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MIXED-LIGAND PLATINUM(II) COMPLEXES OF $[N(SPR_2)_2]^-$ (R = Ph, OPh)

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Abstract—The preparation of complexes of the type $\{Pt(R_3P)_2[(SPR_2)_2N]\}X$($R$ = Ph, OPh, $X = Cl^-$, PF_6^-) and $\{Pt(PR_3)[N(SPR'_2)_2]Cl\}$ is described. The new complexes have been characterized by NMR and IR, microanalyses and in the case of $\{Pt(PPh_3)[N(SPPh_2)_2]Cl\}$ by X-ray crystallography. The PtS_2P_2N ring adopts a pseudo-boat conformation. Copyright © 1996 Elsevier Science Ltd

The coordination of metals by monoanionic bidentate ligands remains a significant topic. For example, β-diketonates form a large class of complexes which have been extensively studied.[1] There are limited examples of metal complexes[2–4] of the neutral bis-chalcogenide $R_2P(E)NHP(E)R_2$ (E = O, S; R = Me or Ph), although the chemistry of tetraorganodithioimidodiphosphinato ligands, $[R_2P(E)NP(E)R_2]^-$ (E = O, S, Se; R = alkyl, aryl, aryloxy), is considerably better understood.[5–9] Anionic ligands of this type have found important uses as metal extractants[10] and are also widely interesting as inorganic analogues of the more familiar β-diketonate ligands. The majority of the complexes reported are homoleptic. Here we describe the synthesis of a range of mixed-ligand platinum complexes containing $[R_2P(S)NP(S)R_2]^-$ (R = Ph, OPh) and phosphines together with the X-ray structure of $\{Pt(PPh_3)[N(SPPh_2)_2]Cl\}$.

EXPERIMENTAL

Hexane and CH_2Cl_2 were dried and distilled under nitrogen before use; all other solvents and reagents were used as received. $(PPh_2)_2NH$, $(SPPh_2)_2NH$ and $Na[(SPPh_2)_2N]$ were prepared by literature methods.[11,12] ^{31}P [^1H] (109.4 MHz) and ^{195}Pt [^1H] (57.9 MHz) NMR spectra were recorded in CD_2Cl_2 on a Jeol JNM EX270 spectrometer, IR spectra (as KBr discs) on a Perkin–Elmer 1720X FT–IR spectrometer. Microanalyses were performed by the Imperial College Microanalytical Service, while FAB$^+$ mass spectra (3-nitrobenzylalcohol matrix) were recorded on a Vacuum Generators Autospec Q instrument.

Bis-phosphine platinum tetraphenylimidodiphosphinates $\{Pt(PR_3)_2[(Ph_2PS)_2N]\}X$

$Na[N(SPPh_2)_2]$ (50 mg 0.1 mmol) was added to a solution of $Pt(PEt_3)_2Cl_2$, $Pt(PPhMe_2)_2Cl_2$ or $Pt(dppe)Cl_2$ in CH_2Cl_2 (5 cm^3) and stirred for 2 days. The solution was filtered and the solvent removed *in vacuo*. The dppe derivative was recrystallized from CH_2Cl_2/hexane as the chloride, $NaPF_6$ (20 mg) was added to hot CH_2Cl_2 solutions of the triethylphosphine and dimethylphenylphosphine derivatives to give the hexafluorophosphates, which were recrystallized from CH_2Cl_2/hexane. $\{Pt(PEt_3)_2[(Ph_2PS)_2N]\}PF_6$ (**1**): yield 21 mg, 42%. Microanalysis: Found: C, 41.7; H, 4.3; N, 1.8. Calc. for

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$C_{36}H_{50}F_6NP_5PtS_2$: C, 42.1; H, 4.9; N, 1.45%; *m/z* 879 (cation). $\{Pt(PPhMe_2)_2[(Ph_2PS)_2N]\}PF_6$ (**2**): not isolated as analytically pure solid. $\{Pt(dppe)[(Ph_2PS)_2N]\}Cl$ (**3**): Yield 68 mg, 59%. Microanalysis: Found: C, 55.8; H, 3.7; N, 1.45. Calc. for $C_{50}H_{44}NP_4S_2PtCl$: C, 55.7; H, 4.1; N, 1.3%, *m/z* 1042. $\{Pt(PPh_3)_2[(Ph_2PS)_2N]\}Cl$ (**4**): decomposed in solution.

Bis-phosphine platinum tetraphenylimidodiphosphinates

A mixture of $[SP(OPh)_2]_2NH$ (60 mg) and KO^tBu (15 mg) was added to solutions of $Pt(PR_3)_2Cl_2[PR_3 = PMe_3, PEt_3, PBu_3, PPhMe_2, PPh_3$ and 1.2dppe (each 0.1 mmol)] in $CDCl_3$ (3 cm^3) and the mixtures were stirred for 2 h. The solutions were then filtered and $NaPF_6$ (20 mg) was added to each of the solutions and the products crystallized by the addition of hexane. Further recrystallizations from CH_2Cl_2/hexane gave pure samples of $\{Pt(R_3P)_2[(SP(OPh)_2]_2N\}PF_6$. $\{Pt(PMe_3)_2[(SP(OPh)_2)_2N]\}PF_6$ (**5**): Yield 40%. Microanalysis: Found: C, 36.1; H, 3.4; N, 1.7. Calc. for $C_{30}H_{38}F_6NO_4P_5PtS_2$: C, 35.9; H, 3.8; N, 1.4%. $\{Pt(PEt_3)_2[(SP(OPh)_2)_2N]\}PF_6$ (**6**): Yield 38%. Microanalysis: Found: C, 40.1; H, 4.4; N, 1.7. Calc. for $C_{36}H_{50}F_6NO_4P_5PtS_2$: C, 39.7; H, 4.6; N, 1.3%; *m/z* 943 (cation). $\{Pt(PBu_3)_2[(SP(OPh)_2)_2N]\}Cl$ (**7**): not isolated as analytically pure solid. $\{Pt(PPhMe_2)_2[(SP(OPh)_2)_2N]\}Cl$ (**8**): not isolated as analytically pure solid. $\{Ptdppe[(SP(OPh)_2)_2N]\}Cl$ (**10**): Yield 54%. Microanalysis: Found: C, 48.5; H, 3.8; N, 1.4. $C_{50}H_{44}F_6NO_4P_5PtS_2$ requires: C, 48.0; H, 3.5; N, 1.1%; *m/z* 1106 (cation). $\{Pt(PPh_3)_2[(SP(OPh)_2)_2N]\}Cl$ (**9**): Yield 35%. Microanalysis: Found: C, 52.0; H, 3.9; N, 1.3. Calc. For $C_{60}H_{50}F_6NO_4P_5PtS_2$: C, 52.3; H, 3.6; N, 1.0; *m/z* 1231 (cation). $Pt(PPh_3)[(SPPh_2)_2N]Cl$ (**11**), $Pt(PPhMe_2)[(SPPh_2)_2N]Cl$ (**12**) and $Pt(PPhMe_2)\{[SP(OPh)_2]_2N\}Cl$ (**13**) were obtained by recrystallization from $CHCl_3$ and pentane. The products was deposited as green crystals: Yield *ca* 40%, **11–13** gave the expected *m/z* parent ions.

Crystallography. (**11**) $C_{42}H_{35}ClNP_3S_2Pt$, $M = 941.3$, monoclinic, space group $P2_1/c$, $a = 10.933(6)$, $b = 18.998(14)$, $c = 19.104(12)$ Å, $\beta = 105.97(4)°$, $U = 3815$ Å^3, $Z = 4$, $D_c = 1.64$ g cm^{-3} crystal dimensions $0.43 \times 0.65 \times 0.83$ mm, $\mu(\text{Mo-}K_\alpha) = 4.02$ mm^{-1}, $\lambda(\text{Mo-}K_\alpha) = 0.71073$ Å, $F(000) = 1864$. Siemens *P*4/PC diffractometer, ω-scan method, graphite monochromated $\text{Mo}-K_\alpha$ radiation (2θ range 3.0–50°), 7075 reflections collected, 6708 independent reflections ($R_{int} = 4.8\%$), 5220 observed ($|F_o| > 4.0\sigma|F_o|$), corrected for Lorentz and polarization factors, numerical (face indexed) absorption correction, maximum and minimum transmission factors 0.25 and 0.09, respectively. The structure was solved by direct methods and the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned isotropic thermal parameters, $U(H) = 1.2U_{eo}(C)$, and allowed to ride on their parent carbon/nitrogen atoms. Refinement was by full-matrix least-squares, based on F, to $R = 0.034$ and $wR = 0.036$ [where $w^{-1} = \sigma^2(F) + 0.0007F^2$]. The maximum and minimum residual electron densities in the final ΔF map were 0.62 and -0.44 e Å^{-3} and the mean and maximum shifts/errors in the final refinement were 0.004 and 0.047, respectively.

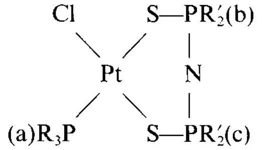
RESULTS AND DISCUSSION

Sodium tetraphenyldithioimidodiphosphinate reacts rapidly with bis-phosphine platinum dichlorides in dichloromethane, displacing the two chlorides to form $\{Pt(PR_3)_2[N(SPPh_2)_2]\}Cl$. Addition of sodium hexafluorophosphate and repeated recrystallization yields colourless $\{Pt(PR_3)_2[N(SPPh_2)_2]\}PF_6$. Similar reactions carried out with $\{[(PhO)_2PS]_2N\}^-$ gave similar initial products. Only $\{Pt(dppe)[N(SPPh_2)_2]\}Cl$ (**3**) and $\{Pt(PPh_3)_2[(SP(OPh)_2)_2N]\}Cl$ (**10**) crystallized readily as the chloride, the other complexes were far harder to purify. Most were initially isolated as oils and proved impossible to crystallize even when they analysed as pure. Some (**1**, **5** and **6**) were crystallized after the introduction of the hexafluorophosphate counter ion. Three of the complexes, $\{Pt(PPhMe_2)_2[(SPPh_2)_2N]\}Cl$ (**2**), $\{Pt(PPhMe_2)_2[(SP(OPh)_2)_2N]\}Cl$ (**8**) and $\{Pt(PBu_3)_2[(SP(OPh)_2)_2N]\}Cl$ (**7**), could not be obtained as analytically pure solids and were only characterized by ^{31}P NMR spectroscopy and mass spectrometry, but comparison of these data with those from the more fully characterized complexes leaves little doubt about their existence. $\{Pt(PPh_3)_2[(Ph_2PS)_2N]\}Cl$ (**4**) decomposed in solution to form another complex and was only identified by ^{31}P NMR.

The arrangement of four phosphorus atoms around a planar platinum centre means that the spin system in the ^{31}P NMR will be AA′XX′. Spectra from this type of system consist of two symmetrical sets of peaks containing 10 lines each. In cases where the coupling constants are small the peaks are frequently overlapping and analysis is difficult, but in cases in which most of the peaks are observed the coupling constants can usually be determined reasonably easily by the application of some simple algebra (Table 1). In some of the examples seen here the complexity of the spin system

Table 1. ^{31}P [^{-1}H] NMR data for complexes $\{(R_3P)_2Pt[(SPR_2)_2N]\}X$ and $\{Pt(PR_3)[N(SPR'_2)_2]Cl\}$

Phosphine	δ ^{31}P ppm A [$^2J(^{31}P-^{195}Pt)$]	δ ^{31}P ppm X [$^1J(^{31}P-^{195}Pt)$]	J_{AX} (Hz)	$J_{AX'}$ (Hz)	$J_{AA'}$ (Hz)	$J_{XX'}$ (Hz)
Complexes of tetraphenyldithioimidodiphosphinate						
(**1**) PEt_3	36.10[60.50]	12.63[3099.5]	9.39	−9.39	5.49	19.02
(**2**) $PPhMe_2$	36.74[63.5]	−10.39[3127]		Other coupling not resolved		
(**3**) dppe	33.54[78.65]	51.35[3103.5]	17.36	−7.91	4.23	4.23
(**4**) PPh_3	32.94[63.48]	17.88[3239.7]	13.84	−6.48	3.47	22.37
Complexes of tetraphenyldithiomidodiphosphonate						
(**5**) PMe_3	40.2[64.5]	−19.3[3123.6]		Other coupling not resolved		
(**6**) PEt_3	38.9[66.46]	13.0[3134.7]				
(**7**) PBu_3	40.2[59.81]	6.2[3128.0]				
(**8**) $PPhMe_2$ (**46**)	41.3[55.13]	−8.8[3176.8]				
(**9**) dppe	43.0[91.75]	50.2[3187.5]	26.69	−2.47	53.73	4.98
(**10**) PPh_3	42.2[54.11]	18.0[3318.6]	19.64	4.21	28.58	21.79



11 **12** **13**

$R_3 = Ph_3$ $R_3 = Me_2PhR_3Me_{2}$-

$R' = Ph$ $R' = Ph$ $PhR' = OPh$

	11	**12**	**13**
δ PR_3 (a)	17.51	−12.42	−11.36
δ P trans to PR_3 (b)	30.37	38.35	46.33
δ P trans to Cl (c)	38.85	29.64	38.20
δ Pt	—	4101	4077
$^1J(^{31}P-^{195}Pt)$ (a)	3473.3	3346.4	3367.5
$^2J(^{31}P-^{195}Pt)$ (b)	52.1	52.6	31.6
$^2J(^{31}P-^{195}Pt)$ (c)	112.9	115.8	126.2
$^3J(^{31}P-^{31}P)$ (a,b)	10.70	8.40	5.1
$^3J(^{31}P-^{31}P)$ (a–c)	12.10	10.15	13.55
$^2J(^{31}P-^{31}P)$ (b,c)	5.00	5.10	67.8

is obvious, in the dppe and PPh_3 derivatives with both the diphosphinate and the diphosphonate most of the peaks are visible even before any attempt at resolution enhancement has been made. In the case of $\{(PEt_3)_2Pt[(SPPh_2)_2N]\}PF_6$, although the normal resolution spectrum appears to contain only two singlets, resolution enhancement reveals that there are in fact two symmetrical sets of seven peaks. In several cases, particularly with the diphosphonates, the resolution of the spectra was not sufficiently good to identify the $^{31}P-^{31}P$ coupling constants. The assignments were made from analysis of the observed spectra and comparison with iteratively refined simulated spectra.[13]

In **3** the two intra-ligand coupling constants are identical. The constant relating to the thiophosphinate is typical, but that of the dppe is much lower than that of the other phosphines. The lower value is almost certainly due to the presence of an alternative intra-ligand route for the coupling, which would be expected to change the $^{31}P-^{31}P$ coupling significantly. This effect is also apparent in the spectrum of **9**, but because the magnitude of the coupling within the diphosphonate is so much larger the spectrum is clearer. The fact that the two constants are identical is coincidental. The simulated spectrum agrees extremely well with the observed spectrum, as can be seen from Fig. 1 below in the half-spectrum due to the dppe. In the ^{31}P NMR spectrum of $\{Pt(Pet_3)_2[N(SP(OPh)_2)_2]\}PF_6$ (**6**) (Fig. 2) some of the peaks are unresolved, but enough detail remains to make a fair assignment. In this case, however, the *cis*- and *trans*-couplings between the ligands turn out to be of the same magnitude, although of different sign. There is no obvious explanation as to why this should happen, but in all the examples of this type these two constants are similar.

Due to the symmetry of the system there is no way from the spectrum alone to determine which of the calculated figures is $J_{AA'}$ and which is $J_{XX'}$ and the same ambiguity exists between J_{AX} and $J_{AX'}$.

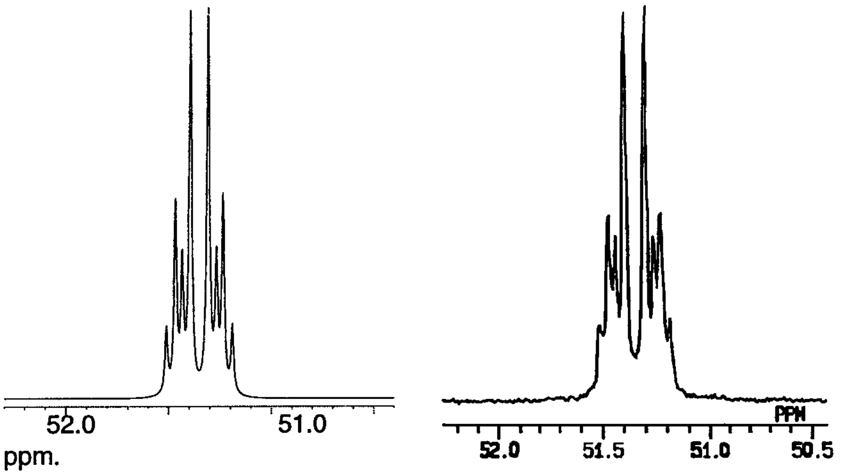


Fig. 1. Part of the simulated (left) and observed (right) ^{31}P [^{-1}H] NMR spectrum of Pt(dppe)[$N(SPPh_2)_2$]Cl.

The assignments above are made by analogy with other related systems[10] as well as by comparison with **11–13**, below.

The IR spectra of the complexes show the same changes in the ligand bands on coordination as were seen in the homoleptic complexes. In the dithiodiphosphinate complexes the P_2N bands are in the ranges 1173–1159 cm^{-1} and 814–806 cm^{-1} compared with 935 and 922 cm^{-1} in the free ligand. In the dithiodiphosphonates the (P_2N) bands are seen at 1297–1262 and 755–735 cm^{-1} compared with 840 cm^{-1} in the free ligand. As in the earlier complexes these changes reflect the increased P—N bond order and are accompanied by a reduction in ν(PS) due to the increased P—S bond order [ν(PS) in the range 575–569 cm^{-1} for **1–4** and 558–526 cm^{-1} for **5–10**, cf. 645 and 659 cm^{-1} for the ligands].

The crystal structures of $\{PT(PEt_3)_2$ [$N(SPPh_2)_2]\}PF_6$ and $\{Pt(PMe_3)_2[SP(OPh)_2)_2N]\}PF_6$ have already been described.[14] In both cases the ligand chelates the metal via the two sulfur atoms with the MS_2P_2N ring being twisted, but there are significant differences in the conformations. In the $[N(SPPh_2)_2]^-$ case the ring adopts a pseudo-boat conformation similar to that seen in the structure of Ni[N(SPPh2)$_2$]$_2$; however, the $[(SP(OPh)_2)_2N]^-$ complex adopts a conformation which more closely resembles a flattened chair.

As mentioned above the reaction of bis-triphenylphosphine platinum dichloride with sodium tetraphenyldithioimidodiphosphinate initially gives $\{Pt(PPh_3)_2[N(SPPh_2)_2]\}Cl$ in the same way as all the others; however, attempted crystallization of the complex from the original reaction solution

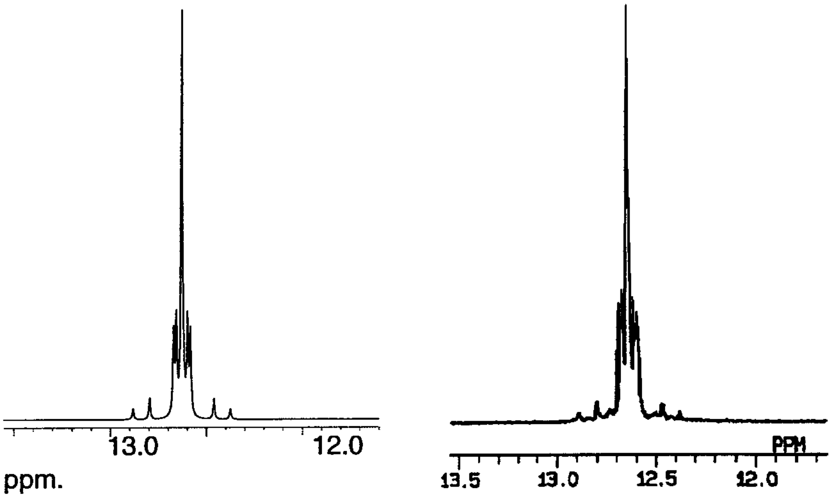


Fig. 2. Part of the simulated (left) and observed (right) ^{31}P [^{-1}H] NMR spectrum of $\{Pt(PEt_3)_2[N(SPPh_2)_2]\}^+$.

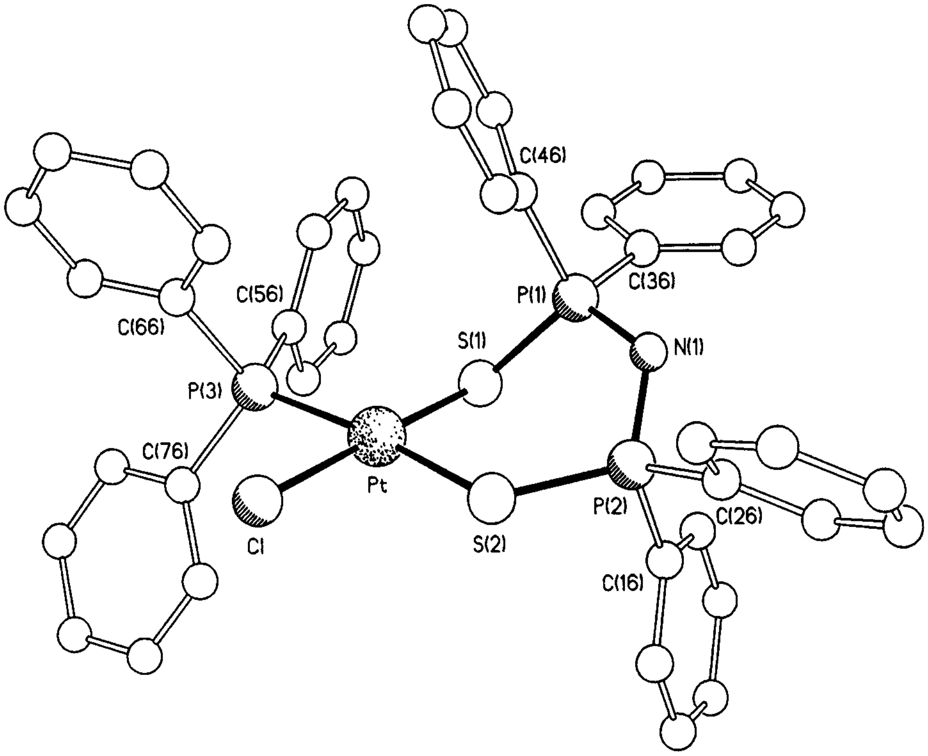


Fig. 3. The X-ray structure of $\{Pt(PPh_3)[N(SPPh_2)_2]Cl\}$.

results in a rearrangement and the formation of a new complex, deposited as bright green crystals which analysed as $\{Pt(PPh_3)[N(SPPh_2)_2]Cl\}$ (**11**). The ^{31}P NMR spectrum of **11** consists of three main peaks, two due to the diphosphinate and one due to the coordinated triphenylphosphine. The symmetry of the system having been destroyed, the two phosphorus atoms in the diphosphinate are now more obviously inequivalent and had different coupling constants to the platinum. The X-ray structure of **11** (Fig. 3, Table 2) reveals a square-planar geometry about platinum with the two Pt—S distances being markedly different as a result of the differing *trans* effects of PPh_3 and Cl^- [Pt—S(1) 2.30(2) and Pt—S(2) 2.372(2) Å] i.e. sulfur *trans* to PPh_3 less strongly bound. The P—N bonds are shortened and the P—S bond lengthened compared with the free ligand. The PtS_2P_2N ring adopts the more commonly observed boat conformation.

Similar complexes containing both the dithiodiphosphinate and the dithiodiphosphonate can be prepared for comparison. Addition of either

Table 2. Selected bond lengths (Å) and angles (°) for $\{Pt(PPh_3)[N(SPPh_2)_2]Cl\}$

Pt—Cl	2.334(3)	P(1)—N(1)	1.590(4)
Pt—S(1)	2.301(2)	N(1)—P(2)	1.599(5)
Pt—S(2)	2.372(2)	P(2)—S(2)	2.022(3)
Pt—P(3)	2.253(2)	mean P(1)C	1.797
S(1)—P(1)	2.029(2)	mean P(2)C	1.799
Cl—Pt—S(1)	177.8(1)	Pt—S(1)—P(1)	103.9(1)
Cl—Pt—S(2)	82.1(1)	S(1)—P(1)—N(1)	116.6(2)
S(1)—Pt—S(2)	98.8(1)	P(1)—N(1)—P(2)	124.6(3)
Cl—Pt—P(3)	88.2(1)	N(1)—P(2)—S(2)	116.8(2)
S(1)—Pt—P(3)	91.0(1)	Pt—S(2)—P(2)	110.9(1)
S(2)—Pt—P(3)	170.1(1)		

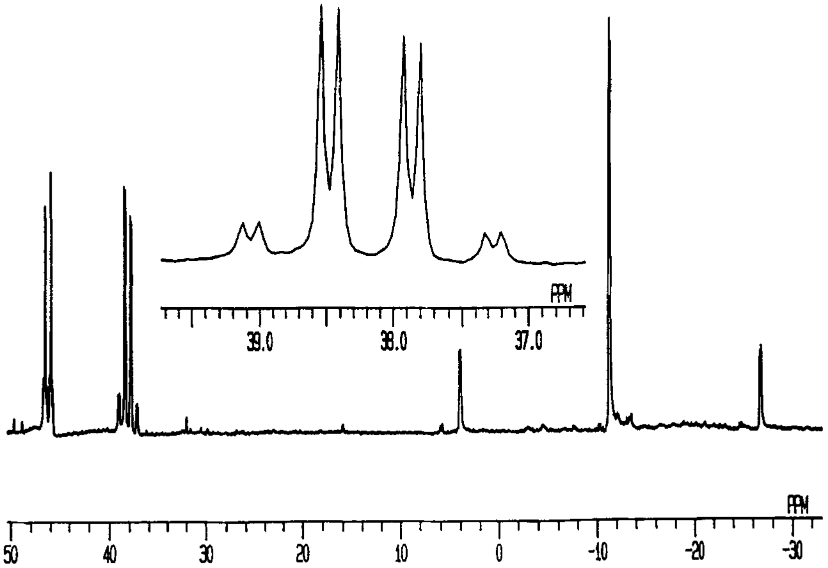


Fig. 4. ^{31}P [$-^{1}$H] NMR spectrum of Pt(PMe$_2$Ph)[N(SP(OPh)$_2$)$_2$].

sodium tetraphenyldithioimidodiphosphinate or the potassium salt of the diphosphonate to the dimeric platinum complex [Pt(PhMe$_2$P)Cl$_2$]$_2$ results in the displacement of two of the chlorides and the formation of Pt(PhMe$_2$P)[N(SPR$_2$)$_2$]Cl (**12** R = Ph; **13**, R = Oph). The ^{31}P NMR spectra of these complexes consist of three double doublets, each with platinum satellites [e.g. see the spectrum of Pt(PPhMe$_2$){[SP(OPh)$_2$]$_2$N}Cl (**13**); Fig. 4], although for the triphenylphosphine derivative not all of the lines are clearly visible due to some coincidences. The spectra of **11–13** are clear examples (Table 1) of *cis* and *trans* ^{31}P–^{31}P coupling constants across a platinum between a diphosphinate and a phosphine. For all three complexes the *cis* coupling is greater than the *trans* coupling (*cis* 12.1 Hz **11**, 10.2 Hz **12**, 13.6 Hz **13** and *trans* 10.7 Hz **11**, 8.4 Hz **12**, 5.1 Hz **13**), although in the imidodiphosphinate complexes **11** and **12** the difference is not particularly great.

The feature which clearly identifies the peak due to the phosphorus attached to the sulfur in the *trans* position to the chloride is its much larger coupling to the platinum, here the coupling constants are in the range 112–126 Hz compared with 31–51 Hz for the phosphorus bound to the sulfur in the *cis* position to the chloride. This difference reflects the lower *trans* influence of the chloride. These three complexes also give examples of ^{31}P–^{31}P coupling between the two phosphorus atoms within the dithioimidodiphosphinate/phosphonate ligand, helping with the assignment of the AA′XX′ spectra described earlier. The ^{195}Pt NMR spectra of **12** and **13** consist of the expected doublet of double doublets. The IR spectra of **11–13** display the same features as those of the earlier cationic and homoleptic complexes. The ν(PS) bands for **12** and **13** are at 571 and 538 cm^{-1}, respectively, compared with 645 and 578 cm^{-1} in the free ligands.

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