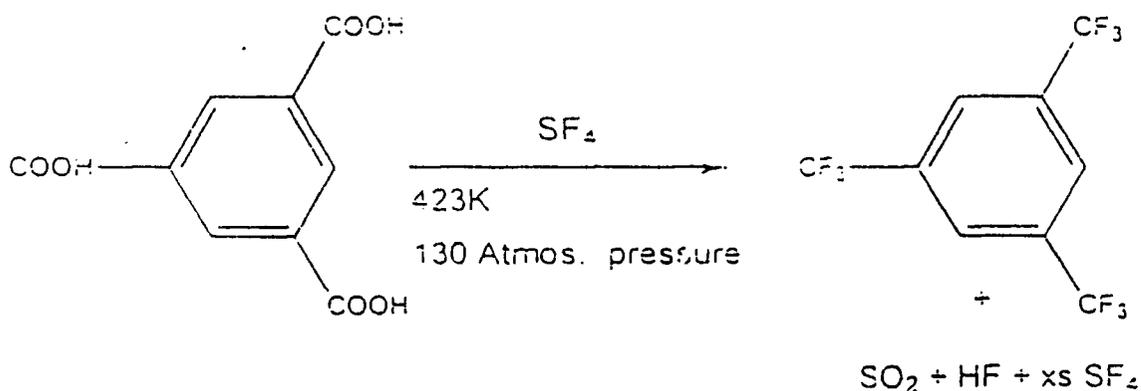
The 2,4,6-tris(trifluoromethyl)phenyl substituent and 2,6-bis(trifluoro-methyl)-phenyl substituent, (Ar and Ar' respectively) are unique amongst all other sterically demanding ligands used so far in the stabilisation of low coordination main group derivatives.⁵²⁻⁵³ A combination of stabilising factors contributes to the unusual stability of Ar derivatives. Sterically, these ligands are not significantly more bulky than 2,4,6-trimethylphenyl and 2,6-dimethylphenyl, certainly less bulky than 2,4,6-tri-'butyl-phenyl and 2,6-di-'butylphenyl. In contrast to most other sterically demanding ligands, however, Ar and Ar' are strongly electron-withdrawing, and therefore should be able to stabilise low oxidation states and consequently low coordination number complexes. Equally important is the potential of the ortho CF₃ groups to form weak interactions with the main group atom, thus blocking possible coordination sites and hence reducing any tendency for the formation of high nuclearity species. This is witnessed by the unusually high stability often encountered in main group Ar derivatives.^{29, 54}

2. Synthesis of 2,4,6-tris(trifluoromethyl)benzene and its lithium derivative, and 2,6-bis(trifluoromethyl)phenyl lithium

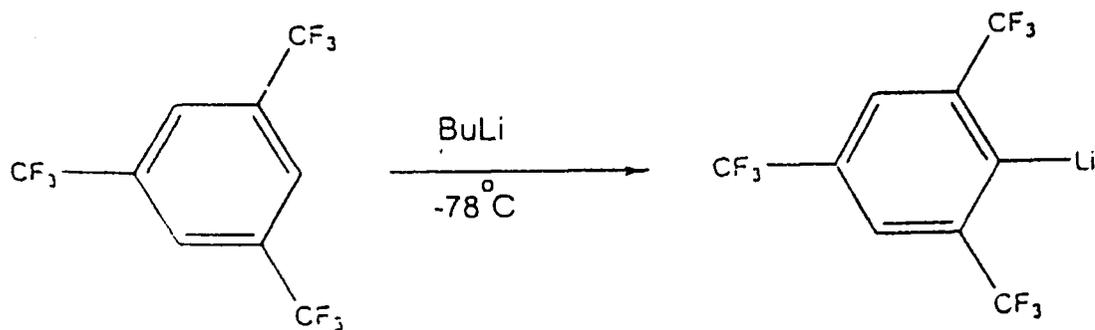
Now commercial 2,6-bis(trifluoromethyl)benzene Ar'H is available, but it has rarely been used as a ligand in main group chemistry, with only two examples found by Roden in the Cambridge structural database⁵⁵. The first is a chromacene analogue containing two Ar' species in a sandwich complex with chromium⁵⁶. The second is

the only substituted example, the diphosphene $\text{Ar}^*\text{P}=\text{PAr}^*$.⁵⁷ So it is interesting to research variation of the 2,6-bis(trifluoromethyl)phenyl substituent and its coordination chemistry.

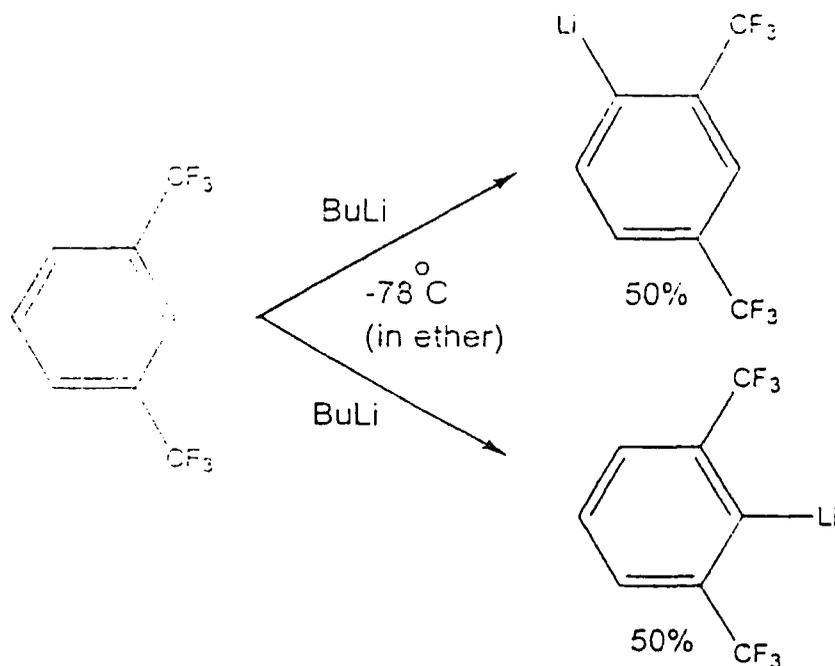
2,4,6-tris(trifluoromethyl)benzene ArH was first prepared in 1947 by McBee and Leech⁵⁸. The modern synthesis for ArH was first described by Chambers et al⁵⁹, involving the reaction of SF_4 and the commercially available trimesic acid [$\text{C}_6\text{H}_3(\text{COOH})_3$] (yield 33%). This method was then subsequently improved dramatically by Edelman et al,⁶⁰ increasing the yield of the reaction to 95%.



The ready availability of the parent fluorocarbon in large quantities has resulted in the rapid development of its derivative chemistry. ArH could be lithiated by treatment with *n*-butyllithium in diethylether;^{59,60} the product 2,4,6-tris-(trifluoromethyl)phenyllithium, (ArLi), is the key precursor to other main group compounds which contain Ar substituents.



Because the aryl ring of 2,6-bis(trifluoromethyl)benzene is not symmetrical, there is more than one potential lithiation site upon reaction with BuLi, as shown below.



^{19}F NMR studies on the reaction mixture formed in the reaction of BuLi and $\text{Ar}'\text{H}$ ⁵⁵ have shown that the ratio of species I ($\text{Ar}'\text{Li}$) to species II ($\text{Ar}''\text{Li}$) is approximately 50:50; however, once this mixture has been reacted with PCl_3 the ratio of products ($\text{PAr}'\text{Cl}_2$: $\text{PAr}''\text{Cl}_2$) is approximately 2:1;⁵⁵ The same ratio of products ($\text{SnAr}'_2\text{Cl}_2$: $\text{SnAr}''_2\text{Cl}_2$) is formed if $\text{Ar}'\text{Li}$ is reacted with SnCl_4 , but if it reacts with GeCl_4 , $\text{GeAr}''_2\text{Cl}_2$ is the main product (90%); with SiCl_4 , similar to Ge, $\text{SiAr}''_2\text{Cl}_2$ is the main product; in reaction with AsCl_3 , however, the ratio of products $\text{Ar}'_2\text{AsCl}$: $\text{Ar}''_2\text{AsCl}$: $\text{Ar}'\text{Ar}''\text{AsCl}$ is almost 1:1:1. This will be discussed in more detail in section V-6.

3. Syntheses of $\text{ER}_{1-2}\text{Cl}_{1-3}$ ($\text{R}=\text{Ar}, \text{Ar}', \text{Ar}''$; $\text{E}=\text{P}, \text{As}, \text{Sn}, \text{Ge}, \text{Si}$)

In recent years there has been considerable and growing interest in the bulky, highly electron-withdrawing 2,4,6-tris(trifluoromethyl)phenyl and 2,6-bis(trifluoromethyl)phenyl ligands for their ability to stabilise low valent, low coordinate main group compounds, examples of which include compounds of metalloids elements such as Ga,⁶¹ Sn⁶², Pb⁶³, Bi⁶⁴, As⁶⁰, Sb^{65,66}, B⁶⁶ and Si⁶⁵.

In this group much work has been done with Ar or Ar' as substituents on phosphorus. Goodwin⁶⁶ has synthesised ArPCl₂, ArPF₂, ArPH₂, ArP(CN)₂, ArPHCl, Ar₂PCl, Ar₂PH, ArP=PAR, ArBCl₂, Ar₂BCl, Ar₃B and some transition metal derivatives, while Roden⁵⁵ prepared Ar'PCl₂, Ar'PF₂, Ar'PH₂, Ar'PBr₂ and Ar''PCl₂, as well as Ar'₂PCl and Ar'₂PH. Sequeira²⁴ has made several transition metal complexes, such as Mo(NBu)₂Ar₂, Cr(NAd)₂Ar₂, VAr₂Cl(thf) and CrAr₂(PMe₃)₂. Roden also used [PtCl₂PEt₃]₂ in a direct reaction with Ar'-substituted species to prepare platinum complexes [Ar'PCl₂-PtCl₂PEt₃], [Ar'PF₂-PtCl₂PEt₃] and [Ar'PH₂-PtCl₂PEt₃].

Very little has been reported about other main group derivatives of groups 14 and 15 with Ar', Ar or Ar'' and halide substituents. The only known compounds are SiAr₂Cl₂ prepared by Buijink⁶⁵, AsAr₂Cl synthesised by Straw⁶⁷, and ArSbCl₂ and Ar₂SbCl prepared by Goodwin⁶⁶ of this group, but no crystal structure has been described so far.

The general method described by Fjelderg et al⁶⁸ has been used in this work, with a heavier metal chloride reacting directly with ArLi or Ar'Li (a mixture of Ar'Li and Ar''Li) at low temperature, then being allowed to warm to room temperature with stirring being continued for a few hours; the products are separated by filtration and removal of solvent. Experimental detail is in the next section.

V. Experimental

1. General Procedures.

All manipulations were carried out by using modified Schlenk techniques under an atmosphere of dry N₂ or in a glove box. All solvents were dried and purified by standard methods, or a special dry solvent was treated with Na wire and 4A molecular sieve. Commercial SnCl₄, GeCl₄, SiCl₄, PCl₃ and AsCl₃ were used without further purification.

2. Synthesis of ArLi, Ar'Li and Ar''Li

Using Goodwin's⁶⁶ and Roden's⁵⁵ methods, ArH was directly reacted with BuLi hexane solution (2.5M) at low temperature (-78 °C) in diethyl ether solvent to produce ArLi. When Ar'H reacts with BuLi under the same condition, a mixture of Ar'Li and Ar''Li is formed.

3. Synthesis of PRCl₂, AsArCl₂, AsR₂Cl, SnR₂Cl₂, GeR₂Cl₂, GeArCl₃, SiR₂Cl₂ (R=Ar, Ar' or Ar'')

a. R₂PCl₂ (R=Ar, Ar' and Ar'')

Similar to Goodwin's and Roden's methods, an ArLi solution (prepared by the described methods) was reacted with PCl₃ in diethyl ether solution at -78 °C, giving a mixture of ArPCl₂ and Ar₂PCl. The precipitated LiCl was then filtered off, and pure ArPCl₂ was obtained by distillation of the mixture. Identical routes were used to synthesise the mixture of Ar'PCl₂ and Ar''PCl₂.

b. AsArCl₂ and AsAr₂Cl

4.35g AsCl₃ (24mmol) and 45ml pentane were introduced into a flask under dry nitrogen protection, and the flask was cooled to almost freezing the solution by a cardice/acetone slush bath with high speed stirring. ArLi-diethyl ether solution (20mmol, about 50 ml) was slowly transferred into the AsCl₃ solution under N₂ pressure (about 20 minutes), then the mixture was allowed to warm to room temperature and stirring continued for about two hours. During this time the colour changed and some white solid formed. The solution was then filtered and the solvent and excess AsCl₃ were removed in vacuo, leaving a yellow sticky oil. This oil was distilled under vacuum, and fractions collected at 80-90 °C and 110-120 °C, giving 1.5g AsArCl₂ (oil) and 1.8g AsAr₂Cl (solid). Elemental analysis: AsArCl₂: Calculated: C, 25.3%; H, 0.47%. AsAr₂Cl: C, 32.2%, H, 0.60%. Found: AsArCl₂: C, 24.1%, H, 1.16%. AsAr₂Cl: C, 31.6%, H, 0.98%

c. AsAr₂Cl

4.35g AsCl₃ (24mmol) and 45ml pentane were placed into a flask under dry nitrogen protection, and the flask was cooled to nearly freeze the solution by a cardice/acetone slush bath with high speed stirring. Ar'Li-diethyl ether solution (20mmol, about 50 ml) was slowly transferred into the AsCl₃ solution under N₂ pressure (about 20 minutes), then the mixture was allowed to warm to room temperature and stirring continued for about 3 hours. During the time the colour changed and some white solid formed. The solution was then filtered and the solvent and excess AsCl₃ were removed in vacuo, leaving a black sticky oil. This oil was distilled under vacuum, and the fraction boiling at 110-120 °C collected, giving 3.4g product (solid), yield 31.7%. Elemental analysis: Calculated C, 35.8%; H, 1.13%. Found: C, 35.7%, H, 1.22%.

d. GeAr₂Cl₂ and GeArCl₃

3.22g GeCl₄ (15mmol) and 50ml pentane were placed in a flask under dry nitrogen protection, and the flask was cooled to -78°C by a cardice/acetone slush bath with high speed stirring. ArLi-diethyl ether solution (30mmol, about 50 ml) was slowly transferred into the GeCl₄ solution under N₂ pressure (about 10 minutes), then the mixture was allowed to warm to room temperature and stirring continued overnight. During this time the colour changed and some white solid formed. The solution was then filtered and the solvent was removed in vacuo, leaving a yellow sticky oil. This oil was distilled under vacuum, and the fractions boiling around 85 °C and 120 °C collected, yielding 2.6g and 1.2g respectively. The 85 °C product corresponds to GeArCl₃ and the 120 °C fraction to GeAr₂Cl₂. Elemental analysis: GeArCl₃: Calculated C, 23.5%; H, 0.44%. Found: C, 24.1%, H, 1.16%. GeAr₂Cl₂: Calculated C, 30.6%; H, 0.57%. Found: C, 28.9%, H, 1.52%. After one month, fine crystals formed in the GeArCl₃, which were taken for structure analysis; at the same time, very small crystals were found in the GeAr₂Cl₂, but unfortunately they were not suitable for X-ray structure analysis.

e. GeAr₂Cl₂

4.29g GeCl₄ (20mmol) and 55ml diethyl ether were placed into a flask under dry nitrogen protection, and the flask was cooled to -78 °C by a cardice/acetone slush bath, with high speed stirring. Ar'Li-diethyl ether solution (40mmol, about 60 ml)

was slowly transferred into the GeCl_4 solution under N_2 pressure in 10 minutes, then the mixture was allowed to warm to room temperature and stirring continued for about 2 hours. During this time the colour changed and some solid formed. The solution was then filtered and the solvent was removed in vacuo, leaving a black sticky oil. This oil was distilled under vacuum, and the fraction boiling at $80\text{-}90^\circ\text{C}$ collected, giving 5.8g product, yield 51%. Elemental analysis: Calculated C, 33.7%; H, 1.06%, Cl, 12.5%. Found: C, 32.4%, H, 1.53%, Cl, 12.8%. After one week, small crystals formed, which were taken for structure analysis.

f. SnAr_2Cl_2

2.6g SnCl_4 (10mmol) and 45ml pentane were placed into a flask under dry nitrogen protection, and the flask was cooled to -78°C by a cardice/acetone slush bath with high speed stirring. ArLi -diethyl ether solution (20mmol, about 50 ml) was slowly transferred into the SnCl_4 solution under N_2 pressure in 20 minutes, then the mixture was allowed to warm to room temperature and stirring continued for about 3 hours. During this time the colour changed and some white solid formed. The solution was then filtered, the solvent was removed under vacuum, and the volume was reduced to 10 ml. The yellow white solid which formed, was filtered off in vacuo, washed three times with 8ml pentane and dried in vacuo, giving 3.8g SnAr_2Cl_2 , yield 51%. Elemental analysis: Calculated C, 28.8%; H, 0.53%. Found: C, 28.2%, H, 1.11%. A small amount of the product was dissolved in diethyl ether solution, and placed in the fridge overnight, producing nice colourless crystals for structure analysis.

g. $\text{SnAr}'_2\text{Cl}_2$

2.6 g SnCl_4 (10mmol) and 35 ml diethyl ether were introduced into a flask under dry nitrogen protection, and the flask was cooled to nearly -78°C by a cardice/acetone slush bath with high speed stirring. $\text{Ar}'\text{Li}$ -diethyl ether solution (20mmol, about 50 ml) was slowly transferred into the SnCl_4 solution under N_2 pressure in 15 minutes, then the mixture was allowed to warm to room temperature and stirring continued overnight. During this time the colour changed and some white solid formed. The lithium salts were filtered off under nitrogen and the solution concentrated to 10ml under vacuum, forming a sticky solid. 5 ml pentane was added and a clear solid formed, which was filtered off, washed 3 time with a small quantity of pentane and dried under vacuum, yield 3.48g (57%). Elemental analysis: Calculated C, 31.21%; H,

0.98%. Found: C, 29.7%, H, 1.26%. A small quantity was dissolved in diethyl ether, or in a mixture of diethyl ether and pentane, and placed in the fridge overnight, yielding nice colourless crystals in the mixed solvent and small crystals in diethyl ether, both of which were taken for structure analysis.

h. SiAr₂Cl₂

1.7g SiCl₄ (10mmol) and 35ml pentane were introduced into a flask under dry nitrogen protection, and the flask was cooled to -70 °C by a cardice/acetone slush bath with high speed stirring. ArLi-diethyl ether solution (20mmol, about 50 ml) was slowly transferred into the SiCl₄ solution under N₂ pressure (about 20 minutes), then the mixture was allowed to warm to room temperature and stirring continued overnight. During this time the colour changed and some white solid formed. The solution was then filtered and the solvent was removed in vacuo, leaving a yellow sticky oil. This oil was distilled under vacuum, and a fraction collected at 110-120 °C, giving 1.6g SiAr₂Cl₂, yield 23.5% Elemental analysis: SiAr₂Cl₂: Calculated: C, 32.7%; H, 0.61%. Found: C, 32.0%, H, 0.93%.

i. SiAr''₂Cl₂

1.7g SiCl₄ (10mmol) and 40ml pentane were introduced into a flask at dry nitrogen protection, and the flask was cooled to -70 °C by a cardice/acetone slush bath with high speed stirring. Ar'Li-diethyl ether solution (20mmol, about 50 ml) was slowly transferred into the SiCl₄ solution under N₂ pressure (about 20 minutes), then the mixture was allowed to warm to room temperature and stirring continued for about 3 hours. During this time the colour changed and some white solid formed. The solution was then filtered and the solvent was removed in vacuo, leaving a black sticky oil. This oil was distilled under vacuum, and fractions collected at 120 °C and giving 1.8g product, yield 32.4%. Elemental analysis: SiAr''₂Cl₂: Calculated: C, 36.6%; H, 1.15%. Found: C, 36.8%, H, 1.24%. After a few days, very small crystals were found, which were taken for crystal structure analysis.

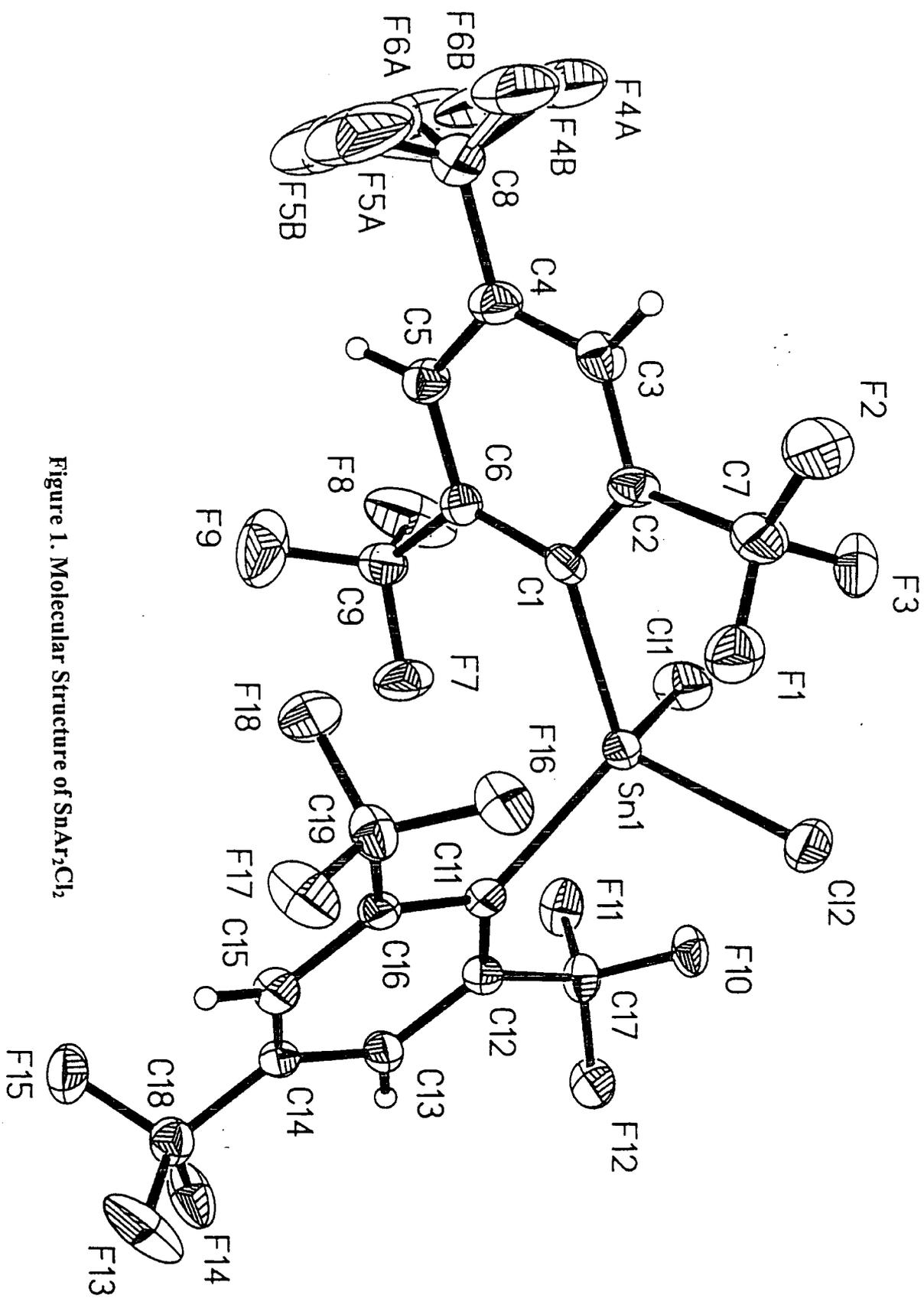


Figure 1. Molecular Structure of SnAr_2Cl_2 .

Table 1. Key bond lengths and angles of SnAr₂Cl₂

Sn(1)-C(11)	2.181(6)	C(9)-F(9)	1.314(8)
Sn(1)-C(1)	2.195(6)	C(9)-F(8)	1.321(9)
Sn(1)-Cl(2)	2.2977(17)	C(9)-F(7)	1.325(8)
Sn(1)-Cl(1)	2.3259(18)	C(11)-C(12)	1.395(8)
C(1)-C(2)	1.403(9)	C(11)-C(16)	1.401(8)
C(1)-C(6)	1.411(9)	C(12)-C(13)	1.389(9)
C(2)-C(3)	1.385(9)	C(12)-C(17)	1.517(8)
C(2)-C(7)	1.503(9)	C(13)-C(14)	1.395(8)
C(3)-C(4)	1.391(9)	C(14)-C(15)	1.386(9)
C(4)-C(5)	1.375(9)	C(14)-C(18)	1.511(9)
C(4)-C(8)	1.487(7)	C(15)-C(16)	1.378(9)
C(5)-C(6)	1.386(9)	C(16)-C(19)	1.506(9)
C(6)-C(9)	1.508(9)	C(17)-F(11)	1.323(8)
C(7)-F(3)	1.340(9)	C(17)-F(12)	1.330(7)
C(7)-F(2)	1.343(8)	C(17)-F(10)	1.353(7)
C(7)-F(1)	1.347(8)	C(18)-F(13)	1.311(8)
C(8)-F(4A)	1.3330	C(18)-F(14)	1.320(8)
C(8)-F(5A)	1.3330	C(18)-F(15)	1.337(8)
C(8)-F(5B)	1.3331	C(19)-F(17)	1.328(8)
C(8)-F(6B)	1.3331	C(19)-F(16)	1.352(7)
C(8)-F(4B)	1.3331	C(19)-F(18)	1.358(8)
C(8)-F(6A)	1.3332		
C(11)-Sn(1)-C(1)	120.3(2)	C(1)-C(2)-C(7)	121.5(6)
C(11)-Sn(1)-Cl(2)	103.80(17)	C(2)-C(3)-C(4)	120.3(6)
C(1)-Sn(1)-Cl(2)	118.94(16)	C(5)-C(4)-C(3)	118.4(6)
C(11)-Sn(1)-Cl(1)	113.89(17)	C(5)-C(4)-C(8)	120.6(6)
C(1)-Sn(1)-Cl(1)	96.14(17)	C(3)-C(4)-C(8)	121.0(6)
Cl(2)-Sn(1)-Cl(1)	102.58(7)	C(4)-C(5)-C(6)	121.3(6)
C(2)-C(1)-C(6)	115.4(6)	C(5)-C(6)-C(1)	121.9(6)
C(2)-C(1)-Sn(1)	125.0(5)	C(5)-C(6)-C(9)	113.7(5)
C(6)-C(1)-Sn(1)	119.4(4)	C(1)-C(6)-C(9)	124.4(6)
C(3)-C(2)-C(1)	122.7(6)	F(3)-C(7)-F(2)	106.7(6)
C(3)-C(2)-C(7)	115.8(6)	F(3)-C(7)-F(1)	107.5(6)

F(2)-C(7)-F(1)	106.3(6)	C(12)-C(11)-Sn(1)	123.5(4)
F(3)-C(7)-C(2)	111.3(6)	C(16)-C(11)-Sn(1)	120.2(4)
F(2)-C(7)-C(2)	112.9(6)	C(13)-C(12)-C(11)	122.5(6)
F(1)-C(7)-C(2)	111.8(6)	C(13)-C(12)-C(17)	114.4(5)
F(4A)-C(8)-F(5A)	106.9	C(11)-C(12)-C(17)	123.1(5)
F(4A)-C(8)-F(5B)	134.6	C(12)-C(13)-C(14)	119.2(6)
F(5A)-C(8)-F(5B)	39.7	C(15)-C(14)-C(13)	119.8(6)
F(4A)-C(8)-F(6B)	73.5	C(15)-C(14)-C(18)	119.6(6)
F(5A)-C(8)-F(6B)	133.6	C(13)-C(14)-C(18)	120.6(6)
F(5B)-C(8)-F(6B)	106.8	C(16)-C(15)-C(14)	119.6(6)
F(4A)-C(8)-F(4B)	37.9	C(15)-C(16)-C(11)	122.7(6)
F(5A)-C(8)-F(4B)	70.9	C(15)-C(16)-C(19)	116.3(5)
F(5B)-C(8)-F(4B)	106.9	C(11)-C(16)-C(19)	121.0(5)
F(6B)-C(8)-F(4B)	106.8	F(11)-C(17)-F(12)	108.0(5)
F(4A)-C(8)-F(6A)	106.8	F(11)-C(17)-F(10)	106.8(5)
F(5A)-C(8)-F(6A)	106.9	F(12)-C(17)-F(10)	106.0(5)
F(5B)-C(8)-F(6A)	71.4	F(11)-C(17)-C(12)	112.9(5)
F(6B)-C(8)-F(6A)	37.5	F(12)-C(17)-C(12)	111.2(5)
F(4B)-C(8)-F(6A)	129.2	F(10)-C(17)-C(12)	111.5(5)
F(4A)-C(8)-C(4)	111.2(3)	F(13)-C(18)-F(14)	108.3(6)
F(5A)-C(8)-C(4)	112.1(3)	F(13)-C(18)-F(15)	106.5(6)
F(5B)-C(8)-C(4)	110.8(3)	F(14)-C(18)-F(15)	106.4(6)
F(6B)-C(8)-C(4)	110.4(3)	F(13)-C(18)-C(14)	112.6(6)
F(4B)-C(8)-C(4)	114.7(3)	F(14)-C(18)-C(14)	112.6(5)
F(6A)-C(8)-C(4)	112.6(3)	F(15)-C(18)-C(14)	110.1(5)
F(9)-C(9)-F(8)	106.3(6)	F(17)-C(19)-F(16)	107.1(5)
F(9)-C(9)-F(7)	107.2(6)	F(17)-C(19)-F(18)	106.3(5)
F(8)-C(9)-F(7)	105.9(6)	F(16)-C(19)-F(18)	105.5(5)
F(9)-C(9)-C(6)	112.1(6)	F(17)-C(19)-C(16)	113.3(5)
F(8)-C(9)-C(6)	111.0(5)	F(16)-C(19)-C(16)	111.8(5)
F(7)-C(9)-C(6)	113.9(5)	F(18)-C(19)-C(16)	112.3(5)
C(12)-C(11)-C(16)	116.1(5)		

2 Molecular Structure of $\text{SnAr}'_2\text{Cl}_2$

The molecule structures determined from the different solvents are very similar. The first molecular crystal structure, and data of key bond distances and angles, are given in figure 2 and table 2. The second is detailed in appendix 2. Data were collected and the structure was solved by Dr. A. Goeta of Durham University.

This compound possesses a pseudo-tetrahedral geometry with C-Sn-C and Cl-Sn-Cl, angles of 116.4° and 101.3° respectively, while C-Sn-Cl angles are 101.4° , 98.5° , 120.2° and 119.5° . Similar to complex SnAr_2Cl_2 , since Ar' is also a bulky group and there are interactions between F of Ar' and Sn, the ligands need to minimise steric interactions, thus causing deviations from regular tetrahedral geometry. The C-Sn-Cl angles are again not identical, possibly because of Sn-F interactions.

The C-Sn distances are 2.178\AA and 2.203\AA , while Sn-Cl bond lengths are 2.321\AA and 2.341\AA . Compared with SnAr_2Cl_2 , the average C-Sn distance is very similar (2.190\AA and 2.188\AA respectively); the average Sn-Cl distance is also similar to that in $\text{SnAr}'_2\text{Cl}_2$ (2.331\AA and 2.312\AA respectively), because there are two $-\text{CF}_3$ groups ortho to Sn in both complexes. It is known that SnAr_2 has a pseudo-sandwich geometry with a Sn-C bond of 2.278\AA ⁶²; this bond is longer than that of SnAr_2Cl_2 and $\text{SnAr}'_2\text{Cl}_2$.

An interesting observation is that $\text{Ar}'\text{Li}$ is known to be a mixture of $\text{Ar}'\text{Li}$ and $\text{Ar}''\text{Li}$ (50:50), although the structure of the product of PCl_3 with $\text{Ar}'\text{Li}$ shows that it is $\text{Ar}'\text{Ar}''\text{PCl}$.⁵⁵ Here the crystal structure shows the product is $\text{SnAr}'_2\text{Cl}_2$. These points are discussed further in section 6.

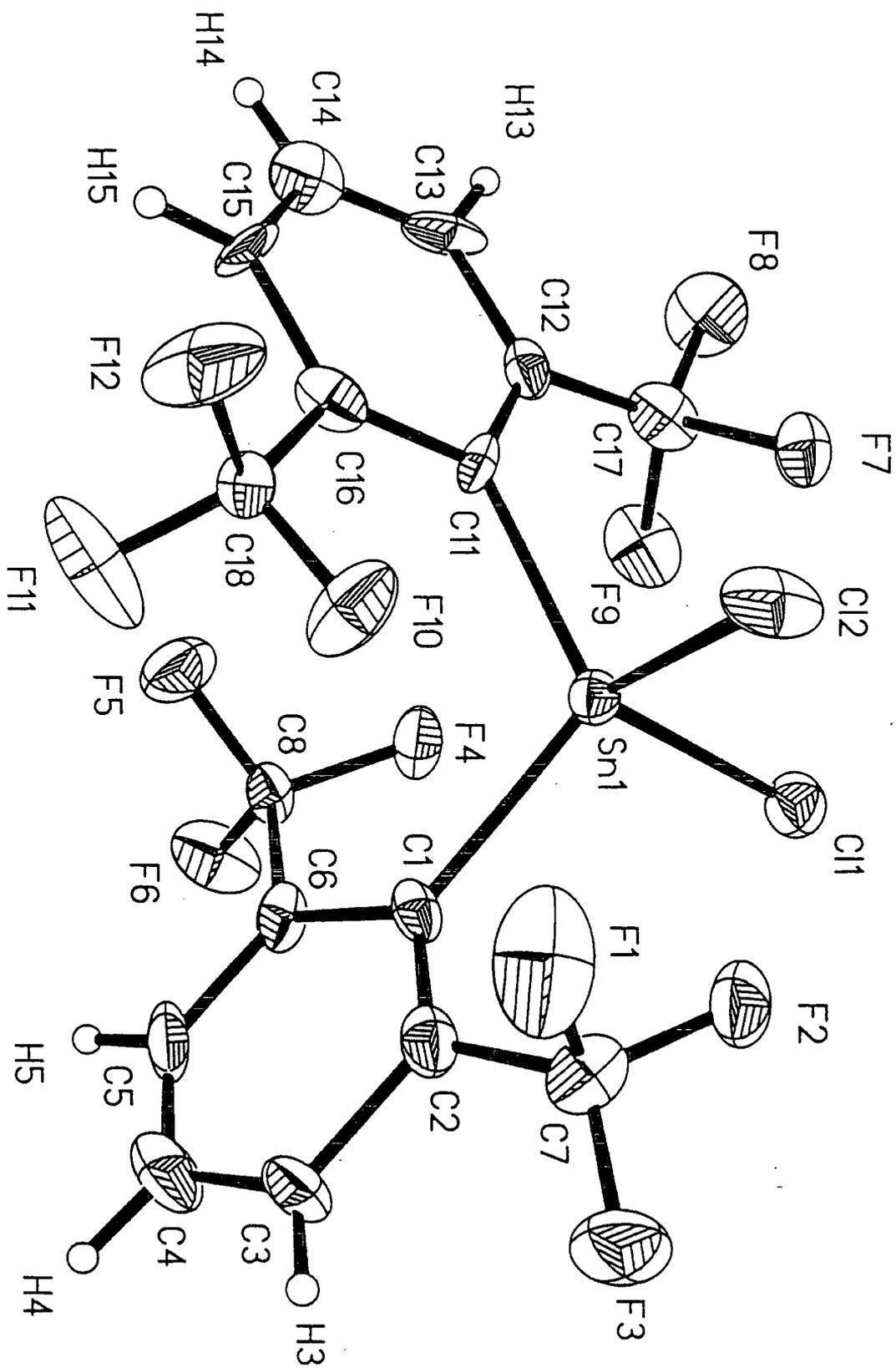


Figure 2. Molecular Structure of SnAr_2Cl_2

Table 2. Key bond lengths and angles of SnAr₂Cl₂

Sn(1)-C(11)	2.178(8)
Sn(1)-C(1)	2.203(7)
Sn(1)-Cl(1)	2.321(3)
Sn(1)-Cl(2)	2.341(2)
C(1)-C(2)	1.325(12)
C(1)-C(6)	1.466(11)
C(2)-C(3)	1.483(12)
C(2)-C(7)	1.543(13)
C(3)-C(4)	1.413(15)
C(3)-H(3)	0.9300
C(4)-C(5)	1.327(16)
C(4)-H(4)	0.9300
C(5)-C(6)	1.366(12)
C(5)-H(5)	0.9300
C(6)-C(8)	1.516(12)
C(7)-F(3)	1.287(12)
C(7)-F(2)	1.335(12)
C(7)-F(1)	1.393(13)
C(8)-F(6)	1.322(10)
C(8)-F(5)	1.328(11)
C(8)-F(4)	1.365(8)
C(11)-C(12)	1.358(12)
C(11)-C(16)	1.413(12)
C(12)-C(13)	1.401(13)
C(12)-C(17)	1.488(13)
C(13)-C(14)	1.334(15)
C(13)-H(13)	0.9300
C(14)-C(15)	1.360(14)
C(14)-H(14)	0.9300
C(15)-C(16)	1.440(12)
C(15)-H(15)	0.9300
C(16)-C(18)	1.584(12)
C(17)-F(8)	1.332(11)
C(17)-F(9)	1.364(12)
C(17)-F(7)	1.409(11)

C(13)-F(12)	1.310(10)
C(18)-F(10)	1.316(12)
C(18)-F(11)	1.326(10)

C(11)-Sn(1)-C(1)	116.4(3)
C(11)-Sn(1)-Cl(1)	119.5(2)
C(1)-Sn(1)-Cl(1)	101.4(2)
C(11)-Sn(1)-Cl(2)	98.5(2)
C(1)-Sn(1)-Cl(2)	120.2(2)
Cl(1)-Sn(1)-Cl(2)	101.03(11)
C(2)-C(1)-C(6)	117.7(7)
C(2)-C(1)-Sn(1)	123.9(6)
C(6)-C(1)-Sn(1)	118.4(6)
C(1)-C(2)-C(3)	122.7(8)
C(1)-C(2)-C(7)	126.2(8)
C(3)-C(2)-C(7)	111.1(8)
C(4)-C(3)-C(2)	116.1(9)
C(4)-C(3)-H(3)	121.9
C(2)-C(3)-H(3)	122.0
C(5)-C(4)-C(3)	120.4(9)
C(5)-C(4)-H(4)	119.8
C(3)-C(4)-H(4)	119.8
C(4)-C(5)-C(6)	124.1(9)
C(4)-C(5)-H(5)	118.0
C(6)-C(5)-H(5)	118.0
C(5)-C(6)-C(1)	118.9(9)
C(5)-C(6)-C(8)	119.6(8)
C(1)-C(6)-C(8)	121.4(7)
F(3)-C(7)-F(2)	107.7(9)
F(3)-C(7)-F(1)	112.9(9)
F(2)-C(7)-F(1)	103.5(8)
F(3)-C(7)-C(2)	115.7(8)
F(2)-C(7)-C(2)	110.8(8)
F(1)-C(7)-C(2)	105.6(8)
F(6)-C(8)-F(5)	109.8(7)
F(6)-C(8)-F(4)	105.3(6)

F(5)-C(8)-F(4)	108.1(6)
F(6)-C(8)-C(6)	110.3(7)
F(5)-C(8)-C(6)	112.6(7)
F(4)-C(8)-C(6)	110.4(6)
C(12)-C(11)-C(16)	113.7(8)
C(12)-C(11)-Sn(1)	128.0(6)
C(16)-C(11)-Sn(1)	118.3(6)
C(11)-C(12)-C(13)	124.5(8)
C(11)-C(12)-C(17)	120.4(8)
C(13)-C(12)-C(17)	115.0(8)
C(14)-C(13)-C(12)	120.8(8)
C(14)-C(13)-H(13)	119.6
C(12)-C(13)-H(13)	119.6
C(13)-C(14)-C(15)	119.4(9)
C(13)-C(14)-H(14)	120.3
C(15)-C(14)-H(14)	120.3
C(14)-C(15)-C(16)	119.2(8)
C(14)-C(15)-H(15)	120.4
C(16)-C(15)-H(15)	120.4
C(11)-C(16)-C(15)	122.0(8)
C(11)-C(16)-C(18)	123.3(8)
C(15)-C(16)-C(18)	114.7(8)
F(8)-C(17)-F(9)	105.6(8)
F(8)-C(17)-F(7)	105.5(8)
F(9)-C(17)-F(7)	103.0(8)
F(8)-C(17)-C(12)	115.9(9)
F(9)-C(17)-C(12)	115.7(8)
F(7)-C(17)-C(12)	109.9(7)
F(12)-C(18)-F(10)	106.0(8)
F(12)-C(18)-F(11)	106.4(7)
F(10)-C(18)-F(11)	106.6(8)
F(12)-C(18)-C(16)	112.6(7)
F(10)-C(18)-C(16)	114.0(7)
F(11)-C(18)-C(16)	110.7(8)

3. Molecular Structure of $\text{GeAr}''_2\text{Cl}_2$

The molecular crystal structure, and data of key bond distances and angles, are given in figure 3 and table 3. Data were collected and the structure was solved by Dr. A.Goeta of Durham University.

This compound possesses a pseudo-tetrahedral geometry with C-Ge-C and Cl-Ge-Cl, angles of 119.9° and 102.6° respectively, while C-Ge-Cl angles are 107.8° , 108.3° , 108.7° and 108.2° . Similar to complexes SnAr_2Cl_2 and $\text{SnAr}'_2\text{Cl}_2$, since Ar'' is also a bulky group, the ligands need to twist in space to minimise steric interaction. The angles are more similar to these in SnAr_2Cl_2 than to these in $\text{SnAr}'_2\text{Cl}_2$, because the radius of Ge is smaller than that of Sn, increasing the steric repulsion between the attached ligands, even though there is only one $-\text{CF}_3$ group ortho to Ge.

The C-Ge bond lengths are 1.957\AA and 1.958\AA , and Ge-Cl bond lengths are 2.148\AA and 2.149\AA . As expected for the smaller germanium atom, both Ge-C and Ge-Cl distances are shorter than the corresponding Sn-C and Sn-Cl bond lengths in $\text{SnAr}'_2\text{Cl}_2$ and SnAr_2Cl_2 .

The most interesting feature of the structure is that both aromatic groups are attached as Ar'' , with the Ge ortho to one CF_3 group only, unlike $\text{SnAr}'_2\text{Cl}_2$, where both ligands are attached to Sn between the two CF_3 groups, and $\text{PAr}'\text{Ar}''\text{Cl}^{55}$, where ligands of both types are present. This is discussed further in section 6.

Figure 3. Molecular Structure of GeAr⁺₂Cl₂

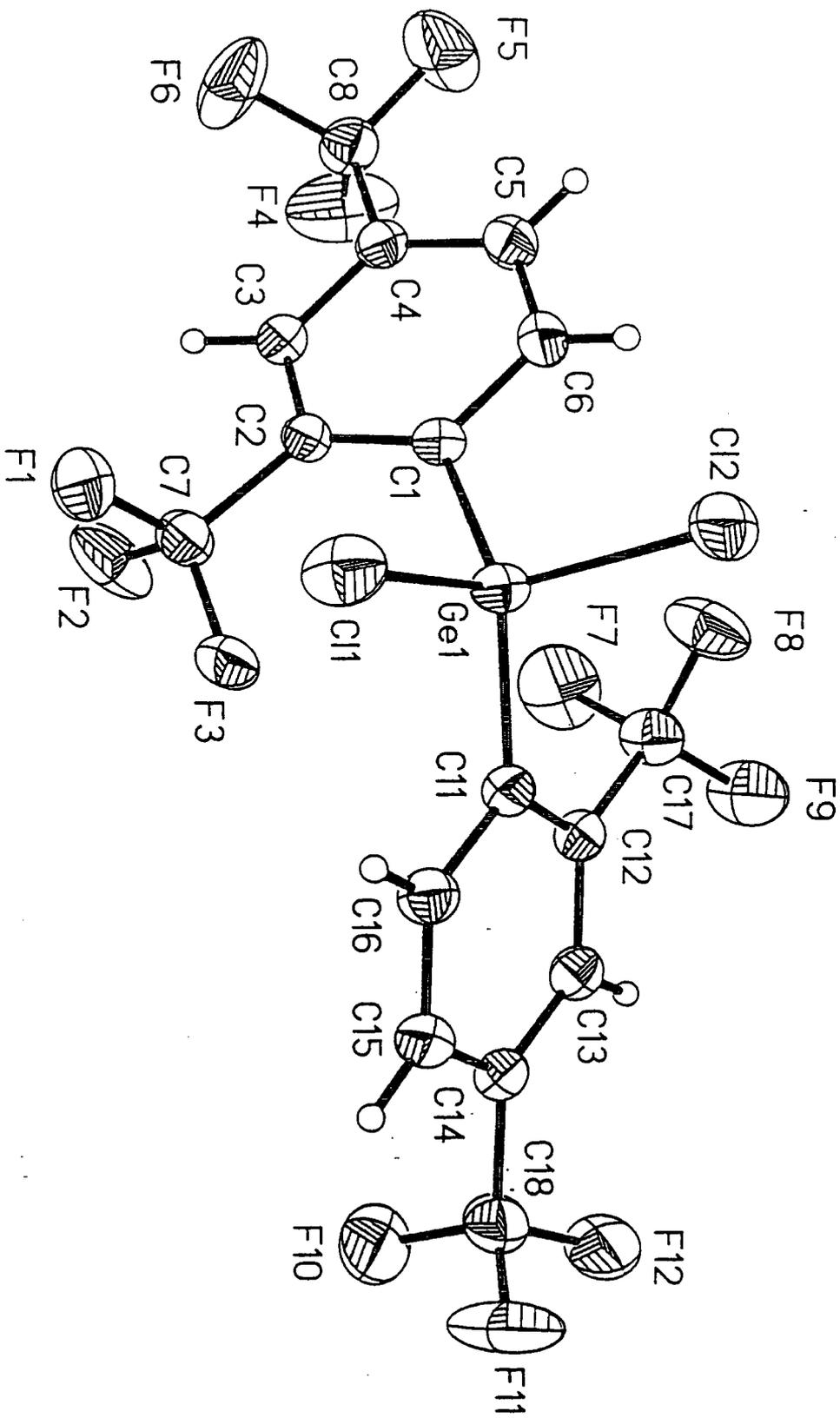


Table 3. Key bond lengths and angles of GeAr''₂Cl₂

Ge(1)-C(1)	1.957(2)	C(8)-F(4)	1.322(3)
Ge(1)-C(11)	1.958(2)	C(8)-F(5)	1.328(3)
Ge(1)-Cl(1)	2.1483(8)	C(11)-C(16)	1.397(3)
Ge(1)-Cl(2)	2.1497(10)	C(11)-C(12)	1.400(3)
C(1)-C(6)	1.399(3)	C(12)-C(13)	1.391(3)
C(1)-C(2)	1.404(3)	C(12)-C(17)	1.507(3)
C(2)-C(3)	1.387(3)	C(13)-C(14)	1.388(4)
C(2)-C(7)	1.505(3)	C(13)-H(13)	0.94(3)
C(3)-C(4)	1.393(3)	C(14)-C(15)	1.387(4)
C(3)-H(3)	0.96(3)	C(14)-C(18)	1.510(4)
C(4)-C(5)	1.372(4)	C(15)-C(16)	1.391(4)
C(4)-C(8)	1.509(4)	C(15)-H(15)	0.94(3)
C(5)-C(6)	1.394(4)	C(16)-H(16)	0.92(3)
C(5)-H(5)	0.89(3)	C(17)-F(9)	1.318(3)
C(6)-H(6)	0.86(3)	C(17)-F(8)	1.328(3)
C(7)-F(3)	1.328(3)	C(17)-F(7)	1.348(3)
C(7)-F(2)	1.334(3)	C(18)-F(10)	1.322(4)
C(7)-F(1)	1.348(3)	C(18)-F(12)	1.330(3)
C(8)-F(6)	1.317(3)	C(18)-F(11)	1.339(4)
C(1)-Ge(1)-C(11)	119.93(10)	C(5)-C(4)-C(3)	120.3(2)
C(1)-Ge(1)-Cl(1)	108.30(7)	C(5)-C(4)-C(8)	121.6(2)
C(11)-Ge(1)-Cl(1)	107.76(7)	C(3)-C(4)-C(8)	118.1(2)
C(1)-Ge(1)-Cl(2)	108.19(7)	C(4)-C(5)-C(6)	120.0(2)
C(11)-Ge(1)-Cl(2)	108.67(7)	C(4)-C(5)-H(5)	121(2)
Cl(1)-Ge(1)-Cl(2)	102.65(4)	C(6)-C(5)-H(5)	119(2)
C(6)-C(1)-C(2)	117.8(2)	C(5)-C(6)-C(1)	121.1(2)
C(6)-C(1)-Ge(1)	116.97(18)	C(5)-C(6)-H(6)	120.0(19)
C(2)-C(1)-Ge(1)	125.20(17)	C(1)-C(6)-H(6)	118.8(19)
C(3)-C(2)-C(1)	120.9(2)	F(3)-C(7)-F(2)	107.7(2)
C(3)-C(2)-C(7)	116.4(2)	F(3)-C(7)-F(1)	105.8(2)
C(1)-C(2)-C(7)	122.6(2)	F(2)-C(7)-F(1)	105.2(2)
C(2)-C(3)-C(4)	119.9(2)	F(3)-C(7)-C(2)	113.7(2)
C(2)-C(3)-H(3)	117.5(15)	F(2)-C(7)-C(2)	112.2(2)
C(4)-C(3)-H(3)	122.6(15)	F(1)-C(7)-C(2)	111.7(2)

F(6)-C(8)-F(4)	106.8(3)	C(14)-C(15)-C(16)	119.3(2)
F(6)-C(8)-F(5)	106.7(2)	C(14)-C(15)-H(15)	119.3(18)
F(4)-C(8)-F(5)	106.3(3)	C(16)-C(15)-H(15)	121.4(18)
F(6)-C(8)-C(4)	112.1(2)	C(15)-C(16)-C(11)	121.5(2)
F(4)-C(8)-C(4)	112.0(2)	C(15)-C(16)-H(16)	119.4(17)
F(5)-C(8)-C(4)	112.5(2)	C(11)-C(16)-H(16)	119.0(17)
C(16)-C(11)-C(12)	118.0(2)	F(9)-C(17)-F(8)	107.5(2)
C(16)-C(11)-Ge(1)	116.80(18)	F(9)-C(17)-F(7)	106.5(2)
C(12)-C(11)-Ge(1)	125.18(17)	F(8)-C(17)-F(7)	105.4(2)
C(13)-C(12)-C(11)	120.9(2)	F(9)-C(17)-C(12)	113.4(2)
C(13)-C(12)-C(17)	117.0(2)	F(8)-C(17)-C(12)	113.1(2)
C(11)-C(12)-C(17)	122.0(2)	F(7)-C(17)-C(12)	110.4(2)
C(14)-C(13)-C(12)	119.7(2)	F(10)-C(18)-F(12)	107.8(3)
C(14)-C(13)-H(13)	122.4(18)	F(10)-C(18)-F(11)	107.2(3)
C(12)-C(13)-H(13)	117.8(18)	F(12)-C(18)-F(11)	105.4(2)
C(15)-C(14)-C(13)	120.5(2)	F(10)-C(18)-C(14)	111.9(2)
C(15)-C(14)-C(18)	119.4(2)	F(12)-C(18)-C(14)	112.5(2)
C(13)-C(14)-C(18)	120.1(2)	F(11)-C(18)-C(14)	111.7(3)

4. Molecular Structure of GeArCl₃

The molecular crystal structure, and data of key bond distances and angles, are given in figure 4 and table 4. Data were collected and the structure was solved by Dr. A. Batsanoc of Durham University.

This compound possesses a pseudo-tetrahedral geometry with C-Ge-Cl angles of 111.9°, 113.7° and 113.7°, while the Cl-Ge-Cl angles are 108.5°, 108.5° and 99.8°. Due to GeArCl₃ having only one bulky ligand, the steric effects are much smaller than with two bulky ligands in GeAr''₂Cl₂; similar to GeAr''₂Cl₂, due to interaction of Ge and F, the ligands still need to twist in space to avoid overlapping, giving some distortion from regular tetrahedral geometry.

The C-Ge bond length is 1.981Å, and the average Ge-Cl bond length is 2.124Å; compared with those of GeAr''₂Cl₂ (1.957 Å and 2.149Å), the Ge-Cl bond length is slightly shorter, while the Ge-C bond is slightly longer; since the Ge of GeArCl₃ is connected to three electronegative chlorines rather than two, as in GeAr''₂Cl₂, the Ge-C bond in GeArCl₃ is slightly weaker.

Figure 4. Molecular Structure of GeArCl₃

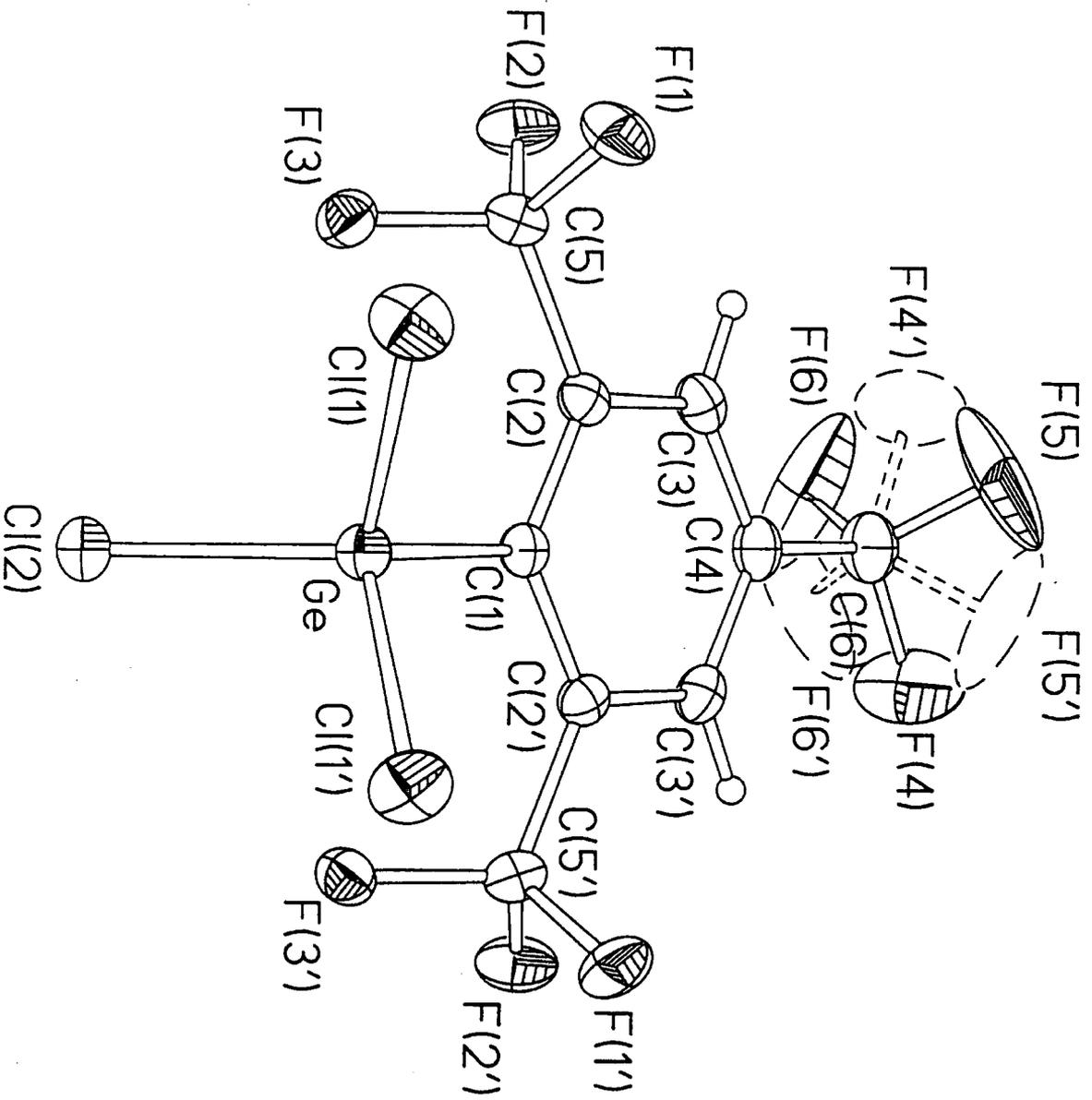


Table 4. Key bond lengths and angles of GeArCl₃

Ge-C(1)	1.981(2)	C(4)-C(6)	1.512(3)
Ge-Cl(2)	2.1117(8)	C(6)-F(5)	1.263(4)
Ge-Cl(1)	2.1277(4)	C(6)-F(5)#1	1.263(4)
Ge-Cl(1)#1	2.1277(4)	C(6)-F(6)	1.274(4)
F(1)-C(5)	1.3370(18)	C(6)-F(6)#1	1.274(4)
F(2)-C(5)	1.3466(17)	C(6)-F(4)	1.329(3)
F(3)-C(5)	1.3464(19)	C(6)-F(4)#1	1.329(3)
C(1)-C(2)#1	1.4117(17)	F(4)-F(5)#1	1.138(6)
C(1)-C(2)	1.4117(17)	F(4)-F(6)#1	1.347(6)
C(2)-C(3)	1.398(2)	F(5)-F(4)#1	1.138(6)
C(2)-C(5)	1.517(2)	F(5)-F(5)#1	1.201(10)
C(3)-C(4)	1.3855(19)	F(6)-F(6)#1	0.966(11)
C(3)-H(3)	0.93(2)	F(6)-F(4)#1	1.347(6)
C(4)-C(3)#1	1.3855(19)		
C(1)-Ge-Cl(2)	111.89(6)	F(1)-C(5)-F(2)	106.72(12)
C(1)-Ge-Cl(1)	113.72(4)	F(3)-C(5)-F(2)	105.97(13)
Cl(2)-Ge-Cl(1)	108.461(17)	F(1)-C(5)-C(2)	112.90(13)
C(1)-Ge-Cl(1)#1	113.72(4)	F(3)-C(5)-C(2)	112.03(12)
Cl(2)-Ge-Cl(1)#1	108.461(17)	F(2)-C(5)-C(2)	110.80(12)
Cl(1)-Ge-Cl(1)#1	99.82(3)	F(5)-C(6)-F(5)#1	56.8(5)
C(2)#1-C(1)-C(2)	116.41(18)	F(5)-C(6)-F(6)	109.9(3)
C(2)#1-C(1)-Ge	121.77(9)	F(5)#1-C(6)-F(6)	134.5(3)
C(2)-C(1)-Ge	121.77(9)	F(5)-C(6)-F(6)#1	134.5(3)
C(3)-C(2)-C(1)	121.71(14)	F(5)#1-C(6)-F(6)#1	109.9(3)
C(3)-C(2)-C(5)	114.18(13)	F(6)-C(6)-F(6)#1	44.6(5)
C(1)-C(2)-C(5)	124.06(13)	F(5)-C(6)-F(4)	105.2(4)
C(4)-C(3)-C(2)	119.81(15)	F(5)#1-C(6)-F(4)	52.0(3)
C(4)-C(3)-H(3)	121.8(13)	F(6)-C(6)-F(4)	103.6(4)
C(2)-C(3)-H(3)	118.4(13)	F(6)#1-C(6)-F(4)	62.3(3)
C(3)#1-C(4)-C(3)	120.2(2)	F(5)-C(6)-F(4)#1	52.0(3)
C(3)#1-C(4)-C(6)	119.87(10)	F(5)#1-C(6)-F(4)#1	105.2(4)
C(3)-C(4)-C(6)	119.87(10)	F(6)-C(6)-F(4)#1	62.3(3)
F(1)-C(5)-F(3)	108.04(12)	F(6)#1-C(6)-F(4)#1	103.6(4)

F(4)-C(6)-F(4)#1	134.7(3)	F(5)#1-F(4)-F(6)#1	113.1(4)
F(5)-C(6)-C(4)	112.6(3)	C(6)-F(4)-F(6)#1	56.9(3)
F(5)#1-C(6)-C(4)	112.6(3)	F(4)#1-F(5)-F(5)#1	123.4(3)
F(6)-C(6)-C(4)	112.5(2)	F(4)#1-F(5)-C(6)	67.0(3)
F(6)#1-C(6)-C(4)	112.5(2)	F(5)#1-F(5)-C(6)	61.6(3)
F(4)-C(6)-C(4)	112.52(16)	F(6)#1-F(6)-C(6)	67.7(3)
F(4)#1-C(6)-C(4)	112.52(16)	F(6)#1-F(6)-F(4)#1	123.5(3)
F(5)#1-F(4)-C(6)	61.0(3)	C(6)-F(6)-F(4)#1	60.9(2)

Symmetry transformations used to generate equivalent atoms:

#1 x, -y+1/2, z

5. Molecular Structure of $\text{SiAr}''_2\text{Cl}_2$

The molecular crystal structure, and data of key bond distances and angles, are given in figure 5 and table 5. Data were collected and the structure was solved by Dr. A. Batsanov of Durham University.

This compound possesses a pseudo-tetrahedral geometry with C-Si-C and Cl-Si-Cl, angles of 117.5° and 104.2° respectively, while C-Si-Cl angles are 109.3° , 108.2° , 108.0° and 108.9° . The structure is similar to that of $\text{GeAr}''_2\text{Cl}_2$, where the C-Ge-C angle is 119.9° and Cl-Ge-Cl is 102.6° . The Cl-E-Cl angle is larger in the Si compound than that in the Ge compound, because the radius of Si is smaller than that of Ge. The C-Si-Cl angles, however, in $\text{SiAr}''_2\text{Cl}_2$ are similar to those of $\text{GeAr}''_2\text{Cl}_2$, because with only one $-\text{CF}_3$ group ortho to E from each Ar'' group, they can approach more closely the ideal tetrahedral angle.

The C-Si bond lengths are 1.884\AA and 1.885\AA , and the Si-Cl bond lengths are 2.048\AA and 2.050\AA . As expected for the smaller silicon atom, both Si-C and Si-Cl distances are shorter than the corresponding Ge-C(1.958\AA) and Ge-Cl(2.149\AA) bond lengths in $\text{GeAr}''_2\text{Cl}_2$. In both of the structures the aromatic groups are attached as Ar'', with the E ortho to one CF_3 group -only, confirming our rationalisation. This will be discussed further in section 6.

Figure 5. Molecular Structure of $\text{SiAr}''''_2\text{Cl}_2$

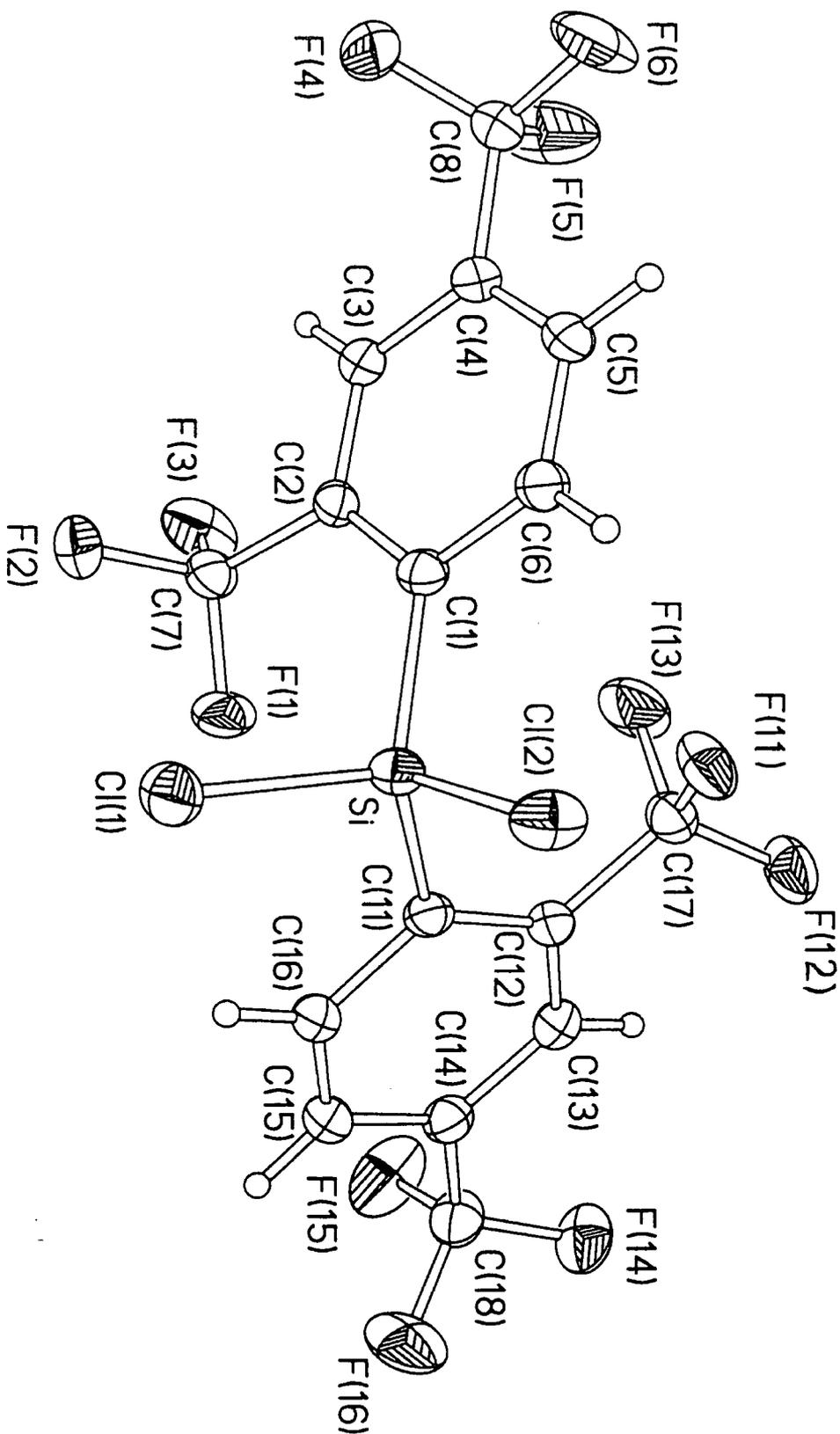


Table 5. Key bond lengths and angles of SiAr''₂Cl₂

Si-C(1)	1.8838(19)	C(2)-C(3)	1.392(2)
Si-C(11)	1.8845(19)	C(2)-C(7)	1.506(2)
Si-Cl(2)	2.0479(13)	C(3)-C(4)	1.395(2)
Si-Cl(1)	2.0497(12)	C(3)-H(3)	0.93(2)
Si-F(1)	2.882(2)	C(4)-C(5)	1.381(3)
Si-F(11)	2.9013(18)	C(4)-C(8)	1.510(2)
F(1)-C(7)	1.338(2)	C(5)-C(6)	1.396(3)
F(2)-C(7)	1.351(2)	C(5)-H(5)	0.96(2)
F(3)-C(7)	1.335(2)	C(6)-H(6)	0.96(2)
F(4)-C(8)	1.326(2)	C(11)-C(16)	1.407(2)
F(5)-C(8)	1.325(3)	C(11)-C(12)	1.411(2)
F(6)-C(8)	1.327(2)	C(12)-C(13)	1.393(2)
F(11)-C(17)	1.340(2)	C(12)-C(17)	1.517(3)
F(12)-C(17)	1.328(2)	C(13)-C(14)	1.392(3)
F(13)-C(17)	1.339(2)	C(13)-H(13)	0.94(2)
F(14)-C(18)	1.334(2)	C(14)-C(15)	1.389(3)
F(15)-C(18)	1.334(3)	C(14)-C(18)	1.503(3)
F(16)-C(18)	1.340(3)	C(15)-C(16)	1.393(3)
C(1)-C(6)	1.406(2)	C(15)-H(15)	0.92(2)
C(1)-C(2)	1.413(2)	C(16)-H(16)	0.95(2)
C(1)-Si-C(11)	117.47(8)	Cl(1)-Si-F(11)	174.30(4)
C(1)-Si-Cl(2)	109.29(6)	F(1)-Si-F(11)	105.64(5)
C(11)-Si-Cl(2)	108.22(7)	C(7)-F(1)-Si	98.52(9)
C(1)-Si-Cl(1)	108.00(7)	C(17)-F(11)-Si	97.00(10)
C(11)-Si-Cl(1)	108.88(6)	C(6)-C(1)-C(2)	116.61(15)
Cl(2)-Si-Cl(1)	104.17(5)	C(6)-C(1)-Si	117.44(13)
C(1)-Si-F(1)	70.51(6)	C(2)-C(1)-Si	125.94(12)
C(11)-Si-F(1)	69.55(7)	C(3)-C(2)-C(1)	121.53(15)
Cl(2)-Si-F(1)	176.92(4)	C(3)-C(2)-C(7)	115.30(15)
Cl(1)-Si-F(1)	78.71(5)	C(1)-C(2)-C(7)	123.10(15)
C(1)-Si-F(11)	77.18(7)	C(2)-C(3)-C(4)	119.92(16)
C(11)-Si-F(11)	69.90(6)	C(2)-C(3)-H(3)	120.0(13)
Cl(2)-Si-F(11)	71.41(5)	C(4)-C(3)-H(3)	120.1(13)

C(5)-C(4)-C(3)	120.16(16)	C(11)-C(12)-C(17)	122.04(15)
C(5)-C(4)-C(8)	121.65(16)	C(14)-C(13)-C(12)	119.86(16)
C(3)-C(4)-C(8)	118.18(16)	C(14)-C(13)-H(13)	119.9(14)
C(4)-C(5)-C(6)	119.63(16)	C(12)-C(13)-H(13)	120.2(14)
C(4)-C(5)-H(5)	121.3(15)	C(15)-C(14)-C(13)	120.18(16)
C(6)-C(5)-H(5)	119.0(15)	C(15)-C(14)-C(18)	119.78(16)
C(5)-C(6)-C(1)	122.16(16)	C(13)-C(14)-C(18)	120.03(16)
C(5)-C(6)-H(6)	119.6(14)	C(14)-C(15)-C(16)	119.55(16)
C(1)-C(6)-H(6)	118.2(14)	C(14)-C(15)-H(15)	119.7(15)
F(3)-C(7)-F(1)	107.21(15)	C(16)-C(15)-H(15)	120.7(15)
F(3)-C(7)-F(2)	105.87(15)	C(15)-C(16)-C(11)	122.04(16)
F(1)-C(7)-F(2)	106.10(15)	C(15)-C(16)-H(16)	119.4(13)
F(3)-C(7)-C(2)	112.28(15)	C(11)-C(16)-H(16)	118.5(13)
F(1)-C(7)-C(2)	113.23(14)	F(12)-C(17)-F(13)	107.55(16)
F(2)-C(7)-C(2)	111.66(15)	F(12)-C(17)-F(11)	106.85(15)
F(5)-C(8)-F(4)	106.71(18)	F(13)-C(17)-F(11)	106.40(16)
F(5)-C(8)-F(6)	106.51(17)	F(12)-C(17)-C(12)	112.56(16)
F(4)-C(8)-F(6)	106.90(17)	F(13)-C(17)-C(12)	110.90(15)
F(5)-C(8)-C(4)	112.10(16)	F(11)-C(17)-C(12)	112.24(15)
F(4)-C(8)-C(4)	111.79(15)	F(15)-C(18)-F(14)	106.99(17)
F(6)-C(8)-C(4)	112.45(16)	F(15)-C(18)-F(16)	106.35(17)
C(16)-C(11)-C(12)	116.77(16)	F(14)-C(18)-F(16)	106.25(17)
C(16)-C(11)-Si	116.93(13)	F(15)-C(18)-C(14)	112.19(17)
C(12)-C(11)-Si	126.30(13)	F(14)-C(18)-C(14)	112.69(16)
C(13)-C(12)-C(11)	121.60(16)	F(16)-C(18)-C(14)	111.95(17)
C(13)-C(12)-C(17)	116.30(15)		

6. Variation of trifluoromethyl group position in bis(trifluoromethyl)phenyl complexes of Sn, Ge, Si, P and As

For the first time, variation in position of trifluoromethyl groups in bis(trifluoromethyl)benzene complexes has been observed. Roden had shown that 2,6-bis(trifluoromethyl)benzene $Ar'H$ reacts with butyl lithium to produce a 2,6-bis(trifluoromethyl)phenyl lithium and 2,4-bis(trifluoromethyl)phenyl lithium mixture (1:1)⁵⁵. The mixed bis(trifluoromethyl)phenyl lithiums react with PCl_3 , generating 2,6-bis(trifluoromethyl)phenyl-2,4-bis(trifluoromethyl)phenyl phosphorus chloride, $Ar'Ar''PCl$, which was confirmed by crystal structure determination and ^{19}F NMR spectra⁵⁵. Initially it was thought that the structure of the tin(IV) complex would be similar, since if the trifluoromethyl group of bis(trifluoromethyl)phenyl can freely arrange its position in space, this is a very likely choice. But the crystal structure shows that it is the di-2,6-bis(trifluoromethyl)phenyl tin dichloride complex, suggesting the possibility of a weak interaction between tin and ortho fluorines making the $-CF_3$ groups more likely to be close to the main group element. The crystal structure of the germanium dichloride complex, on the other hand, shows it is the di-2,4-bis(trifluoromethyl)phenyl germanium dichloride. This suggests that steric factors are becoming more important, because the covalent radius of germanium is just 1.25 Å, hence space around Ge is more important than weak M-F interactions. Since the Si covalent radius of 1.17 Å is slightly shorter than the radius of Ge, the structure should be the same as that of $GeAr''_2Cl_2$. This has been confirmed crystallographically. As expected, the trifluoromethyl groups are again located in positions 2 and 4, in agreement with our rationalisation.

The crystal structures are also backed by ^{19}F NMR spectra. In all the ^{19}F NMR spectra of complexes containing the Ar group, there are only two signals in a 2:1 ratio, but the spectra of complexes with bis(trifluoromethyl)phenyl substituents are very different, according to the trifluoromethyl positions. There will be only one type of F if the trifluoromethyl groups of bis-(trifluoromethyl)-phenyl are all in 2,6 positions (EAr'_2Cl_{1-2}), whereas if the trifluoro-methyl groups are all in 2,4 positions (EAr''_2Cl_{1-2}), there are two kind of fluorine; if the CF_3 groups of one bis(trifluoromethyl)-phenyl

in the 2,6 positions ($\text{EAr}'\text{Ar}''\text{Cl}_2$), there are three kinds of fluorine in a 2:1:1 ratio. If the product is a mixture of all three possible structures, ($\text{EAr}'\text{Ar}''\text{Cl}_2 + \text{EAr}'_2\text{Cl}_2 + \text{EAr}''\text{Cl}_2$), there are 6 kinds of fluorine; if it is a mixture of two structure, there are three possible combinations: a. $\text{EAr}'_2\text{Cl}_2 + \text{EAr}_2''\text{Cl}_2$, 3 kinds of $-\text{CF}_3$. b. $\text{EAr}'\text{Ar}''\text{Cl}_2 + \text{Ar}'_2\text{ECl}_2$, 4 kinds of $-\text{CF}_3$. c: $\text{EAr}_2''\text{Cl}_2 + \text{EAr}'\text{Ar}''\text{Cl}_2$, 5 kinds of $-\text{CF}_3$.

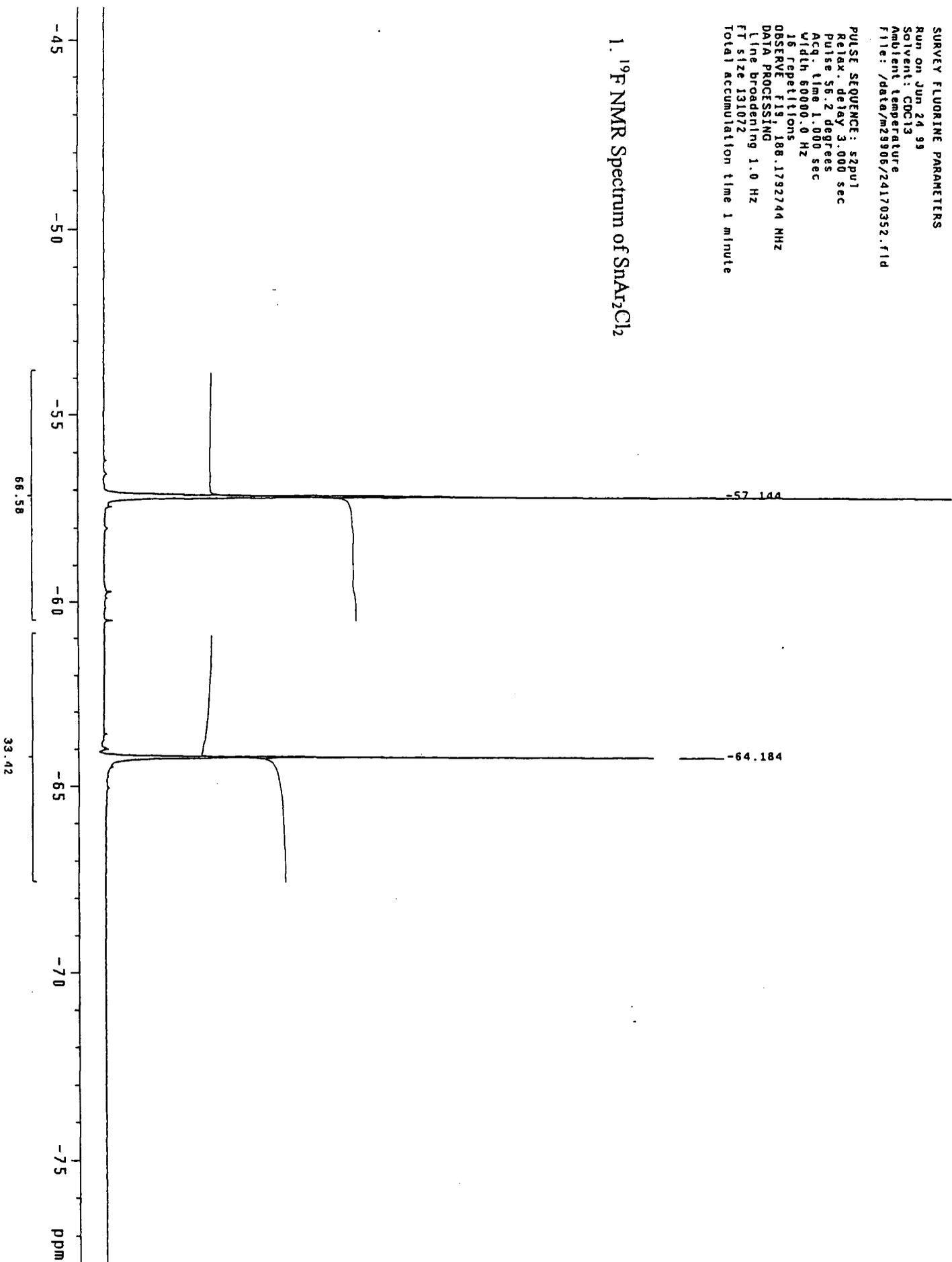
All the ^{19}F NMR spectra of the Sn, Ge, Si and As complexes with tris(trifluoromethyl)-phenyl substituents show two signals in a 2:1 ratio between -53 and -65 ppm; the spectra of SnAr_2Cl_2 and GeArCl_3 are shown as representatives of this types. The ^{19}F NMR spectra of complexes with bis(trifluoromethyl)phenyl substituents are all included. The Sn complex with bis(trifluoromethyl)phenyl substituents shows three signals, corresponding to the mixture $\text{Ar}'_2\text{SnCl}_2 + \text{Ar}_2''\text{SnCl}_2$; $\text{Ar}'_2\text{SnCl}_2$ is about 2/3 of the total. The ^{19}F NMR spectra of the Ge complex show two main signals, the main product (90%) being $\text{GeAr}_2''\text{Cl}_2$, and $\text{SiAr}''_2\text{Cl}_2$ gives rise to a similar spectrum. The ^{19}F NMR spectra of the As complex show 6 signals, indicating a mixture of $\text{Ar}'_2\text{ECl}_2 + \text{Ar}'\text{Ar}''\text{ECl}_2 + \text{Ar}_2''\text{ECl}_2$, with no one species predominant. This is probably because the radius of As is sufficiently large for the bis(trifluoromethyl)phenyl group to choose freely its position in space.

SURVEY FLUORINE PARAMETERS

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Ambient temperature
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Pulse SF: 2 degrees
Acq. time 1.000 sec
Width 60000.0 Hz
16 repetitions
OBSERVE F19, 188.1792744 MHz
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total accumulation time 1 minute

1. ¹⁹F NMR Spectrum of SnAr₂Cl₂

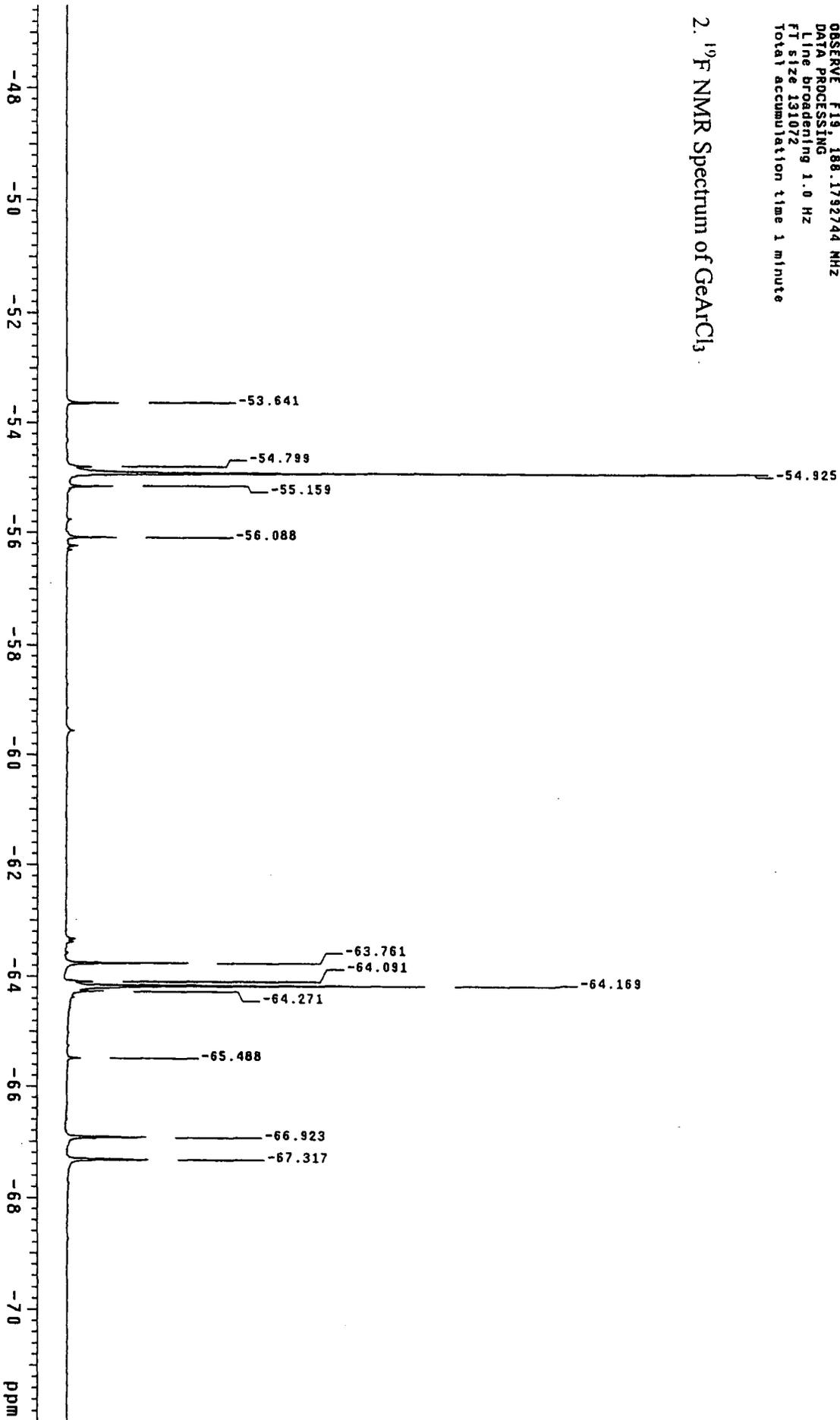


SURVEY FLUORINE PARAMETERS

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Ambient temperature
file: /data/m29907/23115233.fid

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16 repetitions
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DATA PROCESSING
Line broadening 1.0 Hz
Ft size 131072
Total accumulation time 1 minute

2. ¹⁹F NMR Spectrum of GeArCl₃

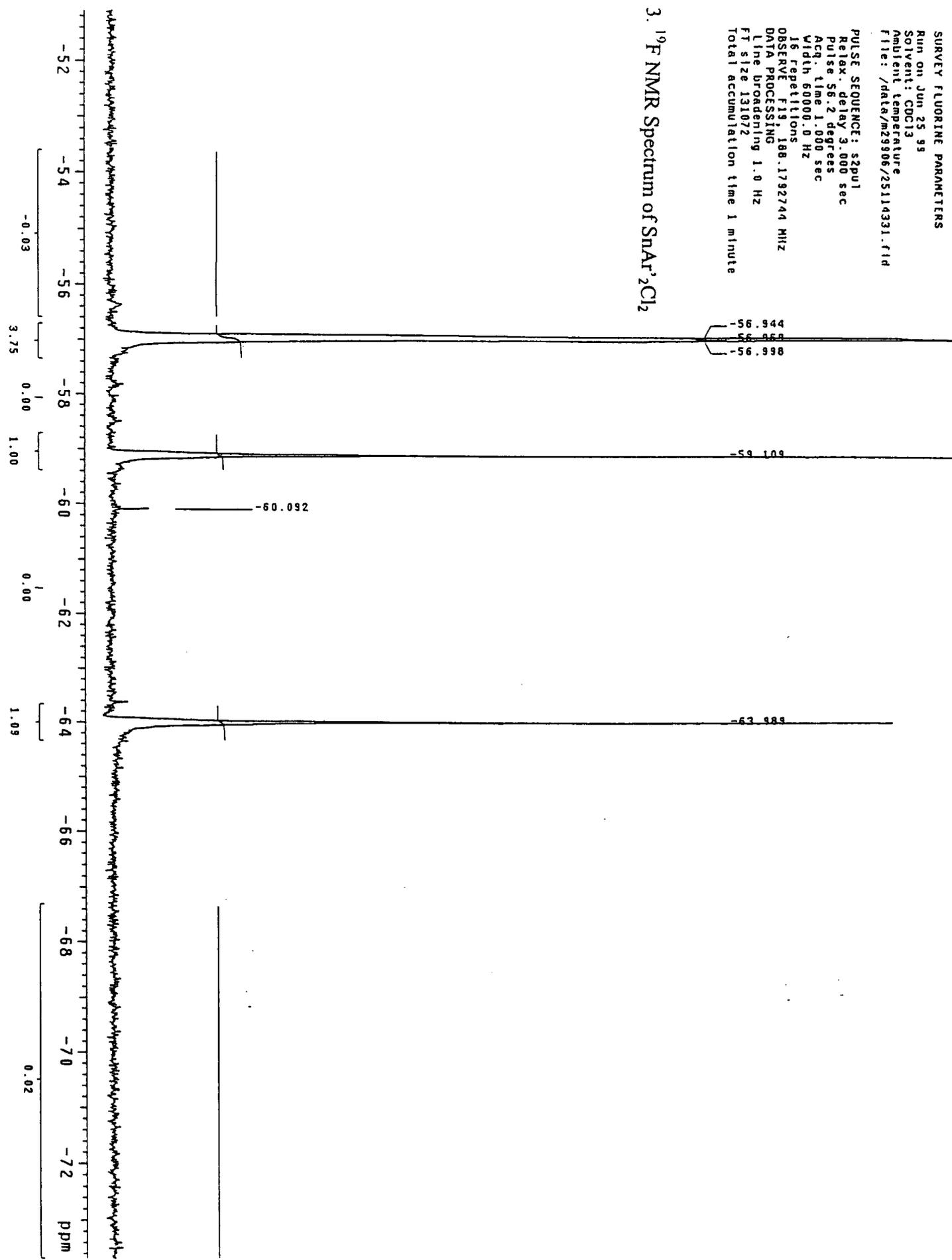


SURVEY FLUORINE PARAMETERS

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Ambient temperature
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Pulse 56.2 degrees
Acq. time 1.000 sec
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16 repetitions
OBSERVE F19, 198.1792744 MHz
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total accumulation time 1 minute

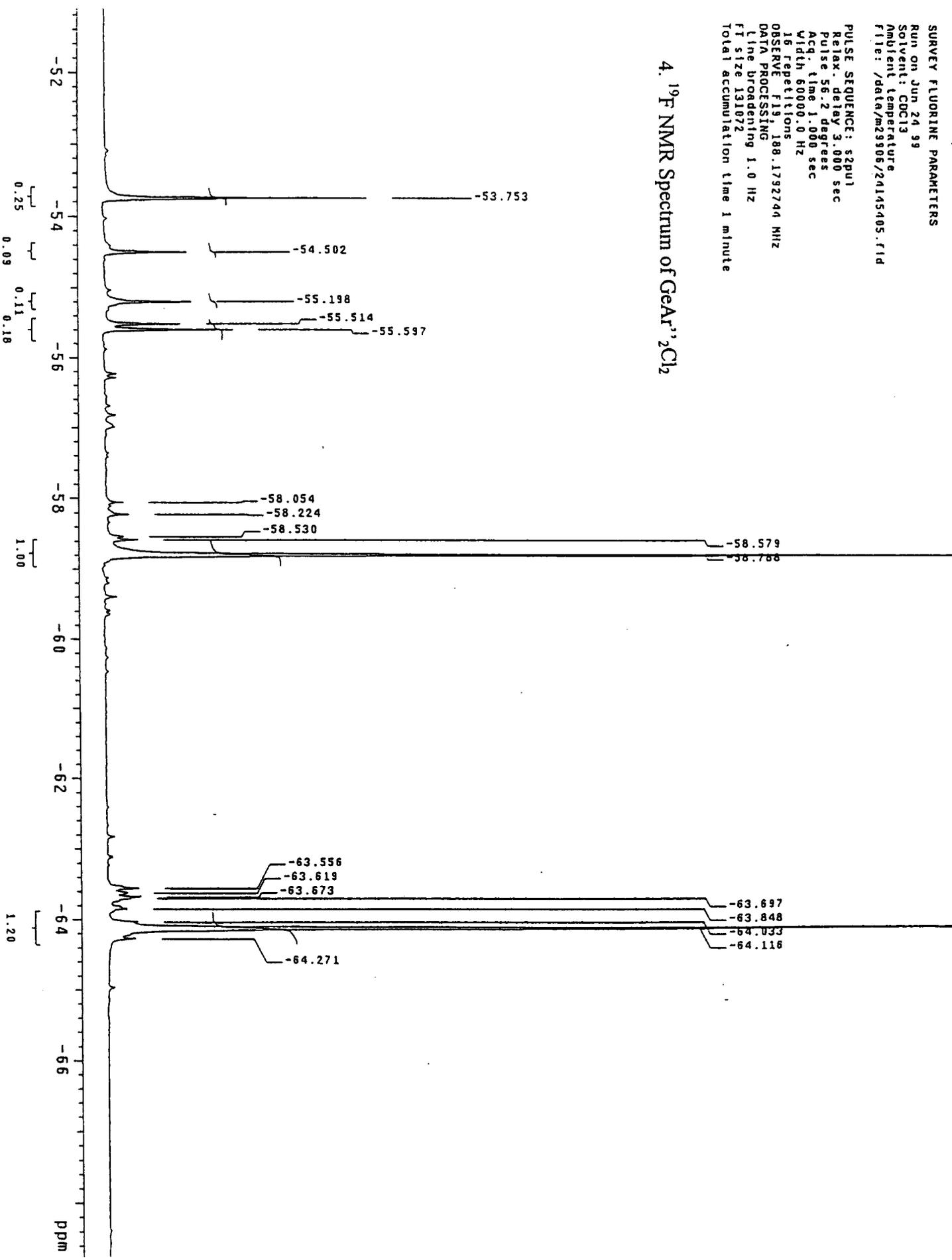
3. ¹⁹F NMR Spectrum of SnAr₂Cl₂



SURVEY FLUORINE PARAMETERS
Run on Jun 24 99
Solvent: CDCl3
Ambient temperature
file: /data/m29906/24145405.fid

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Pulse 56.2 degrees
Acq. time 1.000 sec
Width 60000.0 Hz
16 repetitions
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DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total accumulation time 1 minute

4. ¹⁹F NMR Spectrum of Gear²Cl₂

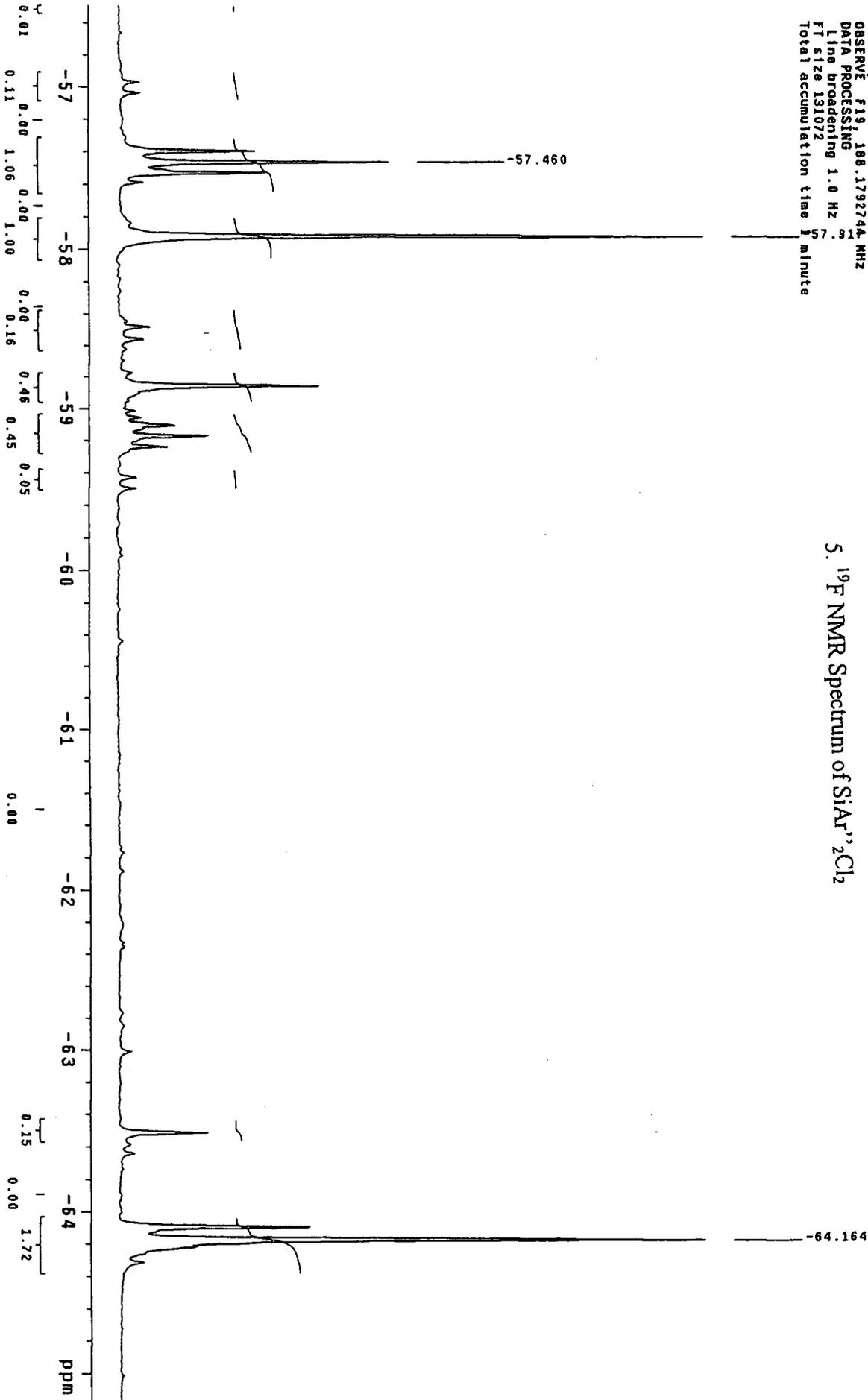


SURVEY FLUORINE PARAMETERS

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Ambient temperature
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Acq. time 1.000 sec
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16 repetitions
OBSERVE F19, 188.1792744 MHz
DATA PROCESSING
Line broadening 1.0 Hz
F1 size 131072
Total accumulation time 1 minute

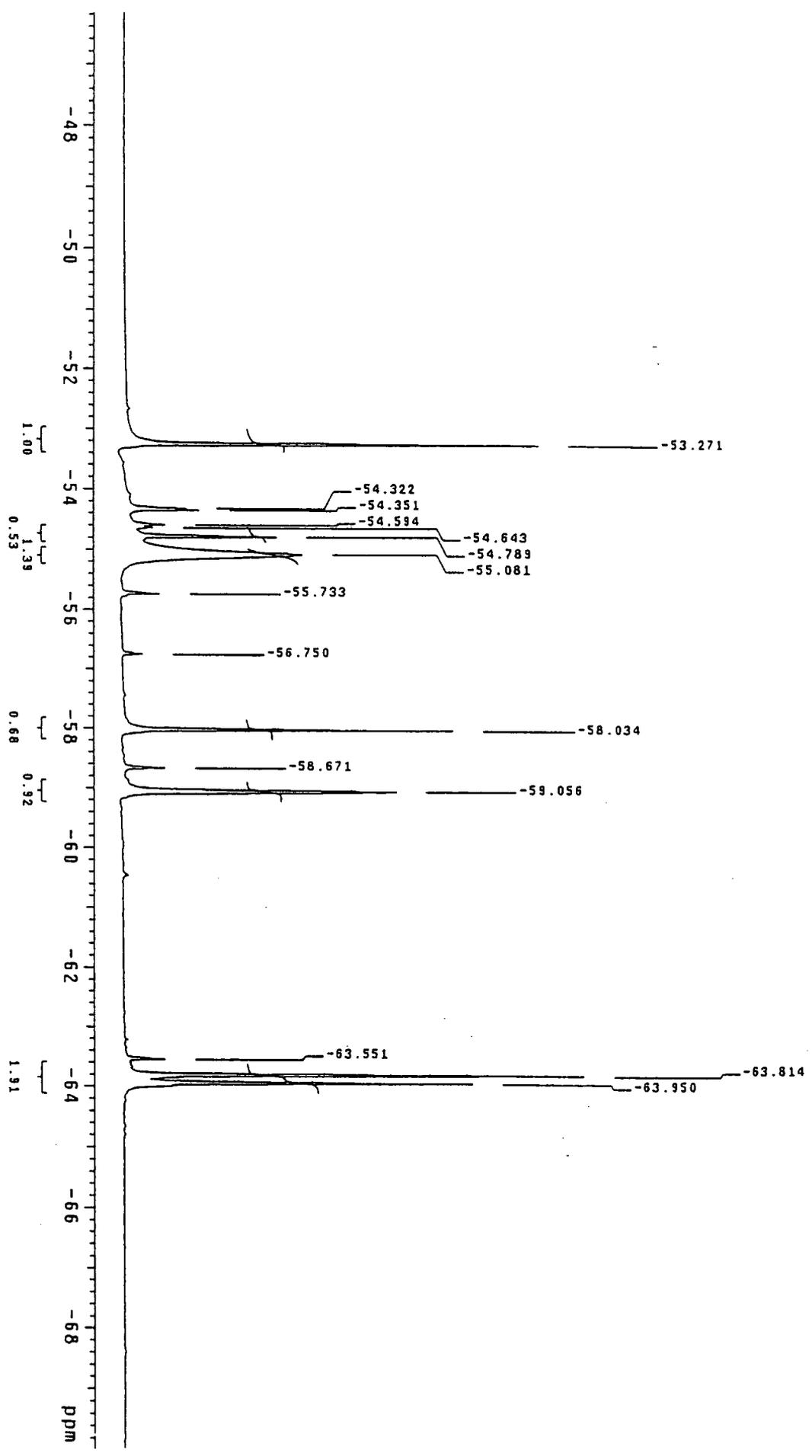
5. ¹⁹F NMR Spectrum of SiAr₂Cl₂



SURVEY FLUORINE PARAMETERS
 Run on Jun 24 99
 Solvent: CDCl3
 Ambient temperature
 File: /data/m29906/24144331.fid

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 Pulse 56.2 degrees
 Acq. time 1.000 sec
 Width 60000.0 Hz
 16 repetitions
 OBSERVE F19, 100.1792744 MHz
 DATA PROCESSING
 Line broadening 1.0 Hz
 FT size 131072
 Total accumulation time 1 minute

6. ¹⁹F NMR Spectrum of AsAr³Ar³Cl₂



7. The interaction between main group elements and fluorine

An interesting feature of these compounds is the possible presence of weak metal-fluorine interactions, which have also been observed widely throughout other main group derivatives.⁶¹⁻⁶⁴ Interaction between the metal atom and the ortho fluorine has been proposed as a significant stabilising effect in main group chemistry. Evidence for these interactions is that the E-F distances lie between the sum of the Van der Waals radii and the covalent distance for E-F Bonds, as shown in the table below.

Comparison of E-F bond distances in Ar or Ar' complexes to the E-F covalent bond distance and to the sum of the Van der Waals radii (Reference 69-71).

Compound	Covalent Distance (Å)	Sum of van der Waals Radii (Å)	Distance in Compound (Å)
SnAr ₂	2.12	1.47+2.17=3.64	2.746
InAr ₃	2.16	3.4	2.762
[LiArEt ₂ O]	1.95	1.47+1.82=3.29	2.252
SnAr ₂ Cl ₂	2.12	1.47+2.18=3.65	2.96
SnAr' ₂ Cl ₂	2.12	1.47+2.18=3.65	2.915
GeAr' ₂ Cl ₂	2.05	1.47+2.12=3.59	2.854
GeArCl ₃	2.05	1.47+2.12=3.59	2.909
SiAr ₂ Cl ₂	2.02	1.47+2.08=3.55	2.892

From the table, it is clear the distances E-F in complexes of Ar, Ar' or Ar'' are shorter than the sum of Van der Waals radii of E and F, strongly suggesting that weak interactions exist in the main group element complexes containing Ar, Ar' or Ar'' ligands.

In the compounds SnAr₂Cl₂ and SnAr'₂Cl₂, the average Sn-F distances are 2.960Å, and 2.915Å respectively, longer than in SnAr₂ (average Sn-F distance 2.746Å), because SnAr₂Cl₂ and SnAr'₂Cl₂ contain two chlorine atoms, reducing the positive charge on Sn and making Sn-F interactions weaker. This also can be seen by comparing the Sn-F distances of SnAr₂Cl₂ and SnAr'₂Cl₂; with three CF₃ groups Ar is more negative than Ar' with two -CF₃ groups, and the Sn-F distance in SnAr₂Cl₂ a

little longer than in $\text{SnAr}'_2\text{Cl}_2$. The average interatomic distance of Ge-F in $\text{GeAr}''_2\text{Cl}_2$ is 2.854\AA , shorter than Sn-F in SnAr_2Cl_2 and $\text{SnAr}'_2\text{Cl}_2$, because the germanium radius is shorter than that of tin. The Ge-F distance in GeArCl_3 is 2.909\AA , a little longer than that of $\text{GeAr}''_2\text{Cl}_2$, because the Ge in GeArCl_3 is connected to three chlorines, making it more negative and its Ge-F interactions slightly weaker. The Si-F distance in $\text{SiAr}''_2\text{Cl}_2$ is 2.892\AA , slightly longer than that in $\text{GeAr}''_2\text{Cl}_2$, since the radius of Si is smaller than that of Ge, this appearing unusual at first glance. In this situation, however, the space factor is very important; the smaller Si may require greater distortion (this can be seen in the structure) to avoid unfavourable steric interactions.

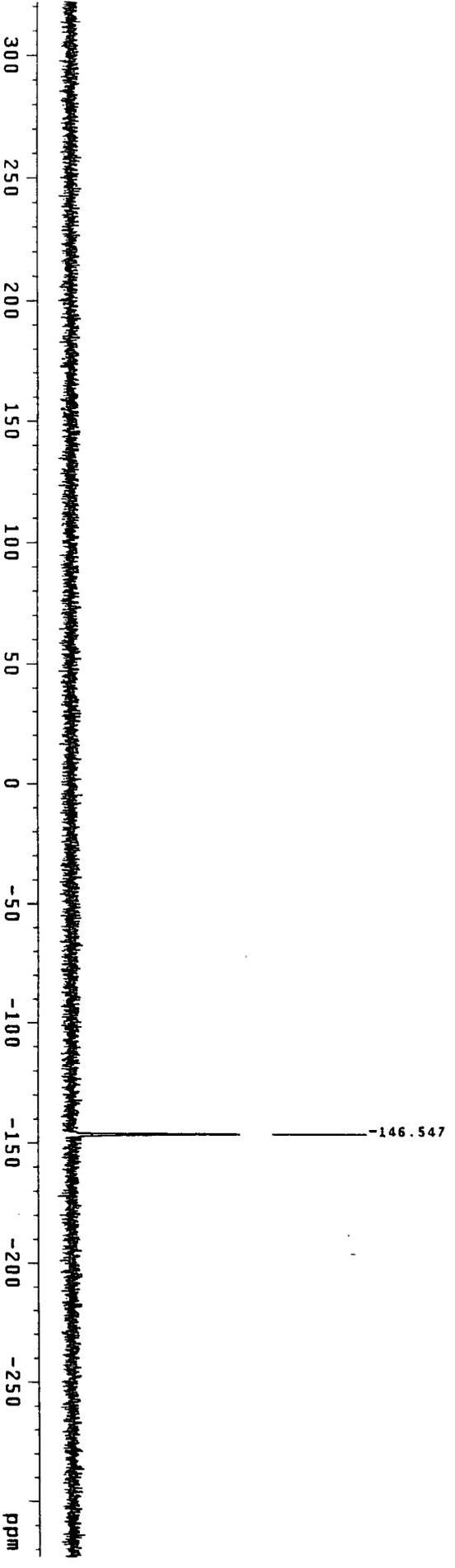
These weak interactions can sometimes be detected in solution by NMR. In SnAr_2 fluorine coupling can be observed in the ^{119}Sn NMR spectra which are split into 13 lines by coupling to the fluorine atoms of the ortho-trifluoromethyl groups.⁶² In BiAr_3 only one signal is seen for all fluorine atoms in the ortho- CF_3 groups at room temperature.⁶⁴ On cooling to $-90\text{ }^\circ\text{C}$ two signals are observed, indicating that rotation about the Bi-C bond is frozen out at this temperature.

The room temperature ^{19}F NMR spectrum (shown in section 4) and low temperature ($-60\text{ }^\circ\text{C}$) ^{19}F NMR of SnAr_2Cl_2 and $\text{SnAr}'_2\text{Cl}_2$ look exactly the same, and no coupling signal could be observed. In the room temperature ^{119}Sn NMR of SnAr_2Cl_2 and $\text{SnAr}'_2\text{Cl}_2$ shown below, only one broad singlet at -146.5 and -141.1 ppm respectively can be seen, and no spin-spin coupling between Sn and F could be resolved. The linewidths were of the order of 60-65Hz, however, compared with a linewidth for the reference of 1-2 Hz. It is therefore possible that some coupling occurs, but is hidden within the overall peak envelope. Since only five of the lines from a 13 line multiplet would appear above the point at which the linewidth is measured (half-height), giving four separations, this indicates a maximum possible value for J of ca. 15Hz. It should be emphasised, however, that no coupling was detected.

BX-Sn1
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30000 repetitions
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DECUPLE H1, 299.9083419 MHz
Power 40 dB
on during acquisition
off during delay
WALTZ-16 modulated
DATA PROCESSING
Line broadening 3.0 Hz
FT size 131072
Total accumulation time 12.5 hours

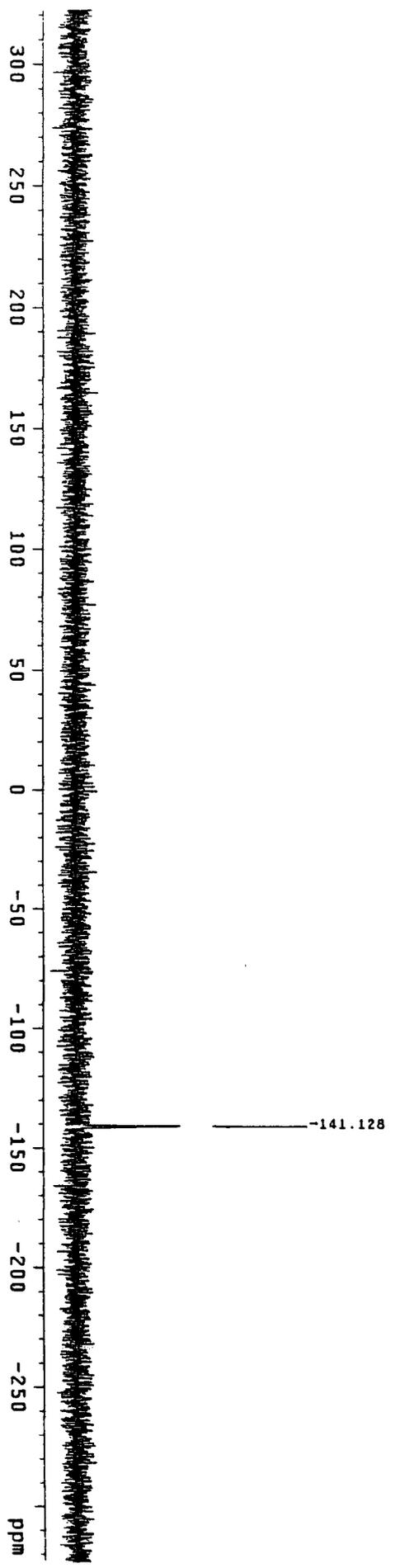
7. ^{119}Sn NMR Spectrum of SnAr_2Cl_2



BX-Sn2
Run on Aug 6 99
Solvent: CDCl3
Ambient temperature
Sample #2
file: /data/u39908/07184453.fid

PULSE SEQUENCE: s2pu1
Relax. delay 1.000 sec
Pulse 57.6 degrees
Acq. time 0.500 sec
Width 72202.2 Hz
30000 repetitions
OBSERVE Sn119, 111.8374326 MHz
DECUPLE H1, 299.9083419 MHz
Power 40 dB
on during acquisition
off during delay
WALTZ-16 modulated
DATA PROCESSING
Line broadening 3.0 Hz
FI size 131072
Total accumulation time 12.5 hours

8. ^{119}F NMR Spectrum of SnAr^2Cl_2



VII. Suggestion for further research

As described in previous sections, the main aim of this project is the synthesis of new double bonded main group elements compounds, which containing bulky electron-withdrawing substituents Ar, Ar' or Ar''.

So far the only double bond compounds of main group elements with such substituents are diphosphenes. Dillon, Gibson and Sequeira used the highly reducing nature and labile coordination sphere of the zerovalent tungsten complex, $W(PMe_3)_6$,²⁶ as an efficient chloride ion abstractor; they found dichlorophosphines reacted with $W(PMe_3)_6$ in benzene at room temperature smoothly over several hours to give the diphosphene $RP=PR$ [R=2,4,6-tris(^tbutyl)phenyl, 2,4,6-tris(trifluoromethyl)phenyl, 2,6-bis(tri-fluoromethyl)phenyl] in virtually quantitative yield.



When different dichlorophosphines ArPCl_2 and Ar^*PCl_2 [$\text{Ar}^*=2,4,6\text{-tris}(\text{}^t\text{butyl})\text{-phenyl}$, $\text{Ar}=2,4,6\text{-tris}(\text{trifluoromethyl})\text{phenyl}$] reacted with $W(\text{PMe}_3)_6$, only the unsymmetrical diphosphene $\text{ArP}=\text{PAr}^*$ was produced in good yield (95%).

Since a series of main group element complexes with substituents Ar, Ar' and Ar'' have been prepared, the next step will react them with $W(\text{PMe}_3)_6$ in an effort to prepare new double bonded compounds. Probably a series of new homonuclear and heteronuclear main group double bonded compounds with bulky electron-withdrawing substituents Ar, Ar' or Ar'' may be synthesised, and their chemistry, particularly with transition metal fragments, can then be explored further.

References

1. H. Kohler and A. Michaelis, *Chem. Ber.*, **10**, 807 (1877).
2. W. Mahler and A. B. Burg, *J. Am. Chem. Soc.*, **79**, 251 (1957); **80**, 6161 (1958).
3. J. J. Daly, *J. Chem. Soc.*, 6147 (1964).
4. P. Erlich, *Lancet*, **173**, 351 (1907).
5. F. S. Kipping, *Proc. Chem. Soc.*, **27**, 143 (1911).
6. P. Jutzi, *Angew. Chem.*, **87**, 269 (1975).
7. T. P. Fehlner, *J. Am. Chem. Soc.*, **88**, 1819 (1966); **90**, 6062 (1968).
8. P. P. Gaspar, *Reactive Intermediates, Vol. 1*, M. Jones and R. S. Moss Eds., Wiley, New York, Ch.7 (1978).
9. M. Yoshifuji, I. Shima, N. Inamoto, K. Hirotsu and T. Higuchi, *J. Am. Chem. Soc.*, **103**, 4587 (1981).
10. R. West, M. J. Fink and J. Michl, *Science*, **214**, 1343 (1981).
11. J. Satge, *Adv. Organomet. Chem.*, **21**, 241 (1982).
12. A. H. Cowley, J. G. Lasch, N. C. Norman, M. Pakulski and B. R. Whittlesey, *J. Chem. Soc., Chem. Commun.* 881 (1983).
13. J. Escudie, C. Couret and J. Satge, *J. Am. Chem. Soc.*, **107**, 3378, 8280 (1985); **109**, 386 (1987).
14. J. Escudie, C. Couret and J. Satge, *Phosphorus Sulfur*, **377** (1987).
15. B. Twamley, C. D. Sofield, M. M. Olmstead and P. P. Power, *J. Am. Chem. Soc.*, **121**, 3357 (1999).
16. T. P. Fehlner, *J. Am. Chem. Soc.*, **89**, 6477 (1967).
17. S. Masamune, Y. Hanzawa, S. Murakami, T. Bally and D. J. Blount, *J. Am. Chem. Soc.*, **104**, 1150 (1982).
18. S. Masamune, S. Murakami and H. Tobita, *Organometallics*, **2**, 1464 (1983).
19. S. Masamune, S. Murakami and H. Tobita, *J. Am. Chem. Soc.*, **105**, 6524 (1983).
20. H. Watanabe, Y. Kougo and Y. Nagai, *J. Chem. Soc., Chem. Commun.*, 66 (1984).
21. C. N. Smit, T. A. Van Der Knaap and F. Bickelhaupt, *Tetrahedron Lett.*, **24**, 2031 (1983).
22. A. H. Cowley, J. E. Kilduff, M. Pakulski and C. A. Stewart, *J. Am. Chem. Soc.*, **105**, 1655 (1983).

23. M. Yoshifuji, S. Sasaki and N. Imamoto, *J. Chem. Soc., Chem. Commun.*, 1732 (1989).
24. L. J. Sequeira, *Ph. D. Thesis*, Durham (1996).
25. K. B. Dillon, V. C. Gibson and L. J. Sequeira, *J. Chem. Soc., Chem. Commun.*, 2429 (1995).
26. D. Rabinovich, R. Zelman and G. Parkin, *J. Am. Chem. Soc.*, *114*, 4611 (1992).
27. P. B. Hitchcock, M. F. Lappert and W. P. Leung, *J. Chem. Soc., Chem. Commun.*, 1282 (1987).
28. C. C. Cummins, R. R. Schrock and W. M. Davis, *Angew. Chem., Int. Ed. Engl.*, *32*, 756 (1993).
29. A. H. Cowley, C. Pellerin, J. L. Atwood and S. G. Bott, *J. Am. Chem. Soc.*, *112*, 6734 (1990).
30. Z. Hou, T. L. Breen and D. W. Stephan, *Organometallics*, *12*, 3158 (1993).
31. M. T. Anthony, M. L. H. Green and D. Young, *J. Chem. Soc., Dalton Trans.*, 1419 (1975); F. W. Benfield, M. L. H. Green, J. S. Ogden and D. Young, *J. Chem. Soc., Chem. Commun.*, 866 (1973); F. G. N. Cloke and M. L. H. Green, *J. Chem. Soc., Dalton Trans.*, 1938 (1981).
32. F. Calderazzo, G. Pampaloni, L. Rocchi, J. Strahle and K. Wurst, *Angew. Chem., Int. Ed. Engl.*, *30*, 102 (1991).
33. R. E. MacKenzie and P. L. Timms, *J. Chem. Soc., Chem. Commun.*, 650 (1974).
34. O. J. Scherer, *Angew. Chem; Int. Ed. Engl.*, *24*, 924 (1985) and references therein.
35. H. Schafer and D. Binder, *Z. Anorg. Allg. Chem.*, *557*, 45 (1988); H. Schafer, D. Binder and D. Fenske, *Angew. Chem; Int. Ed. Engl.*, *24*, 522 (1985); H. Schafer, D. Binder, B. Deppisch and G. Mattern, *Z. Anorg. Allg. Chem.*, *546*, 799 (1987).
36. E. Niecke, B. Kramer and M. Nieger, *Angew. Chem., Int. Ed. Engl.*, *28*, 215 (1989).
37. H. Schafer and D. Binder, *Z. Anorg. Allg. Chem.*, *546*, 55 (1987).
38. J. C. Leblanc and C. Moise, *J. Organomet. Chem.*, *364*, C3-C4, (1989).
39. M. Yoshifuji, T. Hashida, K. Shibayama and N. Inamoto, *Chem. Lett.*, 287 (1985).
40. K. M. Flynn, H. Hope, B. D. Murray, M. M. Olmstead and P. P. Power, *J. Am. Chem. Soc.*, *105*, 7751 (1983).
41. A. H. Cowley, J. E. Kilduff, J. G. Lasch, N. C. Norman, M. Pakulski, F. Ando, T. C. Wright and P. P. Power, *J. Am. Chem. Soc.*, *105*, 7750 (1983).
42. R. A. Bartlett, H. V. R. Disc, K. M. Flynn, M. M. Olmstead and P. P. Power, *J.*

- Am. Chem. Soc.*, 109, 5699 (1987).
43. R. A. Bartlett, H. V. R. Dine and P. P. Power, *J. Organomet. Chem.*, 362, 87 (1989).
44. A-M. Caminade, J. Escudie, C. Couret and M. Koenig, *J. Chem. Soc., Chem. Commun.*, 1622 (1986).
45. G. Huttner, J. Borm and L. Zsolnai, *J. Organomet. Chem.*, 304, 309 (1986).
46. G. Huttner, J. Borm and L. Zsolnai, *Angew. Chem., Int. Ed. Engl.*, 24, 1069 (1989).
47. A-M. Caminade, J-P. Majoral, M. Sanchez, R. Mathieu, S. Attali and A. Grand, *Organometallics*, 6, 1459 (1987).
48. A. G. Del Pozo, A-M. Caminade, F. Dahan, J-P. Majoral and R. Mathieu, *J. Chem. Soc., Chem. Commun.*, 574 (1988).
49. D. Fenske and K. Merzweiler, *Angew. Chem., Int. Ed. Engl.*, 25, 338 (1986).
50. A. H. Cowley, D. M. Giolando, C. M. Nunn, M. Pakulski, D. Westmoreland and N. C. Norman, *J. Chem. Soc., Dalton. Trans.*, 2127 (1988).
51. H. Vahrenkamp and D. Wolters, *Angew. Chem., Int. Ed. Engl.*, 22, 154 (1989).
52. F. T. Edelmann, *Comments Inorg. Chem.*, 12, 259 (1992).
53. W. Witt and H. W. Roesky, *Progr. Inorg. Chem.*, 40, 353 (1992).
54. E. T. Edelman, *Main Group Metal Chemistry*, 17, 67 (1994) and references therein.
55. M. D. Roden, *Ph. D. Thesis*, Durham (1998).
56. M. Y. Eyring, E. C. Zuerner and L. J. Radonovich, *Inorg. Chem.*, 20, 3405 (1981).
57. A. Dubourg, J. P. Declercq, H. Ranaivonjatovo, J. Escudie, C. Couret and M. Lazraq, *Acta. Cryst. Sec. C.*, 44, 2004 (1988).
58. E. T. McBee and R. E. Leech, *Ind. Eng. Chem.*, 39, 393 (1947).
59. G. E Carr, R. D. Chambers, T. F. Holmes and D. G. Parker, *J. Organomet. Chem.*, 325, 13 (1987).
60. M. Scholtz, H. W. Roesky, D. Stalke, K. Keller and F. T. Edelmann, *J. Organomet. Chem.*, 366, 73 (1989).
61. R. D. Schluter, A. H. Cowley, D. A. Atwood, R. A. Jones, M. R. Bond and C. J. Carrano, *J. Am. Chem. Soc.*, 115, 2070 (1993); D. Schluter, H. S. Isom, A. H. Cowley, D. A. Atwood, R. A. Jones, F. Olbrich, S. Corbelin and R. J. Lagow, *Organometallics*, 13, 4058 (1994).



62. H. Gruzmacher, H. Pritzkow and F. T Edelmann, *Organometallics*, 10, 23 (1991).
63. S. Brooker, J-K. Buijink and F. T. Edelmann, *Organometallics*, 10, 25 (1991).
64. K. H. Whitmire, D. Labahn, H. W. Roesky, M. Noltemeyer and G. M. Sheldrick, *J. Organomet. Chem.*, 402, 55 (1989).
65. J-K. Buijink, M. Noltemeyer and F. T Edelmann, *J. Fluorine Chem.*, 61, 51 (1993).
66. H. P. Goodwin, *Ph. D. Thesis*, Durham (1990).
67. T. A. Straw, *Ph. D. Thesis*, Durham (1990).
68. T. Fjeldberg, A. Haaland, M. F. Lappert, B. E. E. Schilling, R. Seip and A. J. Thorne, *J. Chem. Soc., Chem. Commun.*, 1407 (1982).
69. A. Bondi, *J. Phys. Chem.*, 68, 441 (1964).
70. W. W. Porterfield, *Inorganic Chemistry. A unified Approach*, Addison Wesley, P168 (1983).
71. S. S. Batsanov, *J. Mol. Struct.*, in press (1999).

Chapter 4. Attempts to Synthesise Phosphaalkynes with Bulky Electron-Withdrawing Substituents

I. Introduction

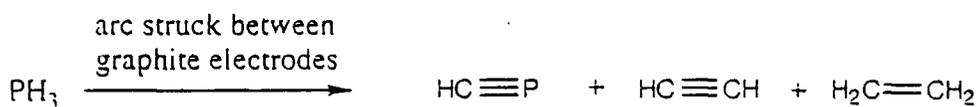
1. Phosphaalkynes and History

Phosphaalkynes are compounds of trivalent phosphorus which contain a $P\equiv C$ triple bond. The first phosphaalkyne was synthesised and characterised in 1961¹ by T.E. Gier of Du Pont in Wilmington. Methynophosphide (HCP) was prepared by passing PH_3 through a low intensity (50-100 amperes, 25volts) rotating arc struck between graphite electrodes, contained in a water cooled copper reactor. HCP is a very reactive colourless gas, stable to storage only in its pure state and below its triple point $-124^\circ C$. The monomer polymerises slowly at $-130^\circ C$ and more rapidly at $-78^\circ C$ to a black solid. Both the monomer and the polymer are extremely pyrophoric.

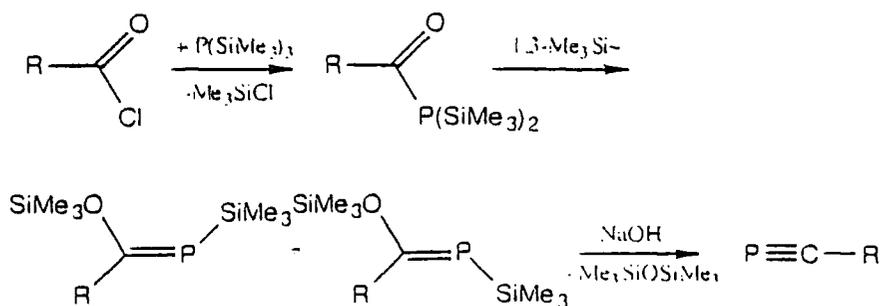
The first stable phosphaalkyne, $tBuCP$, was made by Becker in 1981². This is a colourless liquid which boils at $61^\circ C$ without decomposing. It was made using a base induced disiloxane elimination reaction. Improvements to this reaction have since been made,³ and a variety of stable phosphaalkynes has been synthesised. (e.g. RCP, R= isopropyl, adamantyl, mesityl)

2. Preparation Methods of Phosphaalkynes

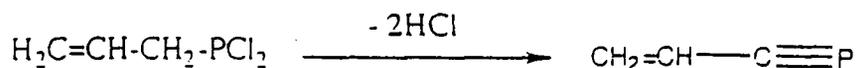
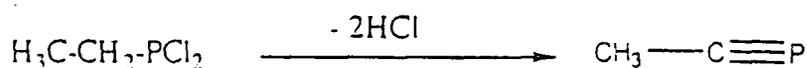
- i) Original prep. of HCP.



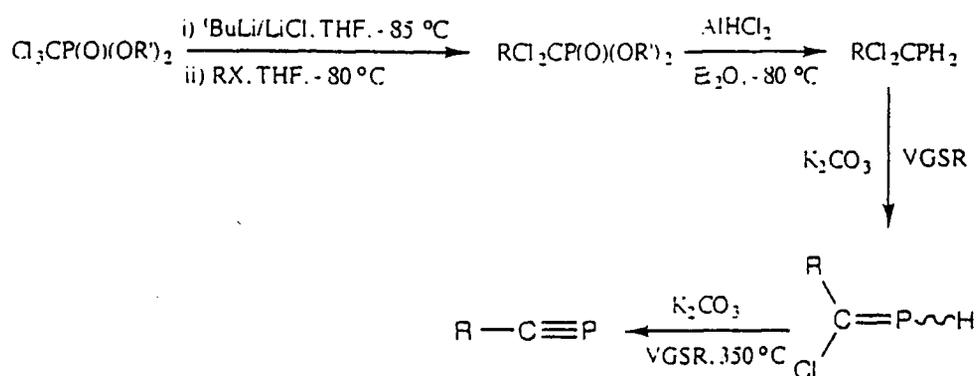
- ii) Preparation from Alkylidenephosphine



iii) Preparation from chlorophosphines.⁴

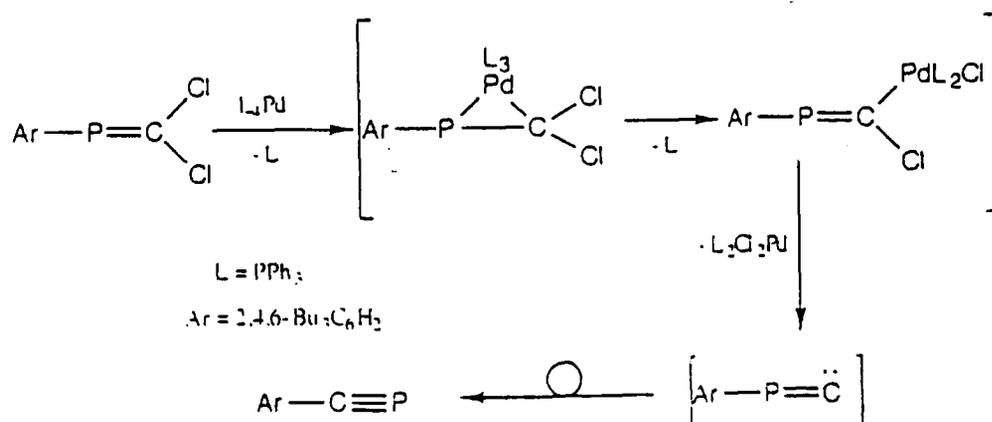


iv) Synthesis of non-stabilised phosphalkynes by Vacuum Gas-Solid HCl Elimination.⁵



VGSR involves heating the materials to a high temperature, under vacuum, and controlling the decomposition, affording the desired product. K_2CO_3 is the base used as it is a solid and stable to high temperature and vacuum.

v) Synthesis of a phosphalkyne via a phosphalkene and a palladium (0) complex.⁶



Yoshifuji and co-workers in 1988 reported that when they reacted phosphalkene, E-2-chloro-1-(2,4,6 tri-butylphenyl)-1-phosphaethylene (RP=CHCl), with butyllithium at -78°C , they obtained the phosphalkyne in 53% yield. In 1989, Romanenko and co-workers used a heterosubstituted phosphalkene to react with butyllithium at -100°C to form the first dialkylaminophosphaethyne, a new kind of phosphalkyne in 7% yield. This reaction is quite straightforward and very important to us.

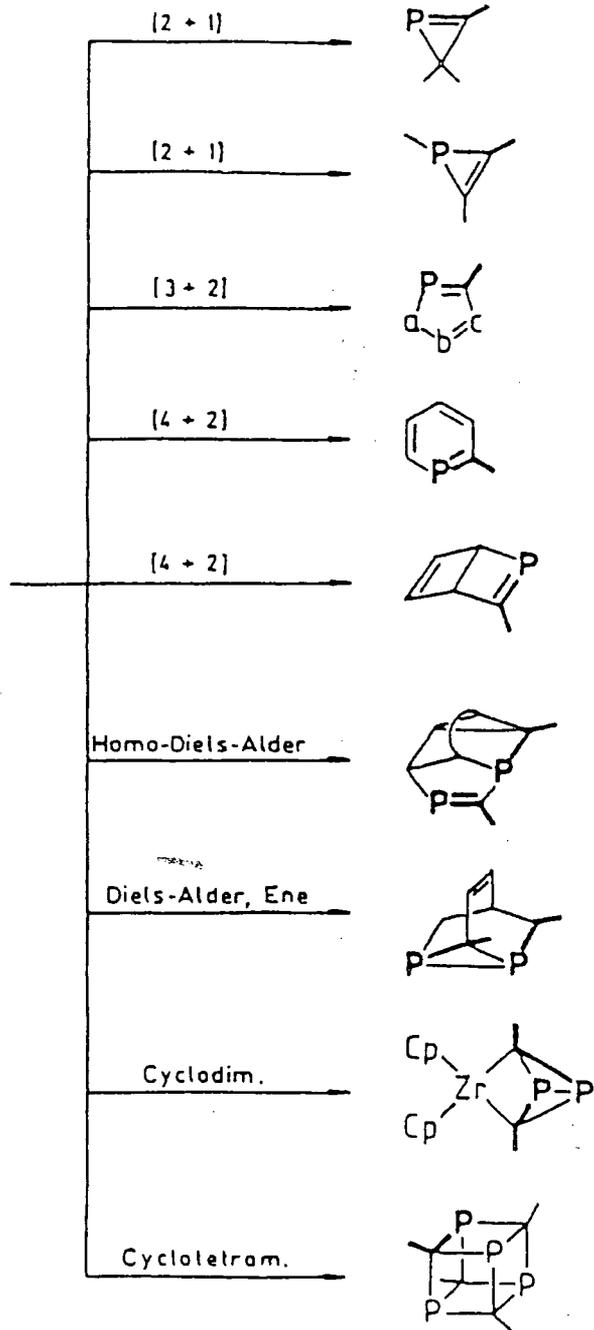
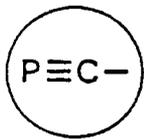
3. Why we are interested in phosphalkynes containing bulky electron-withdrawing substituents.

The inorganic and organic chemistry of phosphalkynes has been extensively developed in recent years, phosphalkynes becoming a very useful synthetic route for incorporating a phosphorus atom into a heterocyclic ring system. Typically [1,2] addition reactions and [2+1], [2+3] and [4+2] cycloadditions occur readily, giving rise to a series of novel types of organophosphorus compounds. Some main types of reaction are summarised on the next page.¹⁰

So far, however, phosphalkyne chemistry has been carried out using electron-donating aryl and alkyl groups connected to $-\text{C}\equiv\text{P}$, which will increase the electron density in the $-\text{C}\equiv\text{P}$ triple bond. However, in the proposed phosphalkynes, the groups connected to $\text{C}\equiv\text{P}$ are highly electron-withdrawing 2,4,6-tris(trifluoromethyl)phenyl (Ar) or 2,6-bis(trifluoromethyl)phenyl (Ar'), while should in theory reduce the electron density in the $-\text{C}\equiv\text{P}$ triple bond, affecting the bonding of the phosphalkynes and the reactions thereof.

In fact the 2,4,6-tris(trifluoromethyl)phenyl (Ar) and 2,6-bis(trifluoromethyl)phenyl (Ar') groups have a number of advantages over other aryl and alkyl groups in phosphorus chemistry, as they are comparatively more oxygen- and moisture-stable than equivalent aryl and alkyl bonded phosphorus species. In the case of phosphorus multiple bonds ($\text{RP}=\text{PR}$, $\text{RP}=\text{CCl}_2$), the compounds are more resistant to polymerisation and formation of dimer and trimer products. This is a great advantage in preparation, and hopefully phosphalkyne chemistry with Ar or Ar' substituents, will lead to the formation of different and novel structures.

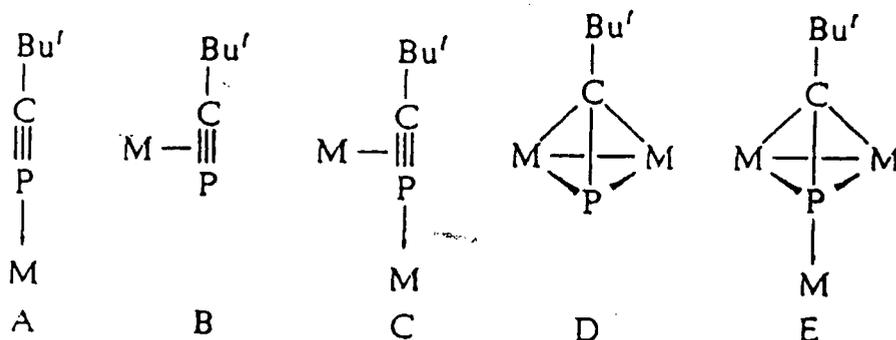
Main Types of
Phosphaalkyne
Reactivity



4. Phosphaalkyne Complexes

As discussed earlier in section 3, phosphaalkynes $RC\equiv P$ have been shown to have a rich organic and inorganic chemistry in which both the triple bond and the P lone-pair electrons can participate; a few reviews have appeared in recent years.¹¹⁻¹⁸ In the field of organometallic chemistry, it is now possible to synthesise a wide variety of stable phosphorus analogues of the better known unsaturated hydrocarbon π -complexes, which have been responsible for the rapid development of organotransition metal chemistry and its importance in homogeneous catalysis. Here only the simple coordination chemistry of the phosphaalkyne is considered.

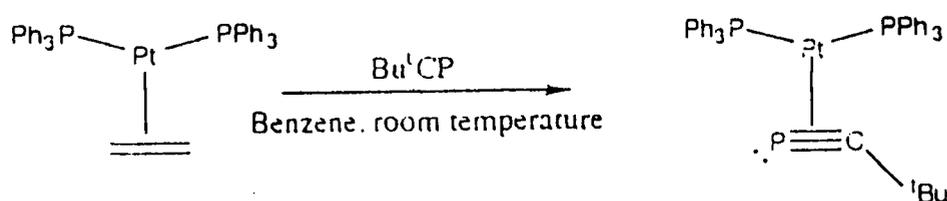
In 1981 the first phosphosphaalkyne complex $[Pt(\eta^2-BuC\equiv P)(PPh_3)_2]$ was reported by Nixon and co-workers¹⁹, in which the η^2 - 'side-on' interaction was established between the $P\equiv C$ triple bond and the transition metal by both NMR and a single crystal X-ray diffraction study. Subsequently, types A-E have been synthesised, using the $RC\equiv P$ moiety as both an η^2 -bridging and/or P lone pair donor ligand.¹⁹⁻²¹



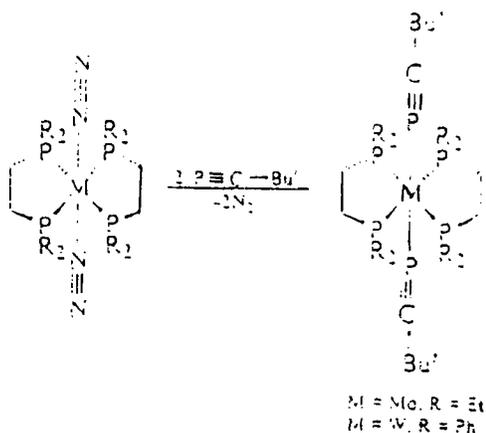
[A]--[E] types of Phosphaalkynes Complexes

Below examples of each type of coordination mode are shown.

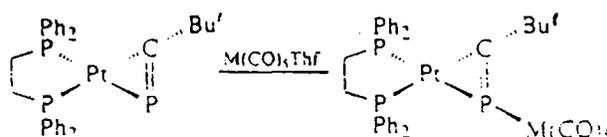
*A type of coordination Mode*¹⁹



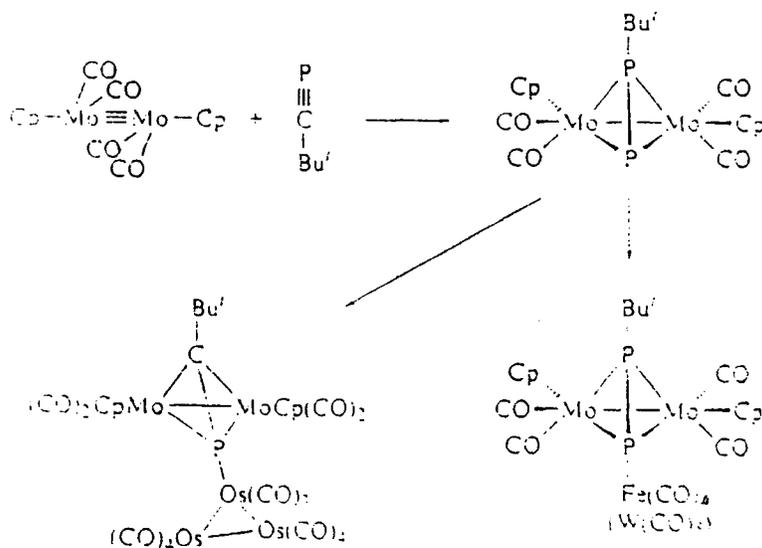
*B type of coordination mode*²²



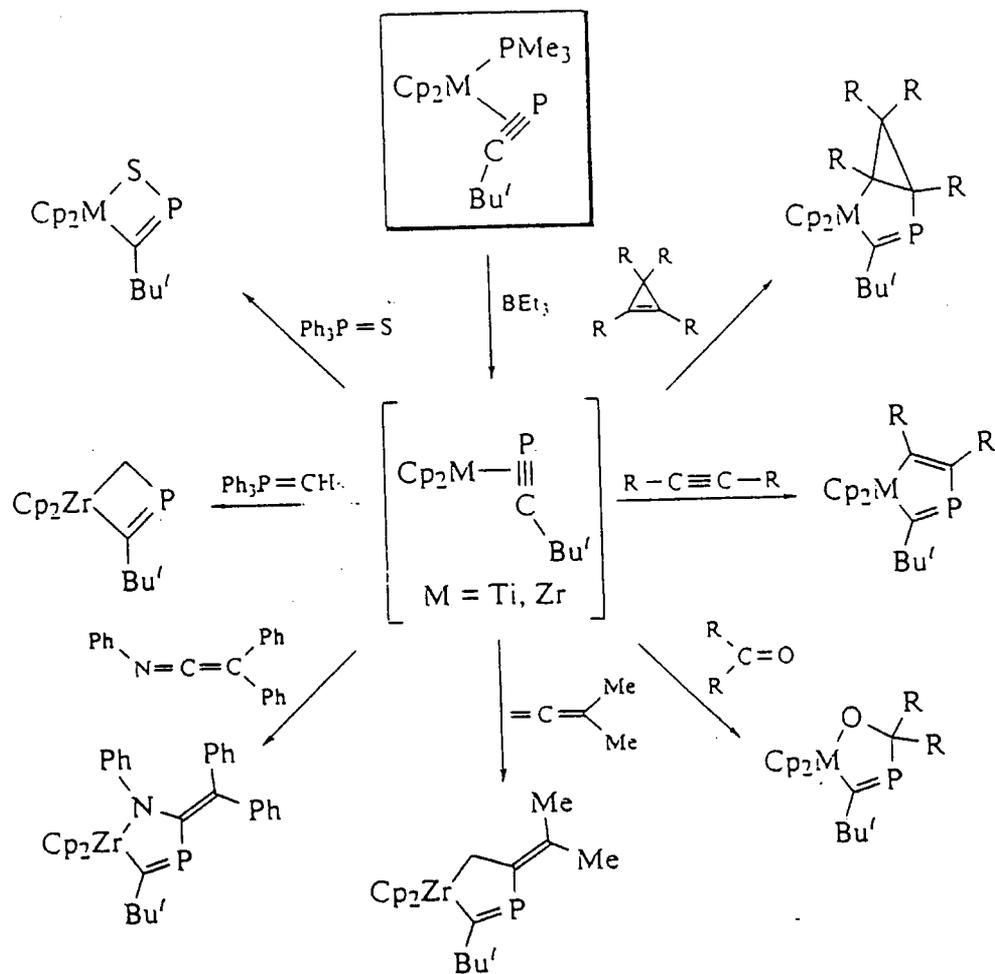
*C type of coordination Mode*²³



*D and E types of coordination Mode*²⁴⁻²⁸



Some complexes can continue to undergo a series of reactions; for example the η^2 complex $[M(\eta^2\text{-C}_5\text{H}_5)_2 \text{BuCP}(\text{PMe}_3)]$, when treated with BEt_3 , loses the PMe_3 to produce a vacant site in the complex. The resulting intermediate complex reacts with itself to give either the dimeric ($M=\text{Ti}$) or trimeric ($M=\text{Zr}$) compounds as the stable products. It also can react with a number of reagents to give a variety of compounds, as shown below.



II. Attempts to synthesise novel phosphalkynes with bulky electron-withdrawing substituents

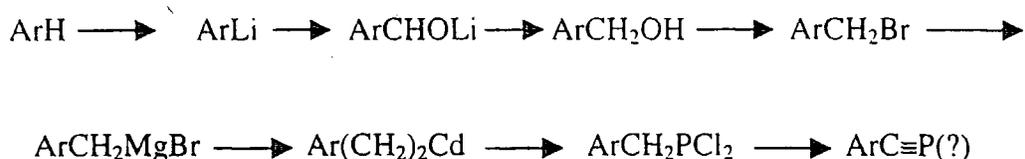
1. Planned Synthesis of Phosphalkynes with bulky electron-withdrawing substituents

There are three possible routes to synthesise the novel phosphalkyne with bulky electron-withdrawing substituents; the first route, like method V, is via a phosphalkene complex. This is being attempted, because previously in this group the phosphalkenes $\text{ArP}=\text{CCl}_2$ and $\text{Ar}'\text{P}=\text{CCl}_2$ had been prepared, and this synthesis route (on paper) looks simpler than using the alkylidenephosphine method which requires the preparation of very volatile compounds.

Roden's work²⁹, however, confirmed that it is not easy to use this route to prepare phosphalkynes; he reacted the phosphalkenes $\text{ArP}=\text{CCl}_2$, $\text{Ar}'\text{P}=\text{CCl}_2$ with the complexes $\text{Pt}(\text{PPh}_3)_4$ and $\text{Pd}(\text{PPh}_3)_4$ to yield the η^2 complexes $[\text{MCl}(\text{CCl}=\text{PR})(\text{PPh}_3)_2]$ ($\text{M}=\text{Pt}, \text{Pd}$, $\text{R}=\text{Ar}$, Ar'), which was confirmed by NMR and a single crystal structure ($\text{M}=\text{Pt}$). These complexes did not convert into $[\text{M}(\text{PPh}_3)_2\text{Cl}_2]$ and phosphalkynes $\text{RC}\equiv\text{P}$ ($\text{M} = \text{Pt}, \text{Pd}$, $\text{R} = \text{Ar}$, Ar'), probably due to the effect of solvent. Roden used toluene as solvent, but Jun et al suggested the reaction occurred in more polar solvents such as CHCl_3 or CH_2Cl_2 ⁷. If our reaction is carried out under different conditions, perhaps the result will be changed. Anyway this route is still the first choice.

The second route was Vi, comprising reaction of a phosphalkene with butyllithium. Yoshifuji used $\text{RP}=\text{PHCl}$, while Romanenko employed a heterosubstituted phosphalkene, $\text{RN}-\text{P}=\text{CCl}_2$; our phosphalkyne is novel, however, with bulky electron-withdrawing substituents. If method 1 does not go smoothly, then we will try to synthesise the phosphalkyne according to this route.

The third route was proposed by Goodwin³⁰, who tried to react $\text{ArCH}_2\text{PCl}_2$ with two mole of base (DBU) to remove HCl leading to the phosphalkyne $\text{ArC}\equiv\text{P}$, but she did not succeed. The reaction scheme is shown below:

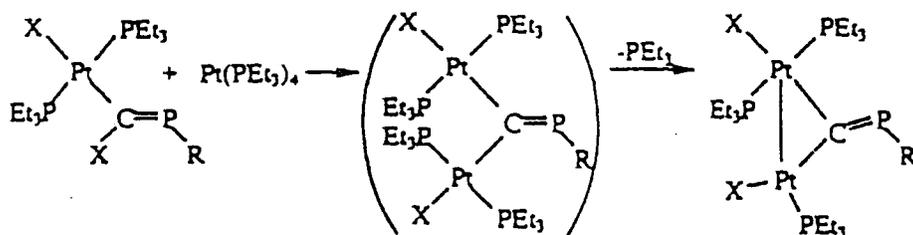


Although this is another probable synthesis method, it requires 8 steps from starting material ArH to product ArC≡P, and some of the reaction conditions are also very harsh. Hence this method is not being considered initially, and routes 1 and 2 will be tried first.

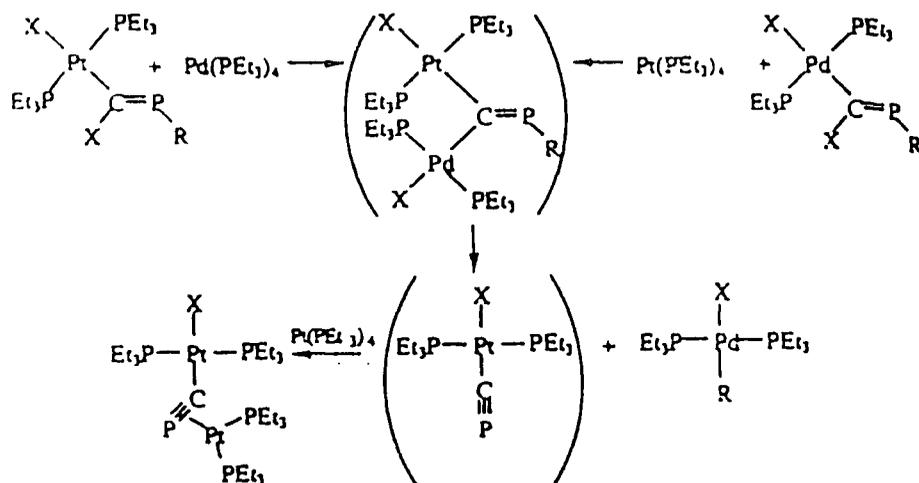
2. Synthesis Plan of Complexes

As discussed earlier in section I-4, using a phosphalkyne RC≡P to synthesise complexes will not be difficult, since there are several ways in which various types of complexes can be prepared. Here we only discuss using a phosphalkene to synthesise semibridged isocyaphide complexes and terminal cyaphide (C≡P) complexes.

In 1994, Jun and co-workers³¹ reported some very interesting reactions of phosphalkenes and the complexes Pt(PEt₃)₄ or Pd(PEt₃)₄. Halophosphalkenes R-P=CX₂ (R=2,4,6-tri-tert-butylphenyl, X=Br, Cl) react with Pt(PEt₃)₄ to form initially the normal complex [PtX(CX=PR)(PEt₃)₂]. This kind of complex can react further with Pd(PPh₃)₄ or Pt(PPh₃)₄ in benzene or hexane at room temperature to give semibridged isocyaphide platinum complexes.



However when these platinum complexes react with Pd(PEt₃)₄, giving the complexes [Pt(C≡P)(PEt₃)₂X] and [RPd(PEt₃)₂X], the species [Pt(C≡P)(PEt₃)] which contains a terminal cyaphide (C≡P-) ligand, reacts further with Pt(PEt₃)₄ rapidly to yield the terminal cyaphide diplatinum complex.



This kind of reaction is seldom reported, and the reaction mechanism looks quite unusual. I am interested in using this route to synthesise new semibridged isocyanide or terminal cyaphide complexes. While the first phosphalkyne with bulky electron withdrawing substituents is still not available, the phosphalkenes with such substituents have been made in this group before; using the phosphalkene to synthesise this semibridged isocyanide or terminal cyaphide complex directly is more rapid and simpler.

3. Attempts to synthesise phosphalkynes with bulky electron withdrawing substituents

The proposed synthesis routes of phosphalkynes with bulky electron withdrawing substituents all need to use a phosphalkene as the starting material, hence the phosphalkene with bulky electron withdrawing substituents is the key compound.

a. General Procedures.

All manipulations were carried out by using modified Schlenk techniques under an atmosphere of dry N_2 or in a glove-box. All solvents were distilled from Na/K alloy, or special dry solvent was treated by Na wire and 4A molecular sieves.

b. Preparation of ArLi , $\text{Ar}'\text{Li}$ and $\text{Ar}''\text{Li}$

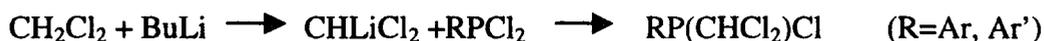
Using the same methods as Goodwin³⁰ and Roden²⁹, ArH was directly reacted with BuLi hexane solution (2.5M) at low temperature (-78 °C) in diethyl ether solvent to produce ArLi. If Ar'H instead of ArH is reacted with BuLi under the same conditions, a mixture of Ar'Li and Ar''Li is generated.

c. Preparation of R₂PCl₂ (R=Ar, Ar' and Ar'')

Similar to the methods of Goodwin³⁰ and Roden²⁹, an ArLi solution was reacted with PCl₃ in diethyl ether solution at -78 °C, giving a mixture of ArPCl₂ and Ar₂PCl; the precipitated LiCl was filtered off and pure ArPCl₂ was obtained by distillation. The same route was used to synthesise a mixture of Ar'PCl₂ and Ar''PCl₂.

d. Attempt to synthesise RP(CHCl₂)Cl (R=Ar, Ar')

i. Via the lithio species (CHLiCl₂)



According to the synthetic route of Goodwin³⁰ and Roden²⁹, CH₂Cl₂ was reacted with butyllithium in a mixed solvent (THF:Et₂O:Pentane = 4:1:1) at -130 °C (Pentane /liquid nitrogen slush), then this lithio reagent was added to a stirred solution of ArPCl₂ in diethyl ether at -130 °C. The mixture was allowed to warm to room temperature; a white precipitate was formed, then stirring was continued for 2 hours. The precipitate was filtered off and the solvent removed in vacuo, giving a crude yellow oil. The crude oil was distilled in vacuo to yield a clear yellow oil at 70 °C. The ³¹P NMR showed two peaks corresponding to ArPCl₂ (145 ppm) and ArP(CHCl₂)Cl (64 ppm).

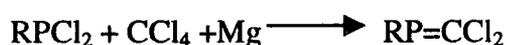
When Ar'PCl₂ was used instead of ArPCl₂, the same result happened, giving a mixture of the starting material Ar'PCl₂ and the required Ar'P(CHCl₂)Cl. Because the boiling points are close, separation is very difficult. This experiment has been repeated over 10 times, but gives a mixture of products, every time.

ii. Via an organocadmium reagent



CHLiCl₂ was prepared as described in d-i. CdCl₂ was added directly to the stirred solution of CHLiCl₂ (Et₂O) at -130 °C, the reaction mixture was allowed to reach 0 °C and stirred for 1 hour, followed by the addition in portions of Ar'PCl₂ in Et₂O. The solution was refluxed for 1 hour, then cooled to room temperature. The precipitate was filtered off and the solution concentrated under vacuum, then distilled in vacuo. Similar to method d-i, a mixture of starting material Ar'PCl₂ and the wanted product Ar'P(CHCl₂)Cl was again obtained.

e. Attempt to synthesise ArP=CCl₂



Goodwin³⁰ found a ³¹P NMR signal possibly corresponding to ArP=CCl₂ in the reaction of ArPCl₂ and CCl₄ with Mg present; but unfortunately she was unsuccessful in her attempts to isolate the products from the reaction. Because I have prepared some ArPCl₂ and Ar'PCl₂, this could be a straightforward route from RPhCl₂ to RPh=CCl₂.

Under nitrogen protection, 4.4 g Ar'PCl₂ (13.93 mmol) and 1.36 ml CCl₄ (13.93 mmol) were placed in a 50ml flask, and 0.668g Mg turnings (27.86 mmol) added at 0 °C, then the mixture was allowed to warm to room temperature and stirring continued overnight. When the ³¹P NMR was recorded, the main signal still corresponded to Ar'PCl₂, and a small signal was found at 460 ppm, attributed to the diphosphene Ar'P=PAR', but no signal for Ar'P=CCl₂ was present.

f. The preparation of Pt(PPh₃)₄

This product is required for the synthesis of phosphalkynes. According to May's method³², K₂PtCl₄ was reacted with PPh₃ first, then NaBH₄ was added; the bright yellow precipitate Pt(PPh₃)₄ formed in the solution, was isolated by filtering and

washing, yield 68.6%. Elemental analysis: calculated, C, 69.50%, H, 4.83%. Found, C, 68.28%, H, 4.58%.

III. Suggestions for future work

1. *Using the crude products to synthesise $RP=Cl_2$ ($R=Ar'$ or Ar)*

Although pure $ArP(CHCl_2)Cl$ and $Ar'P(CHCl_2)Cl$ were not obtained, but certainly these compounds had been made, the next step is direct reaction with DBU to remove HCl and produce the phosphalkene $RP=CCl_2$. The impurities $ArPCl_2$ or $Ar'PCl_2$ should not react with DBU, and thus would not affect the reaction of $Ar'P(CHCl_2)Cl$ [or $ArP(CHCl_2)Cl$] with DBU. The boiling points of the expected products $ArP=CCl_2$ or $Ar'P=CCl_2$ have a larger gap with $ArPCl_2$ or $Ar'PCl_2$ respectively than $ArP(CHCl_2)Cl$ or $Ar'P(CHCl_2)Cl$. So using the crude products to carry out the next step may lead to the isolation of pure $ArP=CCl_2$ or $Ar'P=CCl_2$.

2. *Synthesis of phosphalkynes*

a. Via phosphalkene complex with Pt

Even though the reaction looks straightforward, and the reaction conditions are mild, in fact the conditions are very important, such as the solvent, reaction temperature and other factors; all can affect the reaction mechanism and products. So the experiment needs to be done in different conditions.

B. By reacting a phosphalkene and butyllithium

This method has been used to prepare phosphalkynes, but the phosphalkene used was $RP=CHCl$, not $RP=PCl_2$. Since this reaction is one step, however, and the product is easy to separate, I suggest it should be tried first.

Reference

1. T. E. Gier, *J. Am. Chem. Soc.*, **83**, 1796 (1961).
2. G. Becker, G. Gesser and W. Uhl, *Z. Naturforsch, B* **36**, 16 (1981).
3. M. Regitz, T. Allspach, W. Rosch and U. Vogelbacher, *J. Organomet. Chem.*, **306**, 39 (1986).
4. H. W. Kroto, J. F. Nixon, N. P. C. Simmons and N. P. C. Westwood, *J. Am. Chem. Soc.*, **100**, 446 (1978).
5. J. M. Denis, P. Savignac, P. Puenot, T. Janati and J. C. Guillemin, *Angew. Chem., Int. Ed. Engl.*, **30**, 196 (1991).
6. V. D. Romanenko, M. Sanchez, T. V. Sarina, M. Mazieres and R. Wolf, *Tett. Lett.*, **33**, 2981 (1992).
7. H. Jun, V. C. Young and R. J. Angelici, *Organometallics*, **13**, 2444 (1994).
8. M. Yoshifuji, T. Niitsu and N. Inamoto, *Chemistry Letters*, 1733 (1988).
9. L. N. Markovskii, G. N. Koidan, A. P. Marchenko, V. D. Romanenko, M. I. Povolotskii and A. M. Pinchuk, *Zh. Obshch. Khim.*, **59**, 2133 (1989).
10. K. B. Dillon, F. Mathey and J. F. Nixon, *Phosphorus: The Carbon Copy*. John Wiley & Sons, Chichester (1998).
11. J. F. Nixon, *Chem. Rev.*, **88**, 1327 (1988); *Coord. Chem. Rev.*, **145**, 201 (1995).
12. J. F. Nixon, *Chem. Ind.*, 404 (1993); *Endeavour*, **145**, 49 (1991).
13. M. Regitz, *Chem. Rev.*, **90**, 191 (1990).
14. M. Regitz and P. Binger, *Angew. Chem., Int. Ed. Engl.*, **27**, 1484 (1988).
15. M. Regitz and P. Binger, *Multiple Bonds and Low Coordination in Phosphorus Chemistry*, M. Regitz and O. J. Scherer (eds), Thieme, Stuttgart, Chapter 2 (1990).
16. M. Regitz, *J. Heterocyclic Chem.*, **31**, 663 (1994).
17. M. Regitz, *Proceedings of the 4th symposium on organic synthesis via organometallics*, Aachen, pp93-113 (1992); ref. 7 in chapter 4.3 of ref. 10 above.
18. M. Regitz, *Heteroatom Chemistry*, E. Block (ed.), VCH Publishers, New York, 295 (1990).
19. J. C. T. R. Burckett-St. Laurent, P. B. Hitchcock, H. W. Kroto and J. F. Nixon, *J. Chem. Soc., Chem. Commun.*, 1141 (1981).
20. S. I. Al-Resayes, S. I. Klein, H. W. Kroto, M. F. Meidine and J. F. Nixon,

- J. Chem. Soc., Chem. Commun.*, 930 (1983).
21. S. I. Al-Resayes, P. B. Hitchcock, M. F. Meidine and J. F. Nixon, *J. Chem. Soc., Chem. Commun.*, 1080 (1984).
 22. P. B. Hitchcock, M. J. Maah, J. F. Nixon, J. A. Zora, G. J. Leigh and M. A. Baker, *Angew. Chem., Int. Ed. Engl.*, 26, 1474 (1987).
 23. D. Carmichael, S. I. Al-Resayes and J. F. Nixon, *J. Organomet. Chem.*, 453, 207 (1993).
 24. J. C. T. R. Burckett-St. Laurent, P. B. Hitchcock, H. W. Kroto, M. F. Meidine and J. F. Nixon, *J. Organomet. Chem.*, 238, 82 (1982).
 25. P. B. Hitchcock, M. F. Meidine and J. F. Nixon, *J. Organomet. Chem.*, 333, 337 (1987).
 26. R. Bartsch, P. B. Hitchcock, M. F. Meidine and J. F. Nixon, *J. Organomet. Chem.*, 266, C41 (1984).
 27. M. F. Meidine, C. J. Meir, S. Morton and J. F. Nixon, *J. Organomet. Chem.*, 297, 255 (1985).
 28. G. Becker, W. A. Herrmann, W. Kalcher, G. W. Kriechbaum, C. Pahl, C. T. Wanger and M. L. Ziegler, *Angew. Chem., Int. Ed. Engl.*, 22, 413 (1983).
 29. M. D. Roden, *Ph. D. Thesis*, Durham (1998).
 30. H. P. Goodwin, *Ph. D. Thesis*, Durham (1990).
 31. H. Jun and R. J. Angelici, *Organometallics* 13, 2454 (1994).
 32. I. May, *Ph. D. Thesis*, Durham (1995).

Appendix

I. Instrumentation and apparatus

1. Experimental techniques and solvents

All manipulations of air- and/or moisture-sensitive compounds were performed on a conventional vacuum/inert atmosphere (nitrogen) line, using standard Schlenk and cannular technique, or in an inert atmosphere (nitrogen) filled dry glove box.

The following solvents were dried by prolonged reflux over a suitable drying agent, freshly distilled and deoxygenated prior to use; pentane(lithium aluminium hydride), diethylether (lithium aluminium hydride), tetrahydrofuran (sodium benzophenone ketyl), dichloromethane(calcium hydride), and stored under nitrogen. Special dry solvents were first dried by Na wire and then stored under nitrogen over fresh activated 4Å molecular sieves.

2. Instrumentation and apparatus

a. Elemental analysis

C, H and N were determined by micro-combustion with a CE-440 Elemental Analyser. Chlorine was determined by potentiometric titration against N/100 silver nitrate solution using Ag/AgCl electrodes in an acetone medium.

b. Nuclear magnetic resonance spectroscopy

All ^{31}P NMR spectra were recorded on Varian VXR400 or Varian Mercury 200 MHz Fourier- Transform spectrometers, at 161.91 and 80.96 MHz respectively, with an external reference of 85% H_3PO_4 ; all ^{19}F NMR spectra were recorded on a Varian Mercury 200 MHz instrument at 188.18 MHz, with an internal reference of CFCl_3 ; all ^{119}Sn NMR spectra were recorded on a Varian Unity 300 MHz spectrometer at 111.84 MHz, with external reference of Me_4Sn .

c. X-ray crystallography

All crystal structures and data were collected on a Smart CCD Area Detector Diffractometer at 120K.

II. X-ray crystallographic data

1. Crystal data of SnAr_2Cl_2

Table 1. Crystal data and structure refinement for 99srv178.

Identification code	99srv178	
Empirical formula	$\text{C}_{18}\text{H}_4\text{Cl}_2\text{F}_{18}\text{Sn}$	
Formula weight	751.80	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2(1)/c$	
Number of reflections for cell determination	4663	
Theta range for cell determination	3.09° to 26.56°	
Unit cell dimensions	$a = 8.465(1)$ Å	$\alpha = 90^\circ$.
	$b = 30.409(4)$ Å	$\beta = 96.635(2)^\circ$.
	$c = 8.724(1)$ Å	$\gamma = 90^\circ$.
Volume	2230.6(5) Å ³	
Z	4	
Density (calculated)	2.239 Mg/m ³	
Absorption coefficient	1.543 mm ⁻¹	
F(000)	1432	
Crystal size	0.46 x 0.22 x 0.06 mm ³	
Crystal shape	thin plate	
Crystal colour	colourless	
Diffractometer	Bruker SMART-CCD	
Data collection method	omega scans	
Theta range for data collection	3.09 to 26.56°.	
Index ranges	$-8 \leq h \leq 10$, $-38 \leq k \leq 22$, $-10 \leq l \leq 10$	
Reflections collected	11861	
Independent reflections	4298 [R(int) = 0.0518]	
Completeness to theta = 26.56°	92.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.862 and 0.630	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	4298 / 1 / 346	
Goodness-of-fit on F ²	1.043	
Final R indices [I > 2σ(I)]	R1 = 0.0535, wR2 = 0.1116	
R indices (all data)	R1 = 0.0849, wR2 = 0.1226	
Largest diff. peak and hole	1.626 and -0.970 e.Å ⁻³	

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 99srv178. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
Sn(1)	2418(1)	3822(1)	5437(1)	21(1)
Cl(1)	862(2)	4003(1)	7375(2)	37(1)
Cl(2)	4903(2)	3742(1)	6775(2)	32(1)
C(1)	1076(7)	3231(2)	4645(7)	21(1)
C(2)	1608(7)	2797(2)	4907(8)	23(1)
C(3)	648(8)	2435(2)	4528(7)	26(2)
C(4)	-912(8)	2491(2)	3860(7)	26(2)
C(5)	-1456(8)	2911(2)	3551(7)	25(1)
C(6)	-501(7)	3274(2)	3937(7)	22(1)
C(7)	3240(9)	2699(2)	5704(9)	34(2)
F(1)	4386(5)	2887(1)	4976(5)	35(1)
F(2)	3568(5)	2267(1)	5775(6)	55(1)
F(3)	3407(5)	2848(2)	7160(5)	42(1)
C(8)	-1967(5)	2106(1)	3475(5)	33(2)
F(4A)	-1563(5)	1769(1)	4416(5)	76(4)
F(5A)	-1892(5)	1963(1)	2041(5)	102(5)
F(6A)	-3491(5)	2195(1)	3593(5)	84(4)
F(4B)	-1224(5)	1719(1)	3532(5)	76(4)
F(5B)	-2735(5)	2145(1)	2059(5)	102(5)
F(6B)	-3072(5)	2082(1)	4444(5)	84(4)
C(9)	-1329(8)	3707(2)	3583(8)	30(2)
F(7)	-373(5)	4053(1)	3765(5)	38(1)
F(8)	-2444(6)	3775(2)	4499(7)	65(2)
F(9)	-2045(7)	3722(2)	2164(6)	67(2)
C(11)	2712(7)	4358(2)	3835(7)	20(1)
C(12)	2658(7)	4802(2)	4238(7)	20(1)
C(13)	2592(8)	5137(2)	3150(7)	23(1)
C(14)	2602(7)	5029(2)	1597(7)	20(1)
C(15)	2765(8)	4594(2)	1170(7)	23(1)
C(16)	2823(7)	4269(2)	2275(7)	20(1)
C(17)	2665(8)	4958(2)	5889(7)	24(2)

F(10)	3456(5)	4675(1)	6900(4)	28(1)
F(11)	1218(5)	5002(1)	6303(4)	34(1)
F(12)	3407(5)	5342(1)	6107(4)	35(1)
C(18)	2491(9)	5384(2)	378(8)	27(1)
F(13)	3707(6)	5382(2)	-426(6)	58(1)
F(14)	2365(6)	5782(1)	962(4)	43(1)
F(15)	1194(6)	5324(2)	-629(5)	53(1)
C(19)	3033(8)	3806(2)	1722(7)	28(2)
F(16)	3808(5)	3551(1)	2836(4)	34(1)
F(17)	3836(5)	3783(1)	504(5)	40(1)
F(18)	1622(5)	3602(1)	1311(5)	37(1)

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 99srvt178. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Sn(1)	24(1)	20(1)	18(1)	1(1)	1(1)	-1(1)
Cl(1)	40(1)	42(1)	33(1)	-5(1)	16(1)	-6(1)
Cl(2)	29(1)	30(1)	35(1)	1(1)	-8(1)	1(1)
C(1)	23(3)	19(3)	21(3)	5(2)	4(3)	0(3)
C(2)	17(3)	23(3)	31(4)	3(3)	7(3)	-2(3)
C(3)	30(4)	20(3)	29(4)	1(3)	3(3)	6(3)
C(4)	31(4)	22(3)	27(3)	-4(3)	5(3)	-5(3)
C(5)	26(4)	22(3)	25(3)	-3(3)	1(3)	1(3)
C(6)	20(3)	20(3)	24(3)	3(3)	-1(3)	2(3)
C(7)	35(4)	21(3)	44(4)	6(3)	-2(3)	1(3)
F(1)	27(2)	35(2)	42(2)	1(2)	0(2)	4(2)
F(2)	40(3)	27(2)	92(4)	15(2)	-19(3)	5(2)
F(3)	39(3)	55(3)	31(2)	13(2)	-9(2)	-3(2)
C(8)	34(4)	31(4)	33(4)	1(3)	-3(3)	-2(3)
F(4A)	81(5)	35(3)	104(9)	4(5)	-23(6)	-26(4)
F(5A)	150(12)	109(9)	52(4)	-44(5)	36(6)	-92(9)
F(6A)	25(4)	45(4)	182(13)	-41(6)	7(6)	-11(3)
F(4B)	81(5)	35(3)	104(9)	4(5)	-23(6)	-26(4)
F(5B)	150(12)	109(9)	52(4)	-44(5)	36(6)	-92(9)
F(6B)	25(4)	45(4)	182(13)	-41(6)	7(6)	-11(3)
C(9)	26(4)	28(4)	35(4)	7(3)	1(3)	-4(3)
F(7)	28(2)	23(2)	60(3)	7(2)	-7(2)	-3(2)
F(8)	48(3)	39(3)	115(5)	25(3)	40(3)	17(3)
F(9)	85(4)	43(3)	62(3)	6(2)	-38(3)	13(3)
C(11)	18(3)	21(3)	21(3)	0(2)	0(2)	-1(3)
C(12)	18(3)	23(3)	18(3)	0(2)	4(3)	2(3)
C(13)	28(4)	22(3)	19(3)	1(3)	0(3)	-3(3)
C(14)	16(3)	23(3)	20(3)	2(3)	2(2)	-1(3)
C(15)	27(4)	23(3)	21(3)	-3(3)	4(3)	1(3)
C(16)	20(3)	21(3)	17(3)	-1(2)	3(2)	-4(3)
C(17)	29(4)	24(3)	18(3)	-3(3)	1(3)	6(3)

F(10)	41(2)	24(2)	16(2)	-2(2)	-3(2)	2(2)
F(11)	33(2)	47(2)	23(2)	-6(2)	5(2)	9(2)
F(12)	55(3)	24(2)	23(2)	-7(2)	-4(2)	-9(2)
C(18)	31(4)	28(3)	23(3)	-1(3)	2(3)	-1(3)
F(13)	63(3)	58(3)	62(3)	34(3)	40(3)	18(3)
F(14)	80(3)	23(2)	26(2)	3(2)	3(2)	6(2)
F(15)	71(3)	46(3)	34(2)	16(2)	-24(2)	-18(2)
C(19)	39(4)	25(3)	21(3)	1(3)	3(3)	4(3)
F(16)	51(3)	25(2)	26(2)	-3(2)	8(2)	6(2)
F(17)	65(3)	26(2)	32(2)	-4(2)	23(2)	4(2)
F(18)	49(3)	22(2)	38(2)	-10(2)	1(2)	-9(2)

Table 5. Torsion angles [°] for 99srv178.

C(11)-Sn(1)-C(1)-C(2)	130.5(5)
Cl(2)-Sn(1)-C(1)-C(2)	0.8(6)
Cl(1)-Sn(1)-C(1)-C(2)	-107.2(5)
C(11)-Sn(1)-C(1)-C(6)	-55.6(6)
Cl(2)-Sn(1)-C(1)-C(6)	174.8(4)
Cl(1)-Sn(1)-C(1)-C(6)	66.7(5)
C(6)-C(1)-C(2)-C(3)	-1.3(9)
Sn(1)-C(1)-C(2)-C(3)	172.8(5)
C(6)-C(1)-C(2)-C(7)	-177.7(6)
Sn(1)-C(1)-C(2)-C(7)	-3.6(9)
C(1)-C(2)-C(3)-C(4)	0.0(10)
C(7)-C(2)-C(3)-C(4)	176.7(6)
C(2)-C(3)-C(4)-C(5)	1.7(10)
C(2)-C(3)-C(4)-C(8)	-178.8(6)
C(3)-C(4)-C(5)-C(6)	-2.1(10)
C(8)-C(4)-C(5)-C(6)	178.4(6)
C(4)-C(5)-C(6)-C(1)	0.8(10)
C(4)-C(5)-C(6)-C(9)	-177.0(6)
C(2)-C(1)-C(6)-C(5)	0.9(9)
Sn(1)-C(1)-C(6)-C(5)	-173.6(5)
C(2)-C(1)-C(6)-C(9)	178.5(6)
Sn(1)-C(1)-C(6)-C(9)	4.0(8)
C(3)-C(2)-C(7)-F(3)	-113.2(7)
C(1)-C(2)-C(7)-F(3)	63.5(8)
C(3)-C(2)-C(7)-F(2)	6.8(9)
C(1)-C(2)-C(7)-F(2)	-176.6(6)
C(3)-C(2)-C(7)-F(1)	126.6(6)
C(1)-C(2)-C(7)-F(1)	-56.8(9)
C(5)-C(4)-C(8)-F(4A)	-151.9(5)
C(3)-C(4)-C(8)-F(4A)	28.6(7)
C(5)-C(4)-C(8)-F(5A)	88.5(6)
C(3)-C(4)-C(8)-F(5A)	-91.0(6)
C(5)-C(4)-C(8)-F(5B)	45.8(6)
C(3)-C(4)-C(8)-F(5B)	-133.7(5)

C(5)-C(4)-C(8)-F(6B)	-72.4(6)
C(3)-C(4)-C(8)-F(6B)	108.1(6)
C(5)-C(4)-C(8)-F(4B)	166.9(5)
C(3)-C(4)-C(8)-F(4B)	-12.6(7)
C(5)-C(4)-C(8)-F(6A)	-32.0(6)
C(3)-C(4)-C(8)-F(6A)	148.5(5)
C(5)-C(6)-C(9)-F(9)	-50.0(8)
C(1)-C(6)-C(9)-F(9)	132.2(7)
C(5)-C(6)-C(9)-F(8)	68.6(8)
C(1)-C(6)-C(9)-F(8)	-109.1(7)
C(5)-C(6)-C(9)-F(7)	-171.9(6)
C(1)-C(6)-C(9)-F(7)	10.3(9)
C(1)-Sn(1)-C(11)-C(12)	141.2(5)
Cl(2)-Sn(1)-C(11)-C(12)	-82.7(5)
Cl(1)-Sn(1)-C(11)-C(12)	28.0(6)
C(1)-Sn(1)-C(11)-C(16)	-32.8(6)
Cl(2)-Sn(1)-C(11)-C(16)	103.2(5)
Cl(1)-Sn(1)-C(11)-C(16)	-146.0(4)
C(16)-C(11)-C(12)-C(13)	4.9(9)
Sn(1)-C(11)-C(12)-C(13)	-169.4(5)
C(16)-C(11)-C(12)-C(17)	-175.2(6)
Sn(1)-C(11)-C(12)-C(17)	10.5(9)
C(11)-C(12)-C(13)-C(14)	-0.9(10)
C(17)-C(12)-C(13)-C(14)	179.1(6)
C(12)-C(13)-C(14)-C(15)	-3.6(9)
C(12)-C(13)-C(14)-C(18)	178.5(6)
C(13)-C(14)-C(15)-C(16)	3.8(9)
C(18)-C(14)-C(15)-C(16)	-178.3(6)
C(14)-C(15)-C(16)-C(11)	0.4(10)
C(14)-C(15)-C(16)-C(19)	-178.9(6)
C(12)-C(11)-C(16)-C(15)	-4.7(9)
Sn(1)-C(11)-C(16)-C(15)	169.8(5)
C(12)-C(11)-C(16)-C(19)	174.6(6)
Sn(1)-C(11)-C(16)-C(19)	-10.9(8)
C(13)-C(12)-C(17)-F(11)	89.1(7)
C(11)-C(12)-C(17)-F(11)	-90.9(7)

C(13)-C(12)-C(17)-F(12)	-32.5(8)
C(11)-C(12)-C(17)-F(12)	147.5(6)
C(13)-C(12)-C(17)-F(10)	-150.6(6)
C(11)-C(12)-C(17)-F(10)	29.4(9)
C(15)-C(14)-C(18)-F(13)	-56.2(8)
C(13)-C(14)-C(18)-F(13)	121.8(7)
C(15)-C(14)-C(18)-F(14)	-179.0(6)
C(13)-C(14)-C(18)-F(14)	-1.0(9)
C(15)-C(14)-C(18)-F(15)	62.5(8)
C(13)-C(14)-C(18)-F(15)	-119.6(7)
C(15)-C(16)-C(19)-F(17)	29.3(8)
C(11)-C(16)-C(19)-F(17)	-150.0(6)
C(15)-C(16)-C(19)-F(16)	150.6(6)
C(11)-C(16)-C(19)-F(16)	-28.8(9)
C(15)-C(16)-C(19)-F(18)	-91.1(7)
C(11)-C(16)-C(19)-F(18)	89.5(7)

2. Crystal data of SnAr₂Cl₂

Table 1. Crystal data and structure refinement for 99srv176.

Identification code	99srv176	
Empirical formula	C16 H6 Cl2 F12 Sn	
Formula weight	615.80	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P 1	
Number of reflections for cell determination	507	
Theta range for cell determination	13.66° to 21.77°	
Unit cell dimensions	a = 8.783(2) Å	α = 81.697(4)°.
	b = 9.095(2) Å	β = 83.970(4)°.
	c = 12.162(3) Å	γ = 82.135(4)°.
Volume	948.7(4) Å ³	
Z	2	
Density (calculated)	2.156 Mg/m ³	
Absorption coefficient	1.744 mm ⁻¹	
F(000)	588	
Crystal size	0.50 x 0.40 x 0.38 mm ³	
Crystal shape	irregular shape	
Crystal colour	colourless	
Diffractometer	Bruker SMART-CCD	
Data collection method	omega scans	
Theta range for data collection	1.70 to 30.30°.	
Index ranges	-12 ≤ h ≤ 12, -9 ≤ k ≤ 12, -8 ≤ l ≤ 17	
Reflections collected	7955	
Independent reflections	6451 [R(int) = 0.0134]	
Completeness to theta = 30.30°	88.1 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.604 and 0.416	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	6451 / 3 / 560	
Goodness-of-fit on F ²	1.046	
Final R indices [I > 2σ(I)]	R1 = 0.0226, wR2 = 0.0596	
R indices (all data)	R1 = 0.0251, wR2 = 0.0618	
Absolute structure parameter	0.49(3)	
Largest diff. peak and hole	0.705 and -0.912 e.Å ⁻³	

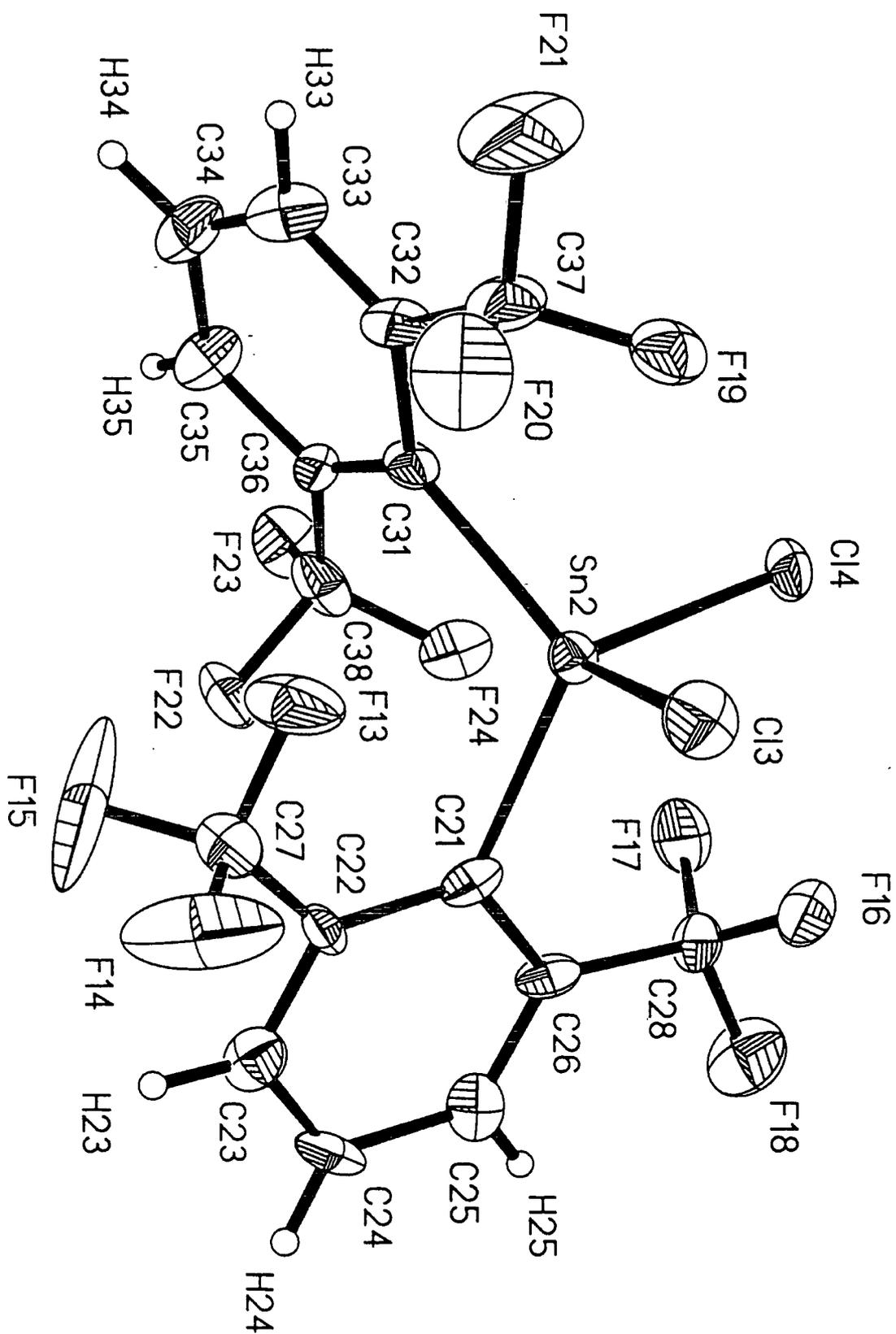


Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 99srvt176. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
Sn(1)	5225(1)	1217(1)	4805(1)	20(1)
Cl(1)	6261(3)	530(3)	6510(2)	31(1)
Cl(2)	7007(3)	2752(3)	3859(3)	40(1)
C(1)	2871(8)	2194(10)	5329(6)	21(2)
C(2)	2493(10)	3615(11)	5483(8)	27(2)
C(3)	885(10)	4257(12)	5791(9)	35(2)
C(4)	-236(11)	3253(14)	5936(10)	39(2)
C(5)	168(9)	1825(12)	5802(8)	36(3)
C(6)	1646(9)	1217(10)	5530(7)	23(2)
C(7)	3615(12)	4798(10)	5408(8)	31(2)
F(1)	3900(11)	5283(11)	4275(8)	70(3)
F(2)	4997(7)	4162(8)	5711(6)	39(2)
F(3)	3170(8)	5882(7)	5987(6)	48(1)
C(8)	1985(8)	-441(8)	5433(7)	22(2)
F(4)	3423(6)	-987(6)	5745(5)	32(1)
F(5)	1907(7)	-736(8)	4404(6)	42(2)
F(6)	1028(7)	-1198(7)	6136(6)	44(2)
C(11)	5417(9)	-413(9)	3635(6)	17(2)
C(12)	6246(9)	-1793(10)	3704(8)	23(2)
C(13)	6256(10)	-2806(9)	2937(8)	30(2)
C(14)	5423(11)	-2454(12)	2059(9)	35(2)
C(15)	4664(10)	-1049(10)	1855(7)	31(2)
C(16)	4630(10)	-25(10)	2659(8)	27(2)
C(17)	7151(11)	-2369(10)	4678(9)	33(2)
F(7)	8104(6)	-1307(7)	4843(5)	33(1)
F(8)	8092(8)	-3636(8)	4598(7)	55(2)
F(9)	6310(8)	-2592(8)	5683(6)	42(2)
C(18)	3710(10)	1576(10)	2332(7)	24(2)
F(10)	3977(8)	2599(7)	2926(6)	44(1)
F(11)	2202(5)	1513(8)	2465(7)	69(2)
F(12)	4026(9)	2115(8)	1286(5)	58(1)
Sn(2)	-335(1)	-4054(1)	9472(1)	20(1)

CI(3)	-2167(3)	-5546(3)	10378(2)	36(1)
CI(4)	-1365(3)	-3384(3)	7753(2)	29(1)
C(21)	-500(9)	-2482(9)	10702(7)	24(2)
C(22)	254(8)	-2880(10)	11666(6)	20(2)
C(23)	274(10)	-1901(10)	12391(7)	30(2)
C(24)	-555(11)	-472(12)	12256(7)	30(2)
C(25)	-1351(10)	-9(11)	11285(8)	30(2)
C(26)	-1350(10)	-975(9)	10486(8)	24(2)
C(27)	1075(12)	-4299(13)	11988(9)	36(2)
F(13)	1111(9)	-5305(7)	11270(6)	56(2)
F(14)	483(10)	-4980(8)	12939(5)	87(3)
F(15)	2534(7)	-4277(9)	12117(9)	123(4)
C(28)	-2326(10)	-510(11)	9534(8)	30(2)
F(16)	-3249(6)	-1463(8)	9423(6)	37(2)
F(17)	-1427(8)	-252(8)	8598(6)	42(2)
F(18)	-3241(8)	787(8)	9679(7)	53(2)
C(31)	1982(9)	-4963(9)	8943(7)	21(2)
C(32)	2445(11)	-6531(9)	8791(8)	23(2)
C(33)	3890(11)	-7040(9)	8539(8)	31(2)
C(34)	5058(11)	-6195(12)	8419(9)	36(2)
C(35)	4711(10)	-4635(10)	8480(8)	32(2)
C(36)	3129(8)	-4108(9)	8762(7)	23(2)
C(37)	1255(11)	-7562(11)	8996(10)	36(2)
F(19)	-90(7)	-6946(7)	8532(5)	35(1)
F(20)	887(10)	-8134(9)	9986(7)	55(2)
F(21)	1724(9)	-8794(8)	8470(8)	82(3)
C(38)	2897(10)	-2469(11)	8803(7)	33(2)
F(22)	3036(7)	-2100(8)	9830(5)	39(1)
F(23)	3897(7)	-1663(7)	8131(5)	39(2)
F(24)	1468(6)	-1819(6)	8578(5)	30(1)

Table 3. Bond lengths [\AA] and angles [$^\circ$] for 99sr176.

Sn(2)-C(31)	2.158(8)
Sn(2)-C(21)	2.195(9)
Sn(2)-Cl(3)	2.332(3)
Sn(2)-Cl(4)	2.332(2)
C(21)-C(22)	1.385(12)
C(21)-C(26)	1.471(11)
C(22)-C(23)	1.343(12)
C(22)-C(27)	1.414(14)
C(23)-C(24)	1.397(13)
C(23)-H(23)	0.9300
C(24)-C(25)	1.418(13)
C(24)-H(24)	0.9300
C(25)-C(26)	1.400(13)
C(25)-H(25)	0.9300
C(26)-C(28)	1.491(12)
C(27)-F(15)	1.311(12)
C(27)-F(14)	1.321(12)
C(27)-F(13)	1.348(13)
C(28)-F(16)	1.294(12)
C(28)-F(17)	1.327(12)
C(28)-F(18)	1.356(11)
C(31)-C(36)	1.337(11)
C(31)-C(32)	1.461(10)
C(32)-C(33)	1.310(13)
C(32)-C(37)	1.477(14)
C(33)-C(34)	1.348(14)
C(33)-H(33)	0.9300
C(34)-C(35)	1.421(14)
C(34)-H(34)	0.9300
C(35)-C(36)	1.429(11)
C(35)-H(35)	0.9300
C(36)-C(38)	1.484(13)
C(37)-F(20)	1.268(13)
C(37)-F(21)	1.363(12)
C(37)-F(19)	1.377(12)
C(38)-F(23)	1.352(10)
C(38)-F(24)	1.350(11)
C(38)-F(22)	1.361(10)

C(31)-Sn(2)-Cl(4)	100.5(2)
C(21)-Sn(2)-Cl(4)	122.2(2)
Cl(3)-Sn(2)-Cl(4)	99.37(10)
C(22)-C(21)-C(26)	119.4(8)
C(22)-C(21)-Sn(2)	120.2(6)
C(26)-C(21)-Sn(2)	120.3(6)
C(23)-C(22)-C(21)	121.5(8)
C(23)-C(22)-C(27)	113.4(7)
C(21)-C(22)-C(27)	125.1(8)
C(22)-C(23)-C(24)	121.9(8)
C(22)-C(23)-H(23)	119.1
C(24)-C(23)-H(23)	119.1
C(23)-C(24)-C(25)	118.8(8)
C(23)-C(24)-H(24)	120.6
C(25)-C(24)-H(24)	120.6
C(26)-C(25)-C(24)	121.0(8)
C(26)-C(25)-H(25)	119.5
C(24)-C(25)-H(25)	119.5
C(25)-C(26)-C(21)	117.2(8)
C(25)-C(26)-C(28)	119.6(7)
C(21)-C(26)-C(28)	122.8(8)
F(15)-C(27)-F(14)	105.8(10)
F(15)-C(27)-F(13)	103.6(9)
F(14)-C(27)-F(13)	103.7(9)
F(15)-C(27)-C(22)	114.6(9)
F(14)-C(27)-C(22)	112.8(8)
F(13)-C(27)-C(22)	115.3(8)
F(16)-C(28)-F(17)	109.9(9)
F(16)-C(28)-F(18)	105.8(8)
F(17)-C(28)-F(18)	107.3(8)
F(16)-C(28)-C(26)	114.1(8)
F(17)-C(28)-C(26)	109.4(8)
F(18)-C(28)-C(26)	110.1(8)
C(36)-C(31)-C(32)	114.7(7)
C(36)-C(31)-Sn(2)	121.1(6)
C(32)-C(31)-Sn(2)	124.2(6)
C(33)-C(32)-C(31)	121.4(8)

C(33)-C(32)-C(37)	120.2(8)
C(31)-C(32)-C(37)	118.3(8)
C(32)-C(33)-C(34)	123.9(9)
C(32)-C(33)-H(33)	118.1
C(34)-C(33)-H(33)	118.1
C(33)-C(34)-C(35)	118.8(8)
C(33)-C(34)-H(34)	120.6
C(35)-C(34)-H(34)	120.6
C(34)-C(35)-C(36)	116.1(8)
C(34)-C(35)-H(35)	121.9
C(36)-C(35)-H(35)	122.0
C(31)-C(36)-C(35)	124.8(8)
C(31)-C(36)-C(38)	123.5(7)
C(35)-C(36)-C(38)	111.6(8)
F(20)-C(37)-F(21)	102.5(9)
F(20)-C(37)-F(19)	107.3(8)
F(21)-C(37)-F(19)	103.7(9)
F(20)-C(37)-C(32)	119.5(10)
F(21)-C(37)-C(32)	110.2(8)
F(19)-C(37)-C(32)	112.1(8)
F(23)-C(38)-F(24)	106.4(7)
F(23)-C(38)-F(22)	103.1(7)
F(24)-C(38)-F(22)	103.2(7)
F(23)-C(38)-C(36)	116.1(8)
F(24)-C(38)-C(36)	113.4(7)
F(22)-C(38)-C(36)	113.3(8)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 99srv176. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Sn(1)	19(1)	21(1)	20(1)	-3(1)	-2(1)	-4(1)
Cl(1)	26(1)	42(1)	24(1)	-3(1)	-3(1)	-7(1)
Cl(2)	44(1)	30(1)	44(1)	-5(1)	22(1)	-17(1)
C(1)	13(3)	33(4)	16(3)	5(3)	-1(2)	-5(3)
C(2)	20(3)	40(5)	21(4)	-1(3)	-4(3)	-5(3)
C(3)	21(3)	43(5)	39(5)	-12(4)	-6(3)	13(3)
C(4)	18(3)	52(6)	44(5)	-2(4)	4(3)	-2(3)
C(5)	18(4)	58(7)	36(5)	-6(5)	-12(3)	-8(4)
C(6)	21(3)	30(4)	20(3)	3(3)	-2(2)	-17(2)
C(7)	42(4)	25(4)	26(3)	1(3)	-1(3)	-13(3)
F(1)	70(4)	81(6)	58(5)	32(4)	-16(4)	-45(4)
F(2)	27(2)	40(3)	56(4)	-14(3)	-11(2)	-10(2)
F(3)	49(3)	32(3)	66(3)	-21(2)	3(2)	-2(2)
C(8)	17(3)	13(3)	40(4)	-6(3)	-7(3)	-5(2)
F(4)	28(2)	25(3)	46(3)	-7(2)	-19(2)	-2(2)
F(5)	46(3)	50(4)	37(3)	-20(3)	2(2)	-19(3)
F(6)	40(3)	30(3)	59(4)	1(3)	18(3)	-13(2)
C(11)	20(3)	23(3)	11(3)	2(2)	-6(2)	-12(2)
C(12)	15(3)	36(4)	17(3)	5(3)	-3(2)	-7(3)
C(13)	33(4)	17(4)	40(5)	-15(3)	20(3)	-7(3)
C(14)	34(4)	26(4)	48(6)	-10(4)	5(4)	-15(3)
C(15)	37(4)	46(4)	21(3)	-22(3)	-2(3)	-19(3)
C(16)	25(4)	20(3)	30(4)	4(3)	2(3)	3(3)
C(17)	31(4)	19(3)	45(5)	-1(3)	4(3)	-6(3)
F(7)	26(2)	40(3)	36(3)	-2(3)	-12(2)	-4(2)
F(8)	57(4)	38(4)	69(5)	-13(3)	-29(3)	29(3)
F(9)	40(3)	46(4)	32(4)	22(3)	-1(3)	-7(3)
C(18)	24(3)	27(3)	17(3)	4(3)	-11(2)	8(2)
F(10)	73(3)	26(2)	36(3)	-1(2)	-30(2)	3(2)
F(11)	22(2)	48(3)	127(4)	16(3)	-3(2)	0(2)
F(12)	94(3)	49(3)	22(2)	2(2)	-12(2)	19(2)
Sn(2)	20(1)	21(1)	19(1)	-2(1)	-2(1)	-5(1)

CI(3)	35(1)	37(1)	39(1)	-3(1)	1(1)	-17(1)
CI(4)	24(1)	43(1)	22(1)	-6(1)	-10(1)	-2(1)
C(21)	19(3)	19(3)	30(4)	-4(3)	3(3)	4(3)
C(22)	18(3)	32(4)	14(3)	-7(3)	-2(2)	-10(3)
C(23)	30(3)	28(3)	28(4)	5(3)	-2(3)	1(3)
C(24)	40(5)	35(5)	18(3)	-14(3)	5(3)	-9(4)
C(25)	28(4)	30(4)	31(4)	4(3)	-6(3)	-8(3)
C(26)	27(3)	12(3)	30(4)	-5(2)	4(3)	2(2)
C(27)	36(4)	44(5)	30(4)	-12(4)	-4(3)	-5(3)
F(13)	93(4)	36(3)	31(2)	-10(2)	-16(2)	33(3)
F(14)	147(6)	44(3)	39(3)	23(2)	44(4)	30(3)
F(15)	65(4)	58(4)	254(10)	9(5)	-110(5)	3(3)
C(28)	27(3)	35(4)	25(3)	0(3)	-13(3)	11(3)
F(16)	22(2)	49(4)	39(4)	-7(3)	-4(2)	-1(2)
F(17)	44(4)	46(4)	35(4)	2(3)	-15(3)	-6(3)
F(18)	50(4)	37(4)	67(5)	-1(3)	-14(3)	16(3)
C(31)	29(4)	12(3)	24(4)	-5(3)	-7(3)	-1(3)
C(32)	34(4)	7(3)	27(4)	-1(3)	-2(3)	1(3)
C(33)	41(4)	20(3)	26(4)	4(3)	8(3)	1(3)
C(34)	31(4)	32(4)	40(5)	2(3)	-2(3)	10(3)
C(35)	26(4)	29(5)	38(5)	4(4)	7(3)	-4(3)
C(36)	19(3)	29(4)	21(3)	-6(3)	-5(2)	5(2)
C(37)	35(4)	21(3)	52(5)	-16(3)	-2(3)	3(3)
F(19)	40(3)	28(3)	40(3)	-12(2)	-1(2)	-10(2)
F(20)	61(4)	49(4)	52(5)	23(3)	-5(3)	-24(3)
F(21)	63(4)	28(3)	161(8)	-47(4)	3(4)	-7(3)
C(38)	34(4)	55(5)	14(3)	-5(3)	3(3)	-23(4)
F(22)	48(3)	46(3)	30(3)	-12(2)	-16(2)	-10(3)
F(23)	38(3)	44(4)	38(3)	0(3)	3(2)	-25(3)
F(24)	32(2)	23(3)	32(3)	4(2)	8(2)	-9(2)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 99srv176.

	x	y	z	U(eq)
H(3)	630	5261	5882	42
H(4)	-1263	3595	6127	47
H(5)	-603	1200	5899	43
H(13)	6852	-3734	3041	36
H(14)	5361	-3163	1591	42
H(15)	4173	-752	1203	38
H(23)	857	-2183	13000	36
H(24)	-585	165	12794	36
H(25)	-1882	951	11176	36
H(33)	4122	-8043	8438	37
H(34)	6074	-6626	8298	44
H(35)	5469	-3994	8344	39

Table 6. Torsion angles [°] for 99srv176.

C(11)-Sn(1)-C(1)-C(2)	-141.5(7)
Cl(1)-Sn(1)-C(1)-C(2)	87.2(7)
Cl(2)-Sn(1)-C(1)-C(2)	-22.9(8)
C(11)-Sn(1)-C(1)-C(6)	39.0(7)
Cl(1)-Sn(1)-C(1)-C(6)	-92.3(6)
Cl(2)-Sn(1)-C(1)-C(6)	157.7(5)
C(6)-C(1)-C(2)-C(3)	-3.1(13)
Sn(1)-C(1)-C(2)-C(3)	177.4(7)
C(6)-C(1)-C(2)-C(7)	174.9(8)
Sn(1)-C(1)-C(2)-C(7)	-4.5(13)
C(1)-C(2)-C(3)-C(4)	1.3(14)
C(7)-C(2)-C(3)-C(4)	-177.1(9)
C(2)-C(3)-C(4)-C(5)	0.2(15)
C(3)-C(4)-C(5)-C(6)	0.5(17)
C(4)-C(5)-C(6)-C(1)	-2.4(14)
C(4)-C(5)-C(6)-C(8)	178.1(10)
C(2)-C(1)-C(6)-C(5)	3.7(12)
Sn(1)-C(1)-C(6)-C(5)	-176.8(7)
C(2)-C(1)-C(6)-C(8)	-176.9(8)
Sn(1)-C(1)-C(6)-C(8)	2.7(10)
C(1)-C(2)-C(7)-F(3)	-153.6(9)
C(3)-C(2)-C(7)-F(3)	24.6(12)
C(1)-C(2)-C(7)-F(2)	-30.7(13)
C(3)-C(2)-C(7)-F(2)	147.6(8)
C(1)-C(2)-C(7)-F(1)	80.7(12)
C(3)-C(2)-C(7)-F(1)	-101.0(10)
C(5)-C(6)-C(8)-F(6)	-31.9(11)
C(1)-C(6)-C(8)-F(6)	148.7(8)
C(5)-C(6)-C(8)-F(5)	91.2(10)
C(1)-C(6)-C(8)-F(5)	-88.3(9)
C(5)-C(6)-C(8)-F(4)	-147.8(8)
C(1)-C(6)-C(8)-F(4)	32.7(11)
C(1)-Sn(1)-C(11)-C(12)	-130.7(7)
Cl(1)-Sn(1)-C(11)-C(12)	-8.5(8)
Cl(2)-Sn(1)-C(11)-C(12)	99.3(7)

C(1)-Sn(1)-C(11)-C(16)	50.8(7)
Cl(1)-Sn(1)-C(11)-C(16)	173.0(5)
Cl(2)-Sn(1)-C(11)-C(16)	-79.2(6)
C(16)-C(11)-C(12)-C(13)	-4.4(12)
Sn(1)-C(11)-C(12)-C(13)	177.1(6)
C(16)-C(11)-C(12)-C(17)	179.6(8)
Sn(1)-C(11)-C(12)-C(17)	1.1(11)
C(11)-C(12)-C(13)-C(14)	0.2(14)
C(17)-C(12)-C(13)-C(14)	176.4(8)
C(12)-C(13)-C(14)-C(15)	5.8(14)
C(13)-C(14)-C(15)-C(16)	-7.1(14)
C(12)-C(11)-C(16)-C(15)	2.9(12)
Sn(1)-C(11)-C(16)-C(15)	-178.5(6)
C(12)-C(11)-C(16)-C(18)	-174.3(7)
Sn(1)-C(11)-C(16)-C(18)	4.4(11)
C(14)-C(15)-C(16)-C(11)	2.7(13)
C(14)-C(15)-C(16)-C(18)	-179.9(8)
C(11)-C(12)-C(17)-F(8)	-171.0(8)
C(13)-C(12)-C(17)-F(8)	12.7(12)
C(11)-C(12)-C(17)-F(9)	64.6(11)
C(13)-C(12)-C(17)-F(9)	-111.8(9)
C(11)-C(12)-C(17)-F(7)	-51.5(11)
C(13)-C(12)-C(17)-F(7)	132.1(8)
C(11)-C(16)-C(18)-F(12)	133.1(9)
C(15)-C(16)-C(18)-F(12)	-44.3(11)
C(11)-C(16)-C(18)-F(10)	12.2(12)
C(15)-C(16)-C(18)-F(10)	-165.1(8)
C(11)-C(16)-C(18)-F(11)	-108.0(10)
C(15)-C(16)-C(18)-F(11)	74.7(10)
C(31)-Sn(2)-C(21)-C(22)	-51.6(8)
Cl(3)-Sn(2)-C(21)-C(22)	80.0(7)
Cl(4)-Sn(2)-C(21)-C(22)	-173.8(5)
C(31)-Sn(2)-C(21)-C(26)	125.5(6)
Cl(3)-Sn(2)-C(21)-C(26)	-102.9(6)
Cl(4)-Sn(2)-C(21)-C(26)	3.3(7)
C(26)-C(21)-C(22)-C(23)	-2.4(13)
Sn(2)-C(21)-C(22)-C(23)	174.7(6)

C(26)-C(21)-C(22)-C(27)	178.2(8)
Sn(2)-C(21)-C(22)-C(27)	-4.7(12)
C(21)-C(22)-C(23)-C(24)	4.8(14)
C(27)-C(22)-C(23)-C(24)	-175.7(9)
C(22)-C(23)-C(24)-C(25)	-4.5(13)
C(23)-C(24)-C(25)-C(26)	1.9(14)
C(24)-C(25)-C(26)-C(21)	0.3(13)
C(24)-C(25)-C(26)-C(28)	173.9(8)
C(22)-C(21)-C(26)-C(25)	-0.1(12)
Sn(2)-C(21)-C(26)-C(25)	-177.3(6)
C(22)-C(21)-C(26)-C(28)	-173.4(8)
Sn(2)-C(21)-C(26)-C(28)	9.5(11)
C(23)-C(22)-C(27)-F(15)	-58.5(12)
C(21)-C(22)-C(27)-F(15)	120.9(11)
C(23)-C(22)-C(27)-F(14)	62.6(12)
C(21)-C(22)-C(27)-F(14)	-118.0(10)
C(23)-C(22)-C(27)-F(13)	-178.6(9)
C(21)-C(22)-C(27)-F(13)	0.8(14)
C(25)-C(26)-C(28)-F(16)	-126.0(9)
C(21)-C(26)-C(28)-F(16)	47.1(12)
C(25)-C(26)-C(28)-F(17)	110.4(10)
C(21)-C(26)-C(28)-F(17)	-76.4(11)
C(25)-C(26)-C(28)-F(18)	-7.2(13)
C(21)-C(26)-C(28)-F(18)	165.9(8)
C(21)-Sn(2)-C(31)-C(36)	-39.9(8)
Cl(3)-Sn(2)-C(31)-C(36)	-158.3(6)
Cl(4)-Sn(2)-C(31)-C(36)	93.3(7)
C(21)-Sn(2)-C(31)-C(32)	137.8(7)
Cl(3)-Sn(2)-C(31)-C(32)	19.5(8)
Cl(4)-Sn(2)-C(31)-C(32)	-88.9(7)
C(36)-C(31)-C(32)-C(33)	2.5(13)
Sn(2)-C(31)-C(32)-C(33)	-175.4(7)
C(36)-C(31)-C(32)-C(37)	178.7(9)
Sn(2)-C(31)-C(32)-C(37)	0.9(12)
C(31)-C(32)-C(33)-C(34)	1.1(15)
C(37)-C(32)-C(33)-C(34)	-175.0(10)
C(32)-C(33)-C(34)-C(35)	-5.1(16)

C(33)-C(34)-C(35)-C(36)	5.1(14)
C(32)-C(31)-C(36)-C(35)	-2.1(13)
Sn(2)-C(31)-C(36)-C(35)	175.8(7)
C(32)-C(31)-C(36)-C(38)	176.2(8)
Sn(2)-C(31)-C(36)-C(38)	-5.9(12)
C(34)-C(35)-C(36)-C(31)	-1.6(14)
C(34)-C(35)-C(36)-C(38)	180.0(9)
C(33)-C(32)-C(37)-F(20)	93.8(12)
C(31)-C(32)-C(37)-F(20)	-82.5(12)
C(33)-C(32)-C(37)-F(21)	-24.3(14)
C(31)-C(32)-C(37)-F(21)	159.4(9)
C(33)-C(32)-C(37)-F(19)	-139.4(9)
C(31)-C(32)-C(37)-F(19)	44.3(13)
C(31)-C(36)-C(38)-F(23)	-149.6(8)
C(35)-C(36)-C(38)-F(23)	28.8(11)
C(31)-C(36)-C(38)-F(24)	-25.9(12)
C(35)-C(36)-C(38)-F(24)	152.6(7)
C(31)-C(36)-C(38)-F(22)	91.3(10)
C(35)-C(36)-C(38)-F(22)	-90.3(9)

Symmetry transformations used to generate equivalent atoms:

3. Crystal data of GeAr²⁺Cl₂

Table 1. Crystal data and structure refinement for 99srv201.

Identification code	99srv201	
Empirical formula	C16 H6 Cl2 F12 Ge	
Formula weight	569.70	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 10.547(1) Å	α = 90°.
	b = 11.658(1) Å	β = 108.20(1)°.
	c = 16.634(1) Å	γ = 90°.
Volume	1943.0(4) Å ³	
Z	4	
Density (calculated)	1.948 Mg/m ³	
Absorption coefficient	1.964 mm ⁻¹	
F(000)	1104	
Crystal size	0.40 × 0.12 × 0.12 mm ³	
Crystal shape	rectangular prism	
Crystal colour	colourless	
Diffractometer	Bruker SMART-CCD	
Data collection method	omega scans	
Theta range for data collection	2.04 to 30.44°.	
Index ranges	-12 ≤ h ≤ 15, -16 ≤ k ≤ 13, -22 ≤ l ≤ 23	
Reflections collected	14930	
Independent reflections	5378 [R(int) = 0.0328]	
Completeness to theta = 30.44°	91.4 %	
Absorption correction	Integration	
Max. and min. transmission	0.806 and 0.633	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	5378 / 0 / 304	
Goodness-of-fit on F ²	1.029	
Final R indices [I > 2σ(I)]	R1 = 0.0361, wR2 = 0.0790	
R indices (all data)	R1 = 0.0616, wR2 = 0.0877	
Largest diff. peak and hole	0.592 and -0.335 e.Å ⁻³	

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 99srv201. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
Ge(1)	6536(1)	225(1)	7100(1)	26(1)
Cl(1)	6872(1)	-475(1)	5989(1)	43(1)
Cl(2)	8516(1)	680(1)	7874(1)	41(1)
C(1)	5888(2)	-1008(2)	7670(2)	25(1)
C(2)	4691(2)	-1613(2)	7324(1)	25(1)
C(3)	4309(2)	-2465(2)	7782(2)	27(1)
C(4)	5120(2)	-2731(2)	8597(2)	28(1)
C(5)	6298(3)	-2155(2)	8947(2)	34(1)
C(6)	6685(3)	-1297(2)	8488(2)	32(1)
C(7)	3786(3)	-1418(2)	6436(2)	33(1)
F(1)	4068(2)	-2140(2)	5882(1)	52(1)
F(2)	2508(2)	-1613(2)	6361(1)	58(1)
F(3)	3871(2)	-369(1)	6146(1)	45(1)
C(8)	4674(3)	-3674(2)	9069(2)	36(1)
F(4)	3611(2)	-3375(2)	9281(2)	80(1)
F(5)	5608(2)	-3957(2)	9784(1)	70(1)
F(6)	4358(3)	-4619(2)	8617(1)	72(1)
C(11)	5487(2)	1630(2)	6768(2)	24(1)
C(12)	4990(2)	2297(2)	7302(2)	26(1)
C(13)	4236(3)	3276(2)	7003(2)	30(1)
C(14)	3960(3)	3594(2)	6162(2)	30(1)
C(15)	4440(3)	2949(2)	5619(2)	33(1)
C(16)	5198(3)	1975(2)	5925(2)	29(1)
C(17)	5182(3)	1960(2)	8208(2)	35(1)
F(7)	4205(2)	1240(2)	8250(1)	69(1)
F(8)	6314(2)	1398(2)	8561(1)	52(1)
F(9)	5152(2)	2838(2)	8701(1)	57(1)
C(18)	3123(3)	4644(2)	5828(2)	43(1)
F(10)	1869(2)	4375(2)	5418(2)	79(1)
F(11)	3590(3)	5239(2)	5292(1)	74(1)
F(12)	3118(2)	5379(2)	6439(1)	56(1)

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 99srv201. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ge(1)	26(1)	23(1)	28(1)	3(1)	9(1)	1(1)
Cl(1)	54(1)	40(1)	43(1)	0(1)	27(1)	9(1)
Cl(2)	25(1)	41(1)	52(1)	8(1)	6(1)	-4(1)
C(1)	27(1)	22(1)	25(1)	2(1)	6(1)	1(1)
C(2)	27(1)	23(1)	22(1)	0(1)	6(1)	3(1)
C(3)	28(1)	25(1)	26(1)	-1(1)	8(1)	1(1)
C(4)	32(1)	23(1)	26(1)	0(1)	8(1)	1(1)
C(5)	41(2)	31(1)	25(1)	5(1)	2(1)	-3(1)
C(6)	31(1)	29(1)	30(1)	1(1)	0(1)	-4(1)
C(7)	30(1)	33(1)	30(1)	6(1)	4(1)	-4(1)
F(1)	74(1)	46(1)	27(1)	-7(1)	4(1)	1(1)
F(2)	29(1)	87(1)	49(1)	25(1)	-3(1)	-8(1)
F(3)	52(1)	35(1)	35(1)	13(1)	-6(1)	-6(1)
C(8)	45(2)	32(1)	32(1)	4(1)	14(1)	-3(1)
F(4)	86(2)	67(1)	114(2)	37(1)	71(2)	14(1)
F(5)	74(1)	72(1)	48(1)	33(1)	-6(1)	-25(1)
F(6)	137(2)	37(1)	46(1)	-5(1)	34(1)	-37(1)
C(11)	24(1)	23(1)	26(1)	1(1)	7(1)	-1(1)
C(12)	26(1)	24(1)	26(1)	0(1)	7(1)	-2(1)
C(13)	33(1)	26(1)	31(1)	-4(1)	9(1)	1(1)
C(14)	30(1)	22(1)	34(1)	-1(1)	4(1)	-1(1)
C(15)	40(1)	28(1)	27(1)	3(1)	6(1)	-1(1)
C(16)	36(1)	27(1)	27(1)	0(1)	11(1)	1(1)
C(17)	40(1)	36(1)	30(1)	2(1)	15(1)	4(1)
F(7)	71(1)	86(2)	55(1)	18(1)	26(1)	-26(1)
F(8)	62(1)	63(1)	30(1)	10(1)	13(1)	27(1)
F(9)	88(2)	50(1)	32(1)	-3(1)	21(1)	20(1)
C(18)	45(2)	34(2)	40(2)	-2(1)	2(1)	9(1)
F(10)	49(1)	52(1)	101(2)	-10(1)	-27(1)	16(1)
F(11)	109(2)	49(1)	68(1)	33(1)	36(1)	34(1)
F(12)	66(1)	39(1)	52(1)	-6(1)	6(1)	22(1)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 99srv201.

	x	y	z	U(eq)
H(3)	3500(30)	-2870(20)	7511(16)	22(6)
H(5)	6830(30)	-2330(30)	9460(20)	48(9)
H(6)	7440(30)	-960(20)	8697(18)	31(7)
H(13)	3950(30)	3710(20)	7391(19)	36(8)
H(15)	4260(30)	3190(30)	5050(20)	41(8)
H(16)	5510(30)	1540(20)	5567(17)	27(7)

Table 6. Torsion angles [°] for 99srv201.

C(11)-Ge(1)-C(1)-C(6)	-118.2(2)
Cl(1)-Ge(1)-C(1)-C(6)	117.67(19)
Cl(2)-Ge(1)-C(1)-C(6)	7.1(2)
C(11)-Ge(1)-C(1)-C(2)	61.4(2)
Cl(1)-Ge(1)-C(1)-C(2)	-62.8(2)
Cl(2)-Ge(1)-C(1)-C(2)	-173.33(19)
C(6)-C(1)-C(2)-C(3)	0.4(4)
Ge(1)-C(1)-C(2)-C(3)	-179.20(18)
C(6)-C(1)-C(2)-C(7)	-177.0(2)
Ge(1)-C(1)-C(2)-C(7)	3.5(3)
C(1)-C(2)-C(3)-C(4)	-0.1(4)
C(7)-C(2)-C(3)-C(4)	177.4(2)
C(2)-C(3)-C(4)-C(5)	-0.1(4)
C(2)-C(3)-C(4)-C(8)	-179.3(2)
C(3)-C(4)-C(5)-C(6)	0.2(4)
C(8)-C(4)-C(5)-C(6)	179.3(3)
C(4)-C(5)-C(6)-C(1)	0.1(4)
C(2)-C(1)-C(6)-C(5)	-0.3(4)
Ge(1)-C(1)-C(6)-C(5)	179.3(2)
C(3)-C(2)-C(7)-F(3)	155.3(2)
C(1)-C(2)-C(7)-F(3)	-27.3(4)
C(3)-C(2)-C(7)-F(2)	32.8(3)
C(1)-C(2)-C(7)-F(2)	-149.8(2)
C(3)-C(2)-C(7)-F(1)	-85.1(3)
C(1)-C(2)-C(7)-F(1)	92.4(3)
C(5)-C(4)-C(8)-F(6)	-128.3(3)
C(3)-C(4)-C(8)-F(6)	50.9(3)
C(5)-C(4)-C(8)-F(4)	111.7(3)
C(3)-C(4)-C(8)-F(4)	-69.1(3)
C(5)-C(4)-C(8)-F(5)	-8.0(4)
C(3)-C(4)-C(8)-F(5)	171.2(2)
C(1)-Ge(1)-C(11)-C(16)	-127.59(19)
Cl(1)-Ge(1)-C(11)-C(16)	-3.2(2)
Cl(2)-Ge(1)-C(11)-C(16)	107.33(18)
C(1)-Ge(1)-C(11)-C(12)	51.2(2)

Cl(1)-Ge(1)-C(11)-C(12)	175.63(18)
Cl(2)-Ge(1)-C(11)-C(12)	-73.8(2)
C(16)-C(11)-C(12)-C(13)	-0.2(4)
Ge(1)-C(11)-C(12)-C(13)	-179.07(18)
C(16)-C(11)-C(12)-C(17)	176.5(2)
Ge(1)-C(11)-C(12)-C(17)	-2.3(3)
C(11)-C(12)-C(13)-C(14)	0.6(4)
C(17)-C(12)-C(13)-C(14)	-176.4(2)
C(12)-C(13)-C(14)-C(15)	-0.6(4)
C(12)-C(13)-C(14)-C(18)	179.0(2)
C(13)-C(14)-C(15)-C(16)	0.3(4)
C(18)-C(14)-C(15)-C(16)	-179.3(2)
C(14)-C(15)-C(16)-C(11)	0.0(4)
C(12)-C(11)-C(16)-C(15)	-0.1(4)
Ge(1)-C(11)-C(16)-C(15)	178.9(2)
C(13)-C(12)-C(17)-F(9)	-28.6(3)
C(11)-C(12)-C(17)-F(9)	154.5(2)
C(13)-C(12)-C(17)-F(8)	-151.5(2)
C(11)-C(12)-C(17)-F(8)	31.6(3)
C(13)-C(12)-C(17)-F(7)	90.7(3)
C(11)-C(12)-C(17)-F(7)	-86.2(3)
C(15)-C(14)-C(18)-F(10)	80.1(4)
C(13)-C(14)-C(18)-F(10)	-99.4(3)
C(15)-C(14)-C(18)-F(12)	-158.4(3)
C(13)-C(14)-C(18)-F(12)	22.1(4)
C(15)-C(14)-C(18)-F(11)	-40.0(4)
C(13)-C(14)-C(18)-F(11)	140.4(3)

4. Crystal data of GeArCl₃

Table 1. Crystal data and structure refinement for 99srv249.

Identification code	99srv249	
Empirical formula	C ₉ H ₂ Cl ₃ F ₉ Ge	
Formula weight	460.05	
Temperature	120(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	<i>Pnma</i>	
Unit cell dimensions	$a = 11.284(1)$ Å	$\alpha = 90^\circ$
	$b = 12.541(1)$ Å	$\beta = 90^\circ$
	$c = 9.710(3)$ Å	$\gamma = 90^\circ$
Volume	1374.1(5) Å ³	
Z	4	
Density (calculated)	2.224 g/cm ³	
Absorption coefficient	2.906 mm ⁻¹	
F(000)	880	
Crystal size	0.40 x 0.28 x 0.28 mm ³	
θ range for data collection	2.65 to 29.10°	
Index ranges	$-15 < h < 14$, $-16 < k < 16$, $-7 < l < 13$	
Reflections collected	11660	
Independent reflections	1921 [R(int) = 0.0219]	
Reflections with $I > 2\sigma(I)$	1743	
Completeness to $\theta = 29.10^\circ$	99.6 %	
Absorption correction	None	
Max. and min. transmission	0.4926 and 0.4371	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	1921 / 6 / 125	
Largest final shift/e.s.d. ratio	0.001	
Goodness-of-fit on F ²	1.064	
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0217$, $wR_2 = 0.0543$	
R indices (all data)	$R_1 = 0.0251$, $wR_2 = 0.0555$	
Largest diff. peak and hole	0.428 and -0.552 e.Å ⁻³	

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^4$) for 99srv249. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	$U(\text{eq})$
Ge	1317(1)	2500	7098(1)	163(1)
Cl(1)	112(1)	1202(1)	6924(1)	276(1)
Cl(2)	2029(1)	2500	9109(1)	251(1)
F(1)	1844(1)	-27(1)	5103(1)	274(2)
F(2)	3706(1)	-209(1)	5524(1)	296(2)
F(3)	2571(1)	473(1)	7070(1)	226(2)
C(1)	2574(2)	2500	5674(2)	153(4)
C(2)	3030(1)	1543(1)	5121(2)	165(3)
C(3)	3808(1)	1542(1)	3999(2)	205(3)
C(4)	4169(2)	2500	3425(2)	217(4)
C(5)	2772(1)	445(1)	5703(2)	200(3)
C(6)	5006(2)	2500	2210(3)	320(6)
F(4)	5254(4)	3478(3)	1769(4)	710(13)
F(5)	4583(4)	2021(4)	1177(3)	992(19)
F(6)	6018(3)	2115(4)	2509(4)	1100(30)

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^4$) for 99srv249. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ge	139(1)	186(1)	163(1)	0	21(1)	0
Cl(1)	184(2)	299(2)	346(2)	-25(2)	42(2)	-79(1)
Cl(2)	338(3)	248(2)	169(2)	0	-18(2)	0
F(1)	265(5)	249(5)	308(5)	-71(4)	-24(4)	-82(4)
F(2)	264(5)	196(5)	427(6)	-1(4)	44(4)	64(4)
F(3)	243(5)	216(4)	217(4)	32(3)	-7(4)	-26(4)
C(1)	122(9)	186(9)	152(9)	0	-15(7)	0
C(2)	144(6)	178(6)	175(6)	-12(5)	-25(5)	-7(5)
C(3)	190(7)	242(7)	181(7)	-41(6)	-6(6)	27(6)
C(4)	177(10)	314(11)	161(9)	0	18(8)	0
C(5)	182(7)	175(6)	242(7)	-26(6)	-3(6)	-2(5)
C(6)	350(13)	400(14)	209(11)	0	97(10)	0
F(4)	1070(30)	436(16)	630(20)	65(15)	650(20)	-50(19)
F(5)	1060(30)	1600(50)	311(15)	-520(20)	339(17)	-830(30)
F(6)	597(18)	2110(80)	590(18)	700(30)	432(16)	860(30)

Table 5. Hydrogen coordinates ($\times 10^3$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 99srv249.

	x	y	z	U(iso)
H(3)	408(2)	89(2)	367(2)	28(5)

5. Crystal data of SiAr''₂Cl₂

Table 1. Crystal data and structure refinement for 99srv253.

Identification code	99srv253	
Empirical formula	C ₁₆ H ₆ Cl ₂ F ₁₂ Si	
Formula weight	525.20	
Temperature	120(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2 ₁ /n (No. 14)	
Unit cell dimensions	$a = 10.429(7)$ Å	$\alpha = 90^\circ$
	$b = 11.534(7)$ Å	$\beta = 107.84(2)^\circ$
	$c = 16.608(10)$ Å	$\gamma = 90^\circ$
Volume	1902(2) Å ³	
Z	4	
Density (calculated)	1.834 g/cm ³	
Absorption coefficient	0.520 mm ⁻¹	
F(000)	1032	
Crystal size	0.40 × 0.40 × 0.26 mm ³	
θ range for data collection	2.06 to 29.13°	
Index ranges	$-14 \leq h \leq 13, -15 \leq k \leq 15, -22 \leq l \leq 22$	
Reflections collected	17420	
Independent reflections	5059 [R(int) = 0.0321]	
Reflections with $I > 2\sigma(I)$	4018	
Completeness to $\theta = 29.13^\circ$	98.6 %	
Absorption correction	None	
Max. and min. transmission	0.8622 and 0.6973	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	5059 / 0 / 304	
Largest final shift/e.s.d. ratio	0.001	
Goodness-of-fit on F ²	1.021	
Final R indices [$I > 2\sigma(I)$]	R ₁ = 0.0356, wR ₂ = 0.0861	
R indices (all data)	R ₁ = 0.0507, wR ₂ = 0.0938	
Largest diff. peak and hole	0.405 and -0.342 e.Å ⁻³	

Table 2. Atomic coordinates ($\times 10^5$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^4$) for 99srv253. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	$U(\text{eq})$
Si	65768(5)	51964(4)	20903(3)	214(1)
Cl(1)	68478(5)	44718(4)	10273(3)	332(1)
Cl(2)	84785(4)	56570(4)	28110(3)	321(1)
F(1)	38437(12)	46368(10)	11266(7)	342(3)
F(2)	40973(13)	28337(11)	8869(7)	380(3)
F(3)	24974(11)	33617(13)	13642(8)	417(3)
F(4)	43326(19)	3922(11)	36202(8)	566(4)
F(5)	36119(17)	16518(14)	43117(12)	628(5)
F(6)	56284(15)	10468(14)	47861(8)	562(4)
F(11)	63963(12)	63895(11)	35897(7)	363(3)
F(12)	51594(14)	78231(11)	37067(7)	400(3)
F(13)	42577(14)	61668(14)	32785(8)	491(4)
F(14)	31684(14)	103746(11)	14684(8)	410(3)
F(15)	18836(14)	93692(13)	4535(10)	574(4)
F(16)	36177(17)	102197(12)	2999(9)	546(4)
C(1)	59136(17)	40370(14)	26564(10)	209(3)
C(2)	47015(16)	34111(14)	23214(10)	200(3)
C(3)	43092(17)	25555(15)	27885(10)	212(3)
C(4)	51215(18)	22985(15)	36062(10)	226(3)
C(5)	63116(19)	28942(16)	39549(11)	262(4)
C(6)	66982(18)	37519(16)	34834(11)	248(3)
C(7)	37848(18)	35707(16)	14309(11)	252(3)
C(8)	46740(20)	13455(16)	40828(11)	278(4)
C(11)	55451(16)	65586(14)	17816(10)	202(3)
C(12)	50306(17)	72449(15)	23154(10)	213(3)
C(13)	42706(18)	82368(15)	20197(11)	237(3)
C(14)	40010(17)	85683(15)	11783(11)	238(3)
C(15)	44899(19)	79143(16)	6340(11)	259(4)
C(16)	52517(18)	69245(15)	9360(11)	237(3)
C(17)	52133(19)	69136(16)	32278(11)	268(4)
C(18)	31670(20)	96296(17)	8539(12)	315(4)

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^4$) for 99srv253. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Si	220(2)	193(2)	233(2)	28(2)	74(2)	16(2)
Cl(1)	423(3)	302(2)	324(2)	3(2)	192(2)	71(2)
Cl(2)	214(2)	327(2)	401(2)	72(2)	64(2)	-21(2)
F(1)	394(6)	266(6)	276(5)	98(4)	-31(5)	-38(5)
F(2)	549(8)	351(6)	201(5)	-48(4)	58(5)	-18(6)
F(3)	233(5)	589(8)	358(6)	155(6)	-17(5)	-61(5)
F(4)	1074(13)	298(7)	353(7)	-43(5)	255(7)	-279(7)
F(5)	683(10)	532(9)	891(12)	272(8)	570(9)	113(8)
F(6)	577(9)	579(9)	387(7)	281(6)	-62(6)	-195(7)
F(11)	440(7)	416(7)	221(5)	55(5)	82(5)	151(5)
F(12)	587(8)	390(7)	241(5)	-30(5)	155(5)	130(6)
F(13)	533(8)	603(9)	377(7)	95(6)	196(6)	-199(7)
F(14)	495(7)	286(6)	391(6)	-49(5)	50(5)	152(5)
F(15)	358(7)	420(8)	722(10)	-68(7)	-162(7)	94(6)
F(16)	818(11)	371(7)	508(8)	234(6)	292(7)	246(7)
C(1)	219(8)	183(7)	213(7)	12(6)	49(6)	11(6)
C(2)	225(8)	187(8)	177(7)	1(6)	46(6)	23(6)
C(3)	230(8)	194(8)	204(7)	-13(6)	56(6)	-10(6)
C(4)	290(9)	180(8)	208(7)	6(6)	75(6)	4(6)
C(5)	306(9)	238(9)	202(7)	32(6)	19(6)	-22(7)
C(6)	246(8)	228(8)	226(8)	17(6)	10(6)	-31(7)
C(7)	261(8)	257(9)	210(8)	24(6)	31(6)	-21(7)
C(8)	364(10)	252(9)	215(8)	25(7)	85(7)	-36(7)
C(11)	207(7)	183(7)	215(7)	7(6)	63(6)	-18(6)
C(12)	224(8)	207(8)	206(7)	2(6)	64(6)	-23(6)
C(13)	247(8)	215(8)	252(8)	-31(6)	79(6)	-3(7)
C(14)	246(8)	198(8)	243(8)	0(6)	34(6)	0(6)
C(15)	326(9)	233(8)	203(8)	26(6)	59(6)	1(7)
C(16)	298(9)	208(8)	210(7)	9(6)	86(6)	8(7)
C(17)	314(9)	271(9)	234(8)	11(7)	108(7)	13(7)
C(18)	352(10)	251(9)	295(9)	-5(7)	31(7)	55(8)

Table 5. Hydrogen coordinates ($\times 10^3$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 99srv253.

	x	y	z	U(iso)
H(3)	351(2)	216(2)	255(1)	27(5)
H(5)	690(2)	270(2)	450(2)	36(6)
H(6)	755(2)	413(2)	371(1)	32(6)
H(13)	392(2)	867(2)	238(1)	27(5)
H(15)	433(2)	815(2)	8(2)	35(6)
H(16)	555(2)	646(2)	56(1)	24(5)

Table 6. Torsion angles [$^\circ$] for 99srv253.

Cl(2)-Si-C(1)-C(6)	6.43(15)
Cl(1)-Si-C(11)-C(16)	-6.23(14)

