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Synthesis and NMR spectra of derivatives of the *polykis*(diphenylphosphino)benzenes, $(Ph_2P)_nC_6H_{6-n}$ [*n*=2 to 4]

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Abstract

111 derivatives of the *polykis*(diphenylphosphino)benzenes, $(Ph_2P)_nC_6H_{6-n}$ [n=2 to 4] obtained by oxidation or reaction with sulfur, selenium, iodomethane, $M(CO)_6$ [M=Cr, Mo, W], [codRh- μ -Cl]₂, or $(PhCN)_2MCl_2$ [M=Pd, Pt], are reported together with their ³¹P and selected other NMR parameters. The reactions generally follow predictable courses, although stereochemical factors affect the range of products obtained and can lead to significant structural distortion in extreme cases. The ³¹P chemical shifts and more particularly vicinal coupling constants are also markedly influenced by such factors, to the extent that in species with three or more adjacent Ph_2P moieties they may be of limited diagnostic value. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Polyphosphine; ³¹P NMR; coupling constant; steric hindrance; metal complex

1. Introduction

We have previously reported [1,2] that the reaction between sodium diphenylphosphide and the appropriate polyfluorobenzene $C_6H_{6-n}F_n$ in refluxing liquid ammonia provides a convenient route to the *polykis*(diphenylphosphino)benzenes, $(Ph_2P)_nC_6H_{6-n}$ [n=2-4], compounds **1** to **7**. These polyphosphines have considerable potential as multi- and ambi-dentate ligands with a rigid skeleton that may facilitate or inhibit chelation to a metal centre or bridging of several metal centres, and a few examples of this diverse behaviour have been described [3,4]. We have also shown [2] how the ³¹P chemical shifts and vicinal coupling constants ³ $J(^{31}P-^{31}P)$ in the parent polyphosphines display trends that can be understood in terms of preferred phosphorus electron lone-pair relative orientations determined by steric interactions between adjacent diphenylphosphino groups.

In order to provide a basis for studying their many types of coordination behaviour we have undertaken a survey of the reactions of these polyphosphines with a range of metal substrates and with the chalcogens. These reactions were conveniently followed by ³¹P NMR spectroscopy, aug-



mented as necessary by ¹H [including COSY and ROESY], ¹³C [including HETCOR], selective ¹H– $\{^{31}P\}$ decoupling, and ³¹P COSY experiments. In general they proceeded in the expected sequential manner, and one of our aims was to establish the extent to which the ³¹P NMR. parameters can be used diagnostically.

In this paper we present ³¹P and selected other NMR. data for 111 distinct derivatives of which 46 have been isolated in analytically pure form. Some data were also obtained on a considerable number of other species detected in the reactions, but as their characterisation was less certain they are not reported in detail. Two other members of the series of parent phosphines, 1,3- and

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1,4-*bis*(diphenylphosphino)benzene, have been made [5–7] without recourse to the corresponding difluorobenzenes, but are not included here since in absence of sterically interacting diphenyl-phosphino groups their behaviour is expected to resemble that of triphenylphosphine.

2. Experimental

2.1. Preparations

The starting polyphosphines 1 to 7 were made as described previously [1,2], and most of their reactions were conducted on a scale of 0.02 to 0.5 mmole. Those with sulfur, selenium, iodomethane, [codRh-µ-Cl]₂, cis-(PhCN)₂PdCl₂, or *cis*-(PhCN)₂PdCl₂ were performed at room temperature in dichloromethane and final products were recrystallised from dichloromethane/diethylether prior to elemental and mass spectroscopic analysis. Oxidations were conducted with ca. 3% aqueous hydrogen peroxide in acetone/dichloromethane at room temperature to give 1a and 5b, and by aerial oxidation in dichloromethane for 5a or refluxing diglyme for 1d and 4a. Reactions with M(CO)₆ [M=Cr, Mo, W] were carried out under nitrogen in refluxing diglyme for approximately 1 h and the isolated products were recrystallised from dichloromethane/methanol.

2.2. NMR spectroscopy

Pulsed Fourier transform ³¹P NMR spectra were obtrichloromethane-d, from solutions in tained dichloromethane- d_2 , or dichloromethane contained in 10 mm o.d. NMR tubes at 24.2 MHz (JEOL FX 60) or 36.2 MHz (JEOL FX 90Q), or in 5 mm o.d. NMR tubes at 202.5 MHz (JEOL LAMBDA 500) and are referenced to external 85% H₃PO₄. Proton (500.15 MHz), ¹³C (125.6 MHz), ⁷⁷Se (95.4 MHz), and ¹⁹⁵Pt (107.0 MHz) NMR spectra were also obtained on the last instrument and are referenced to internal Me4Si, internal Me4Si, external Me₂Se, and a notional $\Xi(^{195}Pt)=21.4$ MHz respectively. ³¹P COSY spectra were acquired at 202.5 MHz from unspun samples with broadband proton decoupling into a $1K \times 1K$ data matrix (digital resolution approximately 10 Hz), a shifted sine-bell weighting function being applied in each dimension prior to Fourier transformation. Other 2D NMR experiments used standard pulse sequences and methods of data treatment [8,9].

3. Results

³¹P chemical shifts and coupling constants for identified species are in Tables 1–7, and microanalytical data, molecular weights determined by mass spectrometry and melting points for isolated products are in Table 8.

Table 1 ³¹P NMR parameters of derivatives of 1,2-*bis*-(diphenylphosphino)benzene

No.	Compound	$\delta(^{31}\text{P})^{a}$	${}^{3}J({}^{31}P_{1}-{}^{31}P_{2})^{b}$
1	1	-13.3	145.2
1a	1 {1,2-O ₂ }	31.8	-
1b	1{1-S}	43.1, -17.5	31.7
1c	$1\{1,2-S_2\}$	47.2	-
1d	$1{1-0,2-Se}^{c}$	27.5, 41.0	4.9
1e	$1{1-Se}^d$	34.6, -18.2	36.6
1f	$1\{1,2-Se_2\}^e$	38.2	7.3
1g	1{1-MeI}	22.2, -14.9	26.9
1h	$1\{1,2-Cr(CO)_{4}\}$	83.3	_
1i	$1{1,2-Mo(CO)_4}$	59.8	_
1j	$1{1,2-W(CO)_4}^f$	46.5	_
1k	$[1{1,2-Rh-\mu-Cl}]_{2}^{g}$	62.3	_
11	$1{1,2-PdCl_2}$	63.8	_
1m	$1{1,2-PtCl_2}^h$	40.1	_
1n	$[1_{2}\{1,1',2,2'-\text{Pt}\}]^{2+}[\text{PtCl}_{4}]^{2-i}$	38.0	_

^a In ppm ± 0.2 ppm. When two values are given the first relates to P₁ and the second to P₂.

^b In Hz ±0.2 Hz. The absence of an entry indicates that the coupling constant is unavailable owing to symmetry or accidental isochronicity.

 $^{c}{}^{1}J(^{77}\text{Se}-^{31}\text{P})=743$ Hz.

 $^{d}{}^{1}J(^{77}\text{Se}{-}^{31}\text{P}) = 739$ Hz.

 $^{e^{-1}}J(^{77}\text{Se}-^{31}\text{P}) = 754$ Hz.

- ${}^{g^{-1}}J({}^{103}\text{Rh}-{}^{31}\text{P}) = 134.3 \text{ Hz}.$
- $^{f_1}J(^{183}W-^{31}P)=232.2$ Hz.
- $^{h-1}J(^{195}\text{Pt}-^{31}\text{P})=3606$ Hz.

ⁱ In the ¹⁹⁵Pt spectrum the resonance at -558 ppm was a quintet with ¹ $J(^{195}Pt-^{31}P)=2502$ Hz.

Table 2 ³¹P NMR parameters of derivatives of 1,2,3-*tris*-(diphenylphosphino)benzene

No	Compound	$\delta({}^{31}P_1)^a$	$\delta({}^{31}P_2)^a$	$\delta({}^{31}P_3)^a$	${}^{3}J({}^{31}P_{1}-{}^{31}P_{2})^{b}$	${}^{4}J({}^{31}P_{1}-{}^{31}P_{3})^{b}$	${}^{3}J({}^{31}P_2 - {}^{31}P_3)^{b}$
2	2	-12.7	-8.9	-12.7	97.5	_	97.5
2a	2 {1-S}	45.8	-9.9	-15.5	55.5	4.9	~0
2b	$2{1,3-S_2}$	46.3	-5.8	46.3	36.6	-	36.6
2c	$2\{1,2,3-S_3\}$	50.1	48.3	50.1	11.0	-	11.0
2d	$2{1-Se}^{c}$	37.3	-10.6	-15.2	63.0	5.3	~1
2e	$2{1,3-Se_2}^d$	37.4	-7.0	37.4	42.1	-	42.1
2f	2 {1-MeI}	21.6	-1.9	-14.4	46.4	4.9	~0
2g	$2{1,2-Cr(CO)_4}$	86.5	89.7	-17.1	22.0	3.6	13.5
2h	$2{1,2-Mo(CO)_4}$	63.9	66.3	-16.0	6.1	3.7	14.7
2i	$2{1,2-W(CO)_4}^e$	48.3	50.5	-17.0	3.7	3.7	15.8

^a In ppm ±0.2 ppm.

^b In Hz ± 0.2 Hz. The absence of an entry indicates that the coupling constant is unavailable owing to symmetry or accidental isochronicity. ^{c 1} $J(^{77}Se^{-31}P) = 735$ Hz.

 $^{e^{-1}}J(^{183}W-^{31}P_1) = 230 \text{ Hz}, \ ^{1}J(^{183}W-^{31}P_2) = 228 \text{ Hz}.$

3.1. Notation

Each reaction product is specified by the number of its parent polyphosphine (as in the introductory section of this paper) printed in bold followed by the position(s) and nature of the added substituent(s) of phosphorus in curly brackets. Thus 1,2,4-*tris*(diphenylthiophosphino)-5-diphenylphosphinobenzene, 1,2,4-[Ph₂P(S)]₃-5-Ph₂P-C₆H₂, is designated **7** {1,2,4-S₃}, and other examples of the use of this system are as follows:



3.2. Reactions with elemental sulfur

These reactions were readily followed by 31 P NMR. because the phosphorus chemical shifts of the resulting tertiary phosphine sulfides are some 50 ppm to high frequency of those of the parent tertiary phosphine. They were generally conducted in toluene or dichloromethane or occasionally chloroform-*d* at room temperature, initially with a single atomic equivalent of sulfur in an attempt to achieve mono-addition, and then with stepwise addition of more sulfur. With **1**, **3**, **4**, **6**, and **7** the fully sulfurised derivatives were isolated in analytically pure form [see Table 8], and satisfactory microanalytical data were also obtained for the monosulfide 5c. In other cases the intermediate products were identified from the patterns of their ³¹P chemical shifts and ³¹P-³¹P coupling constants together with consideration of the sequence of their appearance as the reaction progressed. It was noted that the spectra continued to change over a period of hours after the initial reaction was complete, indicating that that the first products were kinetically determined and that there were subsequent (probably intramolecular) transfers of sulfur to give the thermodynamically preferred products. This approach is exemplified in Fig. 1 which shows part of the $P^{\bar{V}}$ region of proton-decoupled ³¹P spectra resulting from successive additions of sulfur to $1,2,4-(Ph_2P)_3C_6H_3$. Assignments were aided by a proton-decoupled ³¹P COSY spectrum of which the P^{V} part is shown in Fig. 2. This spectrum also showed appropriate correlations with the P^{III} region (0 to -20 ppm). These spectra do not unequivocally distinguish 3a and 3b or 3d and 3e, and the latter pair are assigned on the basis that ${}^{5}J({}^{31}P^{V}-{}^{31}P^{V})$ is likely to be greater than ${}^{4}J({}^{31}P^{V}-{}^{31}P^{V})$ as we have established in the case of 6e [10]. The same reasoning was applied in other cases of pairs showing four- or five-bond ³¹P^V-³¹P^V couplings, but is less well established for the corresponding ${}^{31}P^{III} - {}^{31}P^{V}$ couplings.

3.3. Reactions with elemental selenium

The behaviour was similar to that with sulfur, signals in the ${}^{31}P(Se)$ spectral region (32 to 40 ppm) having satellites due to ${}^{1}J({}^{77}Se{}^{-31}P)$ of 731 to 772 Hz. The reactions generally proceeded with greater difficulty, and the composition of the reaction mixtures continued to change over a period of several days. It was not possible to form species with three adjacent Ph₂P(Se) groups even though

 $J(^{77}Se^{-1}) = 735$ Hz.

Table 3					
³¹ P NMR	parameters of	derivatives of	f 1,2,4- <i>tris</i> -(di	phenylphos	phino)benzene

No	Compound	$\delta({}^{31}P_1)^a$	$\delta({}^{31}P_2)^a$	$\delta({}^{31}P_4)^a$	${}^{3}J({}^{31}P_{1}-{}^{31}P_{2})^{b}$	${}^{5}J({}^{31}P_{1}-{}^{31}P_{4})^{b}$	${}^{4}J({}^{31}P_2 - {}^{31}P_4)^{b}$
3	3	-13.4	-14.9	-6.7	153.3	<3	<3
3a	3 {1-S} ^c	44.1	-17.9	-4.2	29.7	1.0	0
3b	3 {2-S} ^c	-17.6	44.4	-5.6	30.7	0	0
3c	3 {4-S}	-11.9^{d}	-13.9 ^d	42.9	147.0	2.0	0
3d	$3{1,4-S_2}^e$	44.0	-17.9	42.6	31.0	4.7	0
3e	$3{2,4-S_2}^e$	-18.3	44.4	43.0	29.8	1.8	1.8
3f	$3\{1,2,4-S_3\}^e$	47.3 ^f	47.3 ^f	42.2	7.0	4.6	0.5
3g	3 {4-Se}	-11.8^{d}	-13.9^{d}	34.9 ^g	147.0	<5	<5
3h	$3{1,4-Se_2}^c$	34.9 ^g	-18.5	35.1 ^h	35.3	1.4	1.4
3i	$3{2,4-Se_2}^c$	-18.9	34.7 ^g	34.6 ⁱ	35.4	5.1	3.2
3j	$3{1,2,4-Se_3}^j$	39.5°	39.1 ^e	35.1	7.3	5.0	< 0.5
3k	$3{1-Mel}^{c}$	24.1	-14.2	-2.3	24.8	0	0
31	$3{2-MeI}^{\circ}$	-13.6	23.4	-3.6	24.8	0	0
3m	3 {4-MeI}	-12.7	-10.7	22.4	140.2	1.5	0
3n	$3{1,4-(MeI)_2}^c$	23.4	-12.0	22.7	24.8	~2	3.1
30	$3{2,4-(MeI)_2}^c$	-11.7	24.3	23.3	21.7	5.4	~2
3р	$3{1,2-Cr(CO)_4}$	82.7	82.7	-6.1	-	<3	<3
3q	$3{1,2-Cr(CO)_4,4-Cr(CO)_5}$	83.1	83.1	56.6	-	<3	<3
3r	$3{1,2-Mo(CO)_4}$	59.9	59.9	-6.3	-	<5	<5
3s	$3{1,2-Mo(CO)_4,4-Mo(CO)_5}$	59.6	60.2	38.6	4.9	3.7	<3
3t	$3{1,2-W(CO)_4}$	45.0 ^k	45.0 ^k	-6.4	-	<3	<3
3u	$3{1,2-W(CO)_4,4-W(CO)_5}$	45.6 ¹	45.2 ¹	21.6^{1}	<4	<4	<4
3v	$[3{1,2-Rh-\mu-Cl}]_{2}^{m}$	61.0	61.0	-5.9	-	<5	<5
3w	$[3{1,2-Rh-\mu-Cl,4-O}]_{2}^{m}$	62.4	62.4	26.2	-	<5	<5
3x	$3{1,2-PdCl_2}$	63.3	63.3	-4.6	-	<5	<5
3y	$[3\{1,2-\text{PdCl}_2\}]_2^n$	53.5	53.5	-5.3	-	<5	<5
3z	$[3\{1,2-\text{PdCl}_2\}]_2\{4,4'-\text{PdCl}_2\}^\circ$	63.2	63.2	24.1	-	<5	<5
3α	$[3{4,4'-PtCl_2}]_2^p$	-13.4	-13.4	13.8	-	<5	<5
3β	$[3\{1,2-\text{PtCl}_2\}]_2\{4,4'-\text{PtCl}_2\}^{o,q}$	40.8	40.8	15.4	-	<5	<5

^a In ppm ±0.2 ppm.

^b In Hz ±0.2 Hz. The absence of an entry indicates that the coupling constant is unavailable owing to symmetry or accidental isochronicity.

^c It may be necessary to interchange the relative assignments of 3a and 3b, of 3h and 3i, of 3k and 3l, and of 3n and 3o.

 d It may be necessary to interchange $\delta(P_{1})$ and $\delta(P_{2}).$

^e Assigned on the basis that ${}^{5}J(P_{1}^{V}-P_{4}^{V}) > {}^{4}J(P_{2}^{V}-P_{4}^{V})$, see text. ^f Complex multiplet simulated to yield $\delta({}^{31}P_{2}) - \delta({}^{31}P_{1}) = 0.06$ ppm.

 ${}^{g^{-1}}J({}^{77}\text{Se}-{}^{31}\text{P})=745$ Hz.

 ${}^{h}{}^{1}J({}^{77}\text{Se}{-}^{31}\text{P}_{1}, \text{P}_{2}) = 749 \text{ Hz}.$

 $^{11}J(^{77}\text{Se}-^{31}\text{P}_4) = 750$ Hz.

 ${}^{j}{}^{1}J({}^{77}\text{Se}{}^{-31}\text{P}_{1}) = 765 \text{ Hz}; \ \delta({}^{77}\text{Se}) = -191 \text{ ppm}; {}^{1}J({}^{77}\text{Se}{}^{-31}\text{P}_{2}) = 762 \text{ Hz}; \ \delta({}^{77}\text{Se}) = -195 \text{ ppm}. {}^{1}J({}^{77}\text{Se}{}^{-31}\text{P}_{4}) = 754 \text{ Hz}; \ \delta({}^{77}\text{Se}) = -296 \text{ ppm}.$

^{k 1} $J(^{183}W-^{31}P)=230\pm 2$ Hz. ^{1 1} $J(^{183}W-^{31}P_{1,2})=234\pm 2$ Hz; ¹ $J(^{183}W-^{31}P_4)=243\pm 2$ Hz.

 ${}^{m}{}^{1}J({}^{103}\text{Rh}{-}^{31}\text{P}_{1.2}) = 133.5 \pm 1$ Hz.

ⁿ Probable structure, see text.

° See text for structures.

 $^{p-1}J(^{195}\text{Pt}-^{31}\text{P})=3638$ Hz.

 $^{q^{-1}}J(^{195}\text{Pt}-^{31}\text{P}_{1,2})=3607\pm1$ Hz, $\delta(^{195}\text{Pt})=4$ ppm; $^{1}J(^{195}\text{Pt}-^{31}\text{P}_{4})=3636$ Hz, $\delta(^{195}\text{Pt})=84$ ppm.

the corresponding sulfides (2c, 6e and 6f) were identified. 6f was made by sulfurisation of 6g.

3.4. Oxidation reactions

Very marked variations in susceptibility to oxidation were noted for these species. Thus one phosphorus atom of the hindered tetraphosphine 5 was easily oxidised in dichloromethane solution by air at room temperature but hydrogen peroxide was required to yield the tetroxide 5b as the final product. In general with the highly hindered 5 it was easy to add only one atomic equivalent of chalcogen, in each case in the 1-position, so that the products were readily identifiable in spite of the unusual sizes of their vicinal ${}^{31}P-{}^{31}P$ coupling constants (see Fig. 3).

3.5. The addition of iodomethane

This proceeded sequentially and led to the quaternisation of one or more phosphorus atoms as evidenced by the appearance of ³¹P resonances in the range 20 to 27 ppm;

Table 4

³¹P NMR parameters of derivatives of 1,3,5-*tris*-(diphenylphosphino) benzene

No	Compound	$\delta({}^{31}P_1)^a$	$\delta({}^{31}P_3)^a$	$\delta({}^{31}P_5)^a$
4	4	-5.4	-5.4	-5.4
4a	4 {1,3-O ₂ }	23.1	23.1	-5.2
4b	4 {1-S}	42.1	-5.3	-5.3
4c	$4{1,3-S_2}$	42.0	42.0	-5.2
4d	4 {1,3,5-S ₃ }	42.4	42.4	42.4
4e	4 {1-Se}	34.3	-5.7	-5.7
4f	$4{1,3-Se_2}^{b}$	34.2	34.2	-5.5
4g	$4{1,3,5-Se_3}$	34.7	34.7	34.7
4h	4 {1-MeI}	21.5	-4.3	-4.3
4i	$4\{1,3-(MeI)_2\}$	22.4	22.4	-3.5
4j	$4\{1,3,5-(MeI)_3\}$	22.8	22.8	22.8
4k	$4\{1-Mo(CO)_5\}$	39°	-5.6	-5.6
41	$4{1,3-Mo(CO)_5}_2$	39°	39°	-5.0
4m	$4\{1,3,5-Mo(CO)_5\}_3$	40.1	40.1	40.1
4n	$4{1,3,5-W(CO)_5}_3^d$	22.8	22.8	22.8

^a In ppm ±0.2 ppm.

 ${}^{b}{}^{1}J({}^{77}\text{Se}{-}^{31}\text{P}) = 746$ Hz.

^c Overlapped signal, ±1 ppm.

 $^{d^{-1}}J(^{183}W-^{31}P)=244$ Hz.

only in the case of **1** was a persistent species found with a pair of adjacent Ph_2MeP^+ groups. In the cases of **3n** and **3o** the identities of the products were confirmed by their methyl proton resonances which showed characteristic ${}^2J({}^{31}P^{V}-H)$ and ${}^5J({}^{31}P^{III}-H)$ couplings of ca. 14 and 2 Hz respectively, and their methyl ${}^{13}C$ resonances which had ${}^1J({}^{31}P^{V}-{}^{13}C)$ and ${}^4J({}^{31}P^{III}-{}^{13}C)$ couplings of ca. 57 and 24 Hz respectively. A ${}^1H/{}^{13}C$ 2D chemical shift correlation experiment showed the signs of ${}^1J({}^{31}P^{V}-{}^{13}C)$ and ${}^2J({}^{31}P^{V}-H)$ to be opposite, presumably positive and negative respectively [11]. The relative assignments of **3n** and **3o** are based on ${}^5J({}^{31}P-{}^{31}P)$ being greater than ${}^4J({}^{31}P-{}^{31}P)$ as in the case of **3d** and **3e** above, and in an attempt to put this on a more secure basis a proton 2D ROESY spectrum with a spin-locking (mixing) time of 250ms of the reaction mixture containing **3n** and **3o** was

Table 5					
³¹ P NMR	parameters	of	derivatives	of	1.2.3.4-tetrakis-(diphenylphosphino)benzene

No	Compound	$\delta({}^{31}P_1)^a$	$\delta({}^{31}P_2)^a$	$\delta({}^{31}P_3)^a$	$\delta({}^{31}P_4)^a$	${}^{3}J(P_{1}-P_{2})^{b}$	${}^{4}J(P_{1}-P_{3})^{b}$	${}^{5}J(P_{1}-P_{4})^{b}$	${}^{3}J(P_{2}-P_{3})^{b}$	${}^{4}J(P_{2}-P_{4})^{b}$	${}^{3}J(P_{3}-P_{4})^{b}$	_
5	5	-13.5	-2.5	-2.5	-13.5	81.0	4.7	-0.3	35.3	4.7	81.0	
5a	5 {1-O}	31.3	3.4	-4.8	-13.6	37.7	5.0	<3	<3	<3	<3	
5b	5 {1,2,3,4-O ₄ }	38.9	32.4°	32.4°	38.9	<3	<3	<3	<3	<3	<3	
5c	5 {1-S}	45.9	-1.6	-5.2	-15.2	62.5	6.6	1.2	0	1.7	< 0.5	
5d	5 {1-Se} ^d	37.1	-2.6	-5.3	-15.1	70.6	6.7	0	0	2.1	0	
5e	5 {1-MeI}	20.5	7.6	-3.7	-14.9	52.5	6.1	<3	<3	<3	<3	
5f	$\{1, 2-W(CO)_4\}^e$	48.0	57.6	-6.5	-15.3	<10	<10	<5	26 ^g	<5	<5	
5g	5 {1,2-PdCl ₂ }	56.8	77.4	-6.8	-16.2	<10	<10	<10	24 ^g	<10	<10	
5h	5 $\{1, 2-PtCl_2\}^{f}$	34.7	41.4	-7.1	-17.8	<8	<8	<8	12 ^g	<8	<8	

^a In ppm ±0.2 ppm.

^b In Hz ±0.2 Hz. The absence of an entry indicates that the coupling constant is unavailable owing to symmetry or accidental isochronicity.

^c The ³¹P_{2,3} peaks are broader.

 $^{d^{-1}}J(^{77}\text{Se}^{-31}\text{P})=731$ Hz.

 $^{e}{}^{1}J$ ($^{183}W-{}^{31}P$)=230 Hz.

 ${}^{f_1}J({}^{195}\text{Pt}-{}^{31}\text{P}_1) = 3603 \text{ Hz}; {}^{1}J({}^{195}\text{Pt}-{}^{31}\text{P}_2) = 3456 \text{ Hz}.$

 $^{\rm g}$ $\pm 1\,$ Hz.

recorded. This showed clear NOE correlations between the methyl resonances and the *ortho*-resonances of the phenyl groups on the same phosphorus atom, but unfortunately there were no correlations with the proton resonances of the central C_6 ring, and so the spectrum did not provide the required information. In general the products of the quaternisation reactions were of limited stability, but solid materials with satisfactory elemental analyses were isolated in the cases of **4i**, **4j**, and **6l**.

3.6. Reactions with group six metal carbonyls

In refluxing diglyme (160°) either one or two molecules of carbon monoxide were displaced from the hexacarbonyls of chromium, molybdenum, and tungsten to yield complexes with monodentate and/or bidentate chelating polyphosphine. Characterisation is based mainly on the known variations with ring size and metal of ³¹P chemical shifts in analogous complexes of other phosphines and diphosphines [12], together with satisfactory elemental analyses and mass spectra in the cases of **11**, **1m**, **1n**, **2g**, **2i**, **3q**, **3s**, **3w**, **6m**, **6p**, **7n**, **7p**, and **7r**.

3.7. Complexes with platinum group metals

The ³¹P NMR spectra of dichloromethane solutions containing a polyphosphine and $[codRh-\mu-Cl]_2$ showed the presence of many transient species with Rh–P bonds $[^{1}J(^{103}Rh-^{31}P)\sim130$ to 190 Hz], but only **1g**, **3v**, and **3w** (from adventitious aerial oxidation during the preparation of **3v**) were characterised with sufficient confidence to be included in the tables. The palladium and platinum complexes were made by reacting *cis*-(PhCN)₂PdCl₂ and *cis*-(PhCN)₂PtCl₂ respectively with the polyphosphine in dichloromethane at room temperature. The ³¹P NMR spectra of the reaction mixtures changed considerably over periods of several days and indicated transient formation of

Table 6				
³¹ P NMR parameters	of derivatives of	1,2,3,5-tetrakis-	(diphenylphosphine)benzene

No	Compound	$\delta(^{31}P_1)^a$	$\delta(^{31}P_2)^a$	$\delta(^{31}P_3)^a$	$\delta(^{31}P_5)^a$	${}^{3}J(P_{1}-P_{2})^{b}$	${}^{4}J(P_{1}-P_{3})^{b}$	${}^{5}J(P_{1}-P_{5})^{b}$	${}^{3}J(P_{2}-P_{3})^{b}$	${}^{4}J(P_{2}-P_{5})^{b}$	${}^{3}J(P_{3}-P_{5})^{b}$
6	6	-12.7	-9.3	-12.7	-6.0	93.0	-	<3	93.0	<3	<3
6a	6 {5-S}	с	с	c	41.4	с	-	c	c	<3	<3
6b	6 {1,5-S ₂ }	46.3	-10.1	-15.8	41.4	53.7	4.9	<3	2.4	<3	<3
6c	6 {2,5-S ₂ }	-13.1	46.1	-13.1	41.2	36.6	-	<5	36.6	<5	<5
6d	6 {1,3,5-S ₃ }	46.4	-5.3	46.4	41.4	35.4	-	<5	354	<5	<5
6e	6 {1,2,3,5-S ₄ }	51.6	53.8	51.6	42.3	10.9	-	<1	10.9	4.9	<1
6f	6 {1,2,3-S ₃ ,5-Se}	50.4	52.4	50.4	33.3	9.8	-	<2	9.8	4.9	<2
6g	6 {5-Se} ^{d,e}	-12.3	-8.5	-12.3	33.7	94	-	<4	94	<4	<4
6h	6 {1,5-Se ₂ } ^f	37.4	-11.1	-16.2	33.8	61.0	4.9	1.8	2.4	<1	<1
6i	6 {1,3-S ₂ ,5-Se}	46.4	-5.4	46.4	33.5	34.1	-	<2	34.1	<2	<2
6j	6 {1,3,5-Se ₃ }	38.0	-6.0	38.0	33.5	39.5	-	<2	39.5	<2	<2
6k	6 {1,5-(MeI) ₂ }	21.7	-2.5	-13.8	20.6	45.5	4.5	3.3	2.2	3.5	2.2
61	6 {1,3,5-(MeI) ₃ }	26.8	+2.4	26.8	22.8	27.3	-	1.8	27.3	3.7	1.8
6m	$6{1,2-Cr(CO)_4,5-Cr(CO)_5}$	87.5	90.8	-16.2	56.7	23.8	3.7	-	12.8	3.7	1.8
6n	${\bf 6}$ {1,2-Mo(CO) ₄ ,5-Mo(CO) ₅ }	63.9	66.3	-17.0	37.5	8.5	3.4	-	14.4	3.4	1.5
60	6 {1,2-Mo(CO) ₄ ,5-Se} ^g	64.1	66.8	-17.0	33.2	8.2	3.4	-	13.7	4.6	1.5
6p	$6{1,2-W(CO)_4,5-W(CO)_5}^h$	48.9	51.0	-16.6	21.0	1.2	3.4	-	15.3	3.7	1.5
6q	$6{1,2-PdCl_2}_{2}{5,5-PdCl_2}_{2}^{i}$	59.7	70.3	-17.1	24.8	<4	<4	<4	<4	<4	<4
6r	6 {1,2-PtCl ₂ ,5-Se} ^j	38.2	47.2	-17.3	34.0	<4	<4	<4	12.2	<4	<4

 $^{\rm a}$ In ppm ± 0.2 ppm.

^b In Hz ±0.2 Hz. The absence of an entry indicates that the coupling constant is unavailable owing to symmetry or accidental isochronicity.

^c Transient species; peaks in P(III) region overlapped by other signals.

 $^{\rm d}$ From analysis as AB_2X system.

 $^{e^{-1}}J(^{77}\text{Se}-^{31}\text{P})=748$ Hz.

 ${}^{f_1}J({}^{77}\text{Se}-{}^{31}\text{P}_1) = 741 \text{ Hz}; {}^{1}J({}^{77}\text{Se}-{}^{31}\text{P}_5) = 754 \text{ Hz}.$

 $^{g^{-1}}J(^{77}\text{Se}-^{31}\text{P}_5) = 750$ Hz.

$$^{h_1}J(^{183}W-^{31}P_1) = 235$$
 Hz; $^{1}J(^{183}W-^{31}P_2) = 228$ Hz; $^{1}J(^{77}Se-^{31}P_5) = 243$ Hz.

 ${}^{j}{}^{1}J({}^{195}\text{Pt}-{}^{31}\text{P}_{1})\sim 3590 \text{ Hz}; {}^{1}J({}^{195}\text{Pt}-{}^{31}\text{P}_{2})\sim 3535 \text{ Hz}; {}^{1}J({}^{77}\text{Se}-{}^{31}\text{P}_{5})=772 \text{ Hz}.$

species other than those listed. These probably included polymeric and cyclophane-like species such as [1,3,5- $(Ph_2P)_3C_6H_3]_2(PtCl_2)_3$ whose successful characterisation was dependent upon the isolation of suitable crystals [3,4]. Assignments of a *cis* or *trans* geometry at the metal are based upon values of ${}^{1}J({}^{195}\text{Pt}-{}^{31}\text{P})$ of approximately 3500 or 2500 Hz respectively for the platinum complexes [13,14], and by analogy with these in the case of palladium. The structure of 1k was confirmed by the presence of a quintet from coupling to ³¹P with a 1:4:6:4:1 intensity pattern in its ¹⁹⁵Pt spectrum. The reaction of 3 with cis-(PhCN)₂PtCl₂ initially gave mainly 3α which is presumably a chlorine-bridged dimer, but after several days **3B** was the major product and was identified from its characteristic ¹⁹⁵Pt NMR spectrum consisting of a pair of phosphorus-coupled triplets in a 2:1 intensity ratio together with ³¹P resonances in the appropriate regions and allied ¹⁹⁵Pt satellites indicative of *cis* geometry at each type of platinum.

4. Discussion

As already pointed out, the entries in the tables represent only a proportion of species detected in this work, and it is clear that the polyphosphines 1 to 7 can undergo a wide range of reactions with chalcogens, iodomethane, and transition metal substrates to yield products that are generally of the type expected by analogy with the behaviour of such ligands as dppe, but which may vary according to reaction conditions (i.e. for kinetic reasons) as well as their inherent thermodynamic stability. In particular, reactions involving attack on the central Ph₂P moiety of three adjacent ones are significantly hindered. For example, species such as $2{2-MeI}$, and $2{2-Se}$ were not observed, and 2c and 6e formed only with difficulty. Exceptions to this occur with species such as 2g-i, 5f-h, and **6m-r** where additional stability is provided by chelate ring formation, but in these cases it was not then possible to attack the Ph₂P group in the 3-position. It was also found that the highly hindered 5 was considerably less robust than the other polyphosphines and underwent spontaneous decomposition over a period of months at 0° C.

It is of interest to consider the ways in which the different degrees of strain encountered in these species are reflected in their NMR (primarily ³¹P) parameters, particularly with reference to predictive and diagnostic value.

4.1. Phosphorus chemical shifts

As indicated in the introduction, steric interactions between adjacent Ph₂P groups are likely to have a major effect upon $\delta(^{31}P)$, with electronic effects involving more

Table 7 ³¹P NMR parameters of derivatives of 1,2,4,5-tetrakis-(diphenylphosphino)benzene

No	Compound	$\delta({}^{31}P_1)^a$	$\delta({}^{31}P_2)^a$	$\delta({}^{31}P_4)^a$	$\delta({}^{31}P_5)^a$	${}^{3}J({}^{31}P_{1}-{}^{31}P_{2})^{b}$	${}^{3}J({}^{31}P_4 - {}^{31}P_5)^{b}$
7	7	-14.2	-14.2	-14.2	-14.2	-	_
7a	7 {1-S}	43.2	-18.5	-13.5	-13.5	29.3	_
7b	7 $\{1, 4-S_2\}^c$	42.8	-19.7	42.8	-19.7	29.3	29.3
7c	7 $\{1, 5 - S_2\}^c$	42.8	-19.7	-19.7	42.8	29.3	29.3
7d	7 {1,2,4-S ₃ }	45.0	45.0	42.2	-19.3	-	25.4
7e	7 $\{1,2,4,5-S_4\}$	46.0	46.0	46.0	46.0	_	_
7f	7 $\{1-Se\}^d$	33.7	-19.3	-13.4	-13.6	35.4	_
7g	7 $\{1, 4-Se_2\}^c$	34.6	-20.1	34.6	-20.1	34.2	34.2
7h	7 $\{1, 5-Se_2\}^c$	33.3	-19.3	-19.3	33.3	33.3	32.2
7i	7 $\{1,2,4-Se_3\}$	35.6	35.6	33.6	-19.6	_	31.7
7j	7 $\{1,2,4,5-Se_4\}^e$	36.2	36.2	36.2	36.2	-	-
7k	7 $\{1, 4-(MeI)_2\}^c$	22.1	-14.0	22.1	-14.0	22.0	22.0
71	7 $\{1,5-(MeI)_2\}^c$	23.3	-13.3	-13.3	23.3	18.0	18.0
7m	7 $\{1,2-Cr(CO)_4\}$	82.7	82.7	-13.8	-13.8	-	-
7n	7 {1,2-Cr(CO) ₄ , 4,5-Cr(CO) ₄ }	83.4	83.4	83.4	83.4	_	_
70	7 {1,2-Mo(CO) ₄ }	60.0	60.0	-13.9	-13.9	_	-
7p	7 {1,2-Mo(CO) ₄ , 4,5-Mo(CO) ₄ }	59.7	59.7	59.7	59.7	-	-
7q	7 $\{1,2-W(CO)_4\}^f$	45.0	45.0	-14.4	-14.4	_	_
7r	7 {1,2-W(CO) ₄ , 4,5-W(CO) ₄ } ^g	44.0	44.0	44.0	44.0	_	-
7s	7 $\{1,2-PdCl_2, 4,5-PdCl_2\}^h$	61.0	61.0	61.0	61.0	_	-
7t	7 {1,2-PtCl ₂ , 4,5-PtCl ₂ } ⁱ	38.4	38.4	38.4	38.4	_	_

^a In ppm ± 0.2 ppm.

^b In Hz ± 0.2 Hz. The absence of an entry indicates that the coupling constant is unavailable owing to symmetry or accidental isochronicity.

^c It may be necessary to interchange the relative assignments of 7b and 7c, 7g and 7h, and 7k and 7l.

 ${}^{d}{}^{1}J({}^{77}\text{Se} - {}^{31}\text{P}_{1}) = 742 \text{ Hz.}$

 ${}^{e^{-1}}J({}^{77}\text{Se}{}^{-31}\text{P}) = 766 \text{ Hz.}$ ${}^{f^{-1}}J({}^{183}\text{W}{}^{-31}\text{P}) = 234 \text{ Hz.}$

 $^{g^{-1}}J(^{183}W-^{31}P)=238$ Hz.

 $^{h-1}J(^{195}\text{Pt}-^{31}\text{P})=3620$ Hz.

 $^{i} J(^{195}\text{Pt}-^{31}\text{P}) = 3618 \text{ Hz}.$

widely separated groups being much less important. This is supported by the observation that the data for derivatives of 4 (Table 4) and the isolated Ph₂P groups of 3 (Table 3) and 6 (Table 6) are all very similar to those of the corresponding derivatives of triphenylphosphine itself. Similarly, the isolated Ph₂PCCPPh₂ fragments in 1, 3, and 7, show closely parallel behaviour to each other. Thus mono-sulfurisation increases $\delta(^{31}P)$ by approximately 57 ppm (cf. 48 ppm for Ph₂P [15]) and disulfurisation of adjacent Ph₂P groups by approximately 61 ppm, these larger figures being indicative of a significant steric effect. The corresponding figures for mono- and di-selenisation and quaternization with MeI are also greater at 48, 52 and 39 ppm respectively compared with 40, 40, and 27 ppm for isolated Ph_2P groups. The $M(CO)_4$ [M=Mo, W] derivatives of chelating 1 have been referred to previously [16-18], but apparently not fully characterised and the coordination chemical shifts (i.e. the changes in $\delta({}^{31}P)$) accompanying their formation) of 96.6, 73.1, and 59.8 ppm for M = Cr, Mo, and W respectively are all some 6 ppm greater than for the corresponding complexes of dppe which also gives a five-membered chelate ring. This perhaps implies a greater degree of "ring strain" in the former, and it is noteworthy that its greater conformational mobility permits dppe to achieve a smaller angle of bite than 1. However, measurements of heats of formation from

norbornadieneMo(CO)₄ [16] suggest that 1m and dppeMo(CO)₄ are of comparable stability. Similar remarks apply to the five-membered chelate rings in the $M(CO)_4$, $PdCl_2$ and $PtCl_2$ complexes of 3 and 7. The foregoing additions also have minor effects upon the chemical shift(s) of the non-reacting Ph₂P group(s). Thus sulfurisation in an *ortho* position reduces $\delta({}^{31}P)$ of the unreacted Ph₂P group by approximately 4 ppm and selenisation has a somewhat larger effect, while quaternisation leads to small increases. The additional strain that might be expected to be present in derivatives of 2 and 6 with three adjacent Ph₂P groups has little further effect upon $\delta(^{31}P)$, and indeed this generally also applies to the severely hindered 5.

4.2. Phosphorus-phosphorus coupling

In the parent polyphosphines ${}^{3}J({}^{31}P^{III}-{}^{31}P^{III})$ is large and varies considerably with steric factors but nonetheless has considerable diagnostic value. As expected, ${}^{4}J({}^{31}P^{III} - {}^{31}P^{III})$ and ${}^{5}J({}^{31}P^{III} - {}^{31}P^{III})$ are much smaller and any steric dependence is not readily apparent. In the derivatives this also applies to the four and five bond coupling constants but not always to the three-bond couplings. In general terms it can be stated that ${}^{3}J({}^{31}P^{V}-{}^{31}P^{V})$ is always less than 11 Hz, the only apparent exceptions to this being

Table 8				
Microanalytical	data	for	selected	compounds

No	%C	%C			%P		MW		MP °C	
	Calc.	Fd.	Calc.	Fd.	Calc.	Fd.	Calc.	Fd.	C	
1a ^a	_	_	_	_	-	_	478	479	146-147	
1c ^a	70.6	70.0	4.74	4.47	_	_	510	510	266-268	
1d ^a	66.6	66.6	4.47	4.25	_	_	542	542	178 - 180	
1e ^b	68.6	68.8	4.60	4.47	_	_	526	526	209-211	
1f ^c	59.6	59.0	4.00	4.01	_	_	606	526 ⁱ	205-208	
1g ^a	63.3	62.4	4.63	4.41	_	_	_	_	d>235	
$1\mathbf{h}^{d}$	66.9	66.8	3.96	3.98	_	_	_	_	d>235	
1i ^a	62.4	62.4	3.70	3.53	_	_	_	_	d>230	
1j ^⁵	55.0	54.7	3.26	3.07	_	_	_	_	d>275	
1k ^d	61.6	61.8	4.14	4.16	_	_	585	549 ^g	d >140	
1m ^e	50.6	50.5	3.40	3.29	_	_	711	712	d>240	
1n ^e	50.6	49.6	3.40	3.23	_	_	_	_	d>360	
$2d^{b}$	71.1	69.2	4.69	4.76	13.1	12.7	710	710	215-216	
$2\mathbf{g}^{\mathrm{f,h}}$	69.5	71.3	4.19	4.40	11.7	12.2	795	794	d>215	
2 i ^f	59.6	58.2	3.59	3.51	10.0	9.8	926	926	240-245	
3f ^e	69.4	69.1	4.58	4.68	12.8	12.9	727	727	280-283	
3q ^d	62.1	61.8	3.37	3.45	_	_	_	_	d>160	
3s ^b	57.5	57.2	3.10	3.30	_	_	-	_	d>160	
3u ^b	49.0	49.0	2.66	2.67	_	_	_	_	d>180	
$3w^d$	64.2	62.9	4.24	4.10	_	_	785	786	d>160	
$3\alpha^{b}$	49.1	48.6	2.95	3.12	_	_	_	_	d>250	
4d ^a	69.4	67.2	4.58	4.44	12.8	12.2	727	727	220-221	
4e ^a	58.2	58.1	3.83	3.90	_	_	867	867	261-263	
4i ^e	51.1	51.3	2.49	2.72	7.0	7.2	_	_	140-142	
4j°	42.7	42.8	2.08	2.16	5.8	5.8	_	_	158-160	
5b ^a	73.8	71.7	4.82	5.05	_	_	879	877	160-164	
5c ^b	76.6	75.2	5.00	5.12	14.6	14.0	847	847	d>190	
5d ⁱ	72.6	72.1	4.74	5.09	13.9	13.0	893	814 ⁱ	239-242	
5g⁵	65.4	65.0	4.27	4.00	_	_	992	991	d>265	
5h ^b	60.0	58.2	3.92	3.72	_	_	1081	1081	d>260	
6e ^b	68.8	68.6	4.49	4.47	13.1	12.9	943	942	259-260	
6g ^d	72.6	71.8	4.74	4.82	13.9	13.2	894	894	227-230	
6h ^d	66.7	66.3	4.35	4.27	12.7	12.4	-	-	255-258	
61 ^f	55.2	55.5	4.14	4.35	10.0	9.6	_	_	285-290	
6n ^b	60.1	59.6	3.36	3.41	9.8	9.9	_	_	d>160	
6m ^d	64.6	63.3	3.62	3.66	10.6	10.7	-	-	d>180	
6p ^d	52.7	52.8	2.95	2.88	8.6	8.5	_	_	d>205	
6q ^d	60.0	59.5	3.92	3.92	-	_	-	-	d>275	
7e ^a	68.8	67.7	4.49	4.60	13.1	12.6	942	942	d>280	
7g,h ^d	66.7	66.1	4.35	4.14	12.7	12.6	973	973	d>270	
7j ^f	57.4	57.3	3.74	3.88	11.0	11.2	_	_	d>320	
$7n^{d}$	65.2	65.2	3.70	3.71	10.8	10.3	_	_	d>270	
7p ^d −	60.1	60.1	3.41	3.47	10.0	10.2	_	-	d>250	
$\mathbf{7r}^{d}$	52.9	52.7	3.01	2.99	8.8	8.6	_	-	d>260	
$7s^{\circ}$	55.4	55.5	3.62	3.50	_	_	_	_	d>260	
7t ^e	48.2	46.7	3.14	2.89	-	-	_	-	d>360	

^a White.

^b Light yellow.

^c Light tan.

^d Yellow.

^e Off-white.

^f Orange.

^g MW(Calc.) – MW(Fd.) $\equiv 1$ Cl.

^h Unstable compound.

ⁱ MW(Calc.) – $MW(Fd.) \equiv 1$ Se.

the $Cr(CO)_4$ derivatives **2g** and **6m** in which there is an additional coupling pathway via the metal atom. In the absence of serious steric constraints (i.e. in the derivatives

of **1**, **3** and 7) ${}^{3}J({}^{31}P^{V}-{}^{31}P^{III})$ lies in the range 18.0 to 36.5 Hz, the largest values being associated with Ph₂PSe, intermediate ones with Ph₂PS, and the smallest with



Fig. 1. P=S regions of proton-decoupled ³¹P NMR spectra at 202.5 MHz of reaction mixtures resulting from the addition of elemental sulfur to $1,2,4-(Ph_2P)_3C_6H_3$ in CDCl₃. (a) 1 atomic equivalent of sulfur. (b) 1.5 atomic equivalents of sulfur. (c) 2 atomic equivalents of sulfur. (d) 2.5 atomic equivalents of sulfur. The resonances from **3f** at 47.3 ppm are off-scale.

 Ph_2MeP^+ , in a clear parallel with effective electronegativity. In addition ${}^{3}J({}^{31}P^{III}-{}^{31}P^{III})$ remains large and of comparable size to its value in the parent polyphosphine.

The foregoing does not apply to the derivatives of the more severely hindered 2, 4 and 5, and some striking variations in the three-bond couplings are apparent, although it is noteworthy that those in derivatives of 2 are always similar to those of the corresponding derivatives of 5 as expected on the basis that an isolated Ph₂P group will

have little electronic and no steric influence. Thus ${}^{3}J({}^{31}P^{III}-{}^{31}P^{III})$ is close to zero in **2a** and **6b**, while ${}^{3}J({}^{31}P^{V}-{}^{31}P^{III})$ is 55.5 and 53.7 Hz respectively, results which might cast doubts upon the authenticity of these species had not **6e**, the product of complete sulfurisation of **6** been fully characterised by elemental analysis and single-crystal X-ray diffraction [10]. It is known that in **6e** the bulk of the three adjacent Ph₂P(S) groups leads to large structural distortions with dihedral angles of as much as



Fig. 2. Part of the P=S region of the 2D proton-decoupled ³¹P COSY NMR spectrum at 202.5 MHz of the reaction mixture resulting from the addition of 2.5 atomic equivalents of sulfur to $1,2,4-(Ph_2P)_3C_6H_3$ in CDCL₃. The resonance at 47.3 ppm from P₁ in **3f** is off-scale but showed a correlation with the P₄ resonance at 42.2 ppm, and the resonances from **3d** and **3e** at 44.1 and 44.4 ppm were also correlated with corresponding signals in the P^{III} region of the spectrum.

70° for the nominally planar P–C–C–P fragments and that these probably persist in solution. Comparable deviations from planarity can be expected to occur in other derivatives of **2** and **6** and to affect the vicinal ${}^{31}P_{-}{}^{31}P$ couplings both by direct modification of the through-bond pathway and by modifying electron lone-pair interactions. It is difficult to quantify these effects at present, but it may be noted that the values of ${}^{3}J({}^{31}P^{\Pi}_{-}{}^{31}P^{\Pi})$ in **1**, *cis*-Ph₂PCH=CHPPh₂, *trans*- Ph₂PCH=CHPPh₂, and dppe are 145.2, 105.5, 13.4, and 33.6 Hz respectively [19], which illustrates the large potential for variation of this coupling constant; indeed it is possible that the contribu-

tions from through-bond and direct lone-pair interactions are of opposite sign.

The highly hindered **5** has smaller (81.0 and 35.3 Hz) vicinal ${}^{31}P-{}^{31}P$ coupling constants than any of the other polyphosphines studied here, and its derivatives display some remarkably small or even zero values of ${}^{3}J({}^{31}P^{III}-{}^{31}P^{III})$ in conjunction with abnormally large ${}^{3}J({}^{31}P^{V}-{}^{31}P^{III})$, e.g. 70.6 Hz in **5d**. It is particularly striking that in **5a–e** which are substituted in the 1-position not only is the adjacent vicinal $P^{III}-P^{III}$ coupling constant almost zero, but so is that between P₃ and P₄. This is consistent with there being quite severe distortions of the P₄C₆ skeleton in



Fig. 3. Proton-decoupled ³¹P NMR spectrum at 24.2 MHz of $1-Ph_2P(Se)-2,3,4-(Ph_2P)_3C_6H_2$ in CH_2CL_2 showing the pattern of unusual coupling constants.

addition to specific electron lone-pair orientations which are normally regarded as being the main determining factors in vicinal ³¹P^{III}-³¹P^{III} couplings.

4.3. Other couplings to phosphorus

The coupling constants ${}^{1}J(M-{}^{31}P)$ [M = ${}^{77}Se$, ${}^{103}Rh$, ${}^{183}W$, ${}^{195}Pt$] all lie in the ranges expected for derivatives of less sterically demanding ligands, and indicate that the hybridisation and effective nuclear charge on the phosphorus atoms are essentially normal thus confirming that the unusual features shown by the vicinal ${}^{31}P-{}^{31}P$ couplings arise primarily from special dihedral angles and/or coupling paths. These considerations also apply to ${}^{1}J({}^{31}P-{}^{13}C)$ of the methyl groups in the quaternary phosphonium iodides.

5. Conclusions

The *polykis*(diphosphino)benzenes without more than two adjacent Ph₂P moieties react with chalcogens and iodomethane and with transition metal substrates in a predictable manner and the patterns of ³¹P chemical shifts and coupling constants are a valuable guide to the nature of the products. However, the presence of more than two Ph₂P proximate moieties leads to considerable steric strain in the products and this is relieved by significant distortions from planarity of the P_nC₆ skeleton which are reflected in abnormal values of ³J(³¹P^{III}–³¹P^{III}) and ³J(³¹P^V–³¹P^{III}) to the extent that these are of less immediate and direct value as guides to identity.

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