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Coordination Chemistry of Higher Oxidation States. Part 21.* Platinum-195 NMR Studies of Platinum(II) and Platinum(IV) Complexes of Bi- and Multi-dentate Phosphorus, Arsenic and Sulphur Ligands

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Abstract

195-Platinum NMR spectra are reported for a series of complexes of bidentate ligands [Pt(L–L)X_4] (X = Cl, Br; L–L = diphosphine, diarsine, dithioether, diselenoether), [Pt($Me_2PCH_2CH_2PMe_2$)$_2X_2$]X_2, [Pt(*o*-C_6H_4($AsMe_2$)$_2$)$_2X_2$]X_2, and for the Pt(II) analogues. The trends in chemical shifts δ(Pt) and ^1J(Pt–P), ^1J(Pt–Se) coupling constants are discussed, and used to establish the nature of the solution species obtained by oxidation of Pt(II) complexes of some multidentate phosphorus and arsenic ligands. The [Pt(L–L)I_4] materials are shown to exist as [Pt^{II}(L–L)I_2] in dimethylsulphoxide solution, but [Pt(*o*-C_6H_4($AsMe_2$)$_2$)$_2I_2$]$^{2+}$ is a genuine Pt(IV) iodo-complex.

Introduction

Platinum-195 is a moderately sensitive nucleus (^{195}Pt, $I = ½$, 33%, D_p† = 3.36 × 10^{-3}, D_c† = 19.1) and a considerable amount of data is available on Pt(II) and Pt(0) complexes [2, 3]. Data on platinum(IV) complexes is more limited, especially upon complexes of heavier donor atoms. During recent studies of platinum diselenoether complexes [4–6] we required ^{195}Pt NMR spectral data for a variety of other bidentate ligand analogues for comparison purposes, and the data recorded below was obtained. Since data on Pt(IV) complexes is largely restricted to monodentate ligand examples we report the results of our studies here.

Results

The chemical shifts δ(Pt) and coupling constants ^1J(Pt–L) of the Pt(IV) complexes are given in Table I, (along with representative data on diselenoether complexes [6]), and corresponding data on Pt(II) analogues in Table II. Generally the platinum(IV) complexes were less soluble in most solvents than the platinum(II) analogues, and in many cases only dimethylsulphoxide was suitable. Unfortunately a number of the Pt(IV) complexes decomposed in this solvent [7, 8], a problem more often encountered with ligands with vinylic or *o*-phenylene backbones and this restricted the range of complexes studied.

[Pt(L–L)X_2] and [Pt(L–L)X_4] (X = Cl, Br, I)

The chemical shifts of the Pt(L–L)X_2] (Table II) are similar to those of the monodentate ligand analogues *cis*-[PtL_2X_2] [2, 3] indicating that the donor atoms are the predominant influence on δ(Pt). The effect of the ligand backbone is relatively small (<200 ppm), and it is notable that although the ^{31}P [9] and ^{77}Se [4] chemical shifts show marked dependence upon chelate ring size (reflected by the ring parameter Δ*R*) [9], a similar effect is not apparent in the ^{195}Pt shifts. Both the chemical shifts δ(Pt) and ^1J(^{195}Pt–^{31}P) and ^1J(^{195}Pt–^{77}Se) show the usual dependence upon the *trans* ligand (Table II). The linewidths of the platinum resonances are small for complexes of P, Se or S donors, but those of N, Sb and to a lesser extent As ligands are broadened by those quadrupolar nuclei ($W_{1/2} \leqslant 400$ Hz for N or Sb donors).

The [Pt(L–L)X_4] (X = Cl, Br) have much higher frequency resonances than the Pt(II) precursors, and the 'oxidation shift' ΔPt [defined as δ[Pt(L–L)X_4] – δ[Pt(L–L)X_2]] is always greater for X = Cl than X = Br for fixed (L–L) (Table I) being typically *ca.* 2000 ppm (X = Cl) and *ca.* 1200 ppm (X = Br), with nitrogen donors producing rather larger shifts, than sulphur, phosphorus or arsenic. Selenium ligands differ in producing much smaller shifts typically *ca.* 1300 ppm (X = Cl) and *ca.* 650–900 ppm (X = Br). Our attempts to record ^{195}Pt NMR spectra for platinum(IV) distibines failed, as the complexes decomposed immediately

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*Part 20, see ref. 1.

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†Receptivities relative to ^{1}H and ^{13}C [2].

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TABLE I. ^{195}Pt and ^{31}P NMR Data on some Platinum(IV) Complexes

Complex	δ(Pt)[a] (ppm)	δ(P)[b] (ppm)	^1J(Pt–L)[c] (Hz)	ΔPt[d] (ppm)
$[Pt(Me_2NCH_2CH_2NMe_2)Cl_4]$	−113			2145
$[Pt(Me_2NCH_2CH_2NMe_2)Br_4]$	−1073			1447
[Pt(2,2′-bipyridyl)Cl_4]	−311			2004
[Pt(2,2′-bipyridyl)Br_4]	−1410			1134
$[Pt(Ph_2PCH_2CH_2PPh_2)Cl_4]$	−2701(t)	36.7	2183	1847
$[Pt(Ph_2PCH_2CH_2PPh_2)Br_4]$	−3820(t)	27.5	2092	1001
$[Pt(Me_2PCH_2CH_2PMe_2)_2Cl_2]Cl_2$	−4161(q)	35.1	1383	1151
$[Pt(Me_2PCH_2CH_2PMe_2)_2Br_2]Br_2$	−4932(q)	26.0	1382	331
$[Pt(Ph_2PCHCHPPh_2)Cl_4]$[f]	−2470(t)	43.8	2225	1997
$[Pt(Ph_2PCHCHPPh_2)Br_4]$[f]	−3926(t)	36.2	2062	972
$[Pt(PhP(CH_2CH_2PPh_2)_2)Cl_3]BF_4$[f]	−3546(d,t)	22.5, 83.1	1953, 1531	1313
$[Pt(PhP(CH_2CH_2PPh_2)_2)Br_3]Br$[f]	−4546(d,t)	11.5, 78.0	1904, 1544	462
‘$PtP(CH_2CH_2PPh_2)_3Cl_4$’	−3509(d,t)	see text		
[Pt(o-$C_6H_4(AsMe_2)_2)Cl_4$]	−2711			1845
[Pt(o-$C_6H_4(AsMe_2)_2)Br_4$]	−3872			1000
$[Pt(Ph_2AsCH_2CH_2AsPh_2)Cl_4]$	−2482			2068
$[Pt(Ph_2AsCH_2CH_2AsPh_2)Br_4]$	−3695			1217
$[Pt(Me_2As(CH_2)_3AsMe_2)Cl_4]$	−2952			1368
[Pt(o-$C_6H_4(AsMe_2)_2)_2Cl_2]Cl_2$	−4456			950
[Pt(o-$C_6H_4(AsMe_2)_2)_2Br_2]Br_2$	−5202			402
[Pt(o-$C_6H_4(AsMe_2)_2)_2I_2](NO_3)_2$[g]	−5406			191
$[Pt(As(CH_2CH_2CH_2AsMe_2)_3)Cl_4]$	−4348			397
$[Pt(MeSCH_2CH_2SMe)Cl_4]$	−1899, −1910			1865
$[Pt(MeSCH_2CH_2SMe)Br_4]$	−3053, −3065			1073
$[Pt(MeS(CH_2)_3SMe)Cl_4]$	−1630, −1649			1910
$[Pt(MeS(CH_2)_3SMe)Br_4]$	−2760, −2779			1137
$[Pt(PhSCH_2CH_2SPh)Cl_4]$	−1749, −1754			2057
$[Pt(PhSCH_2CH_2SPh)Br_4]$	−2945, −2949			1259
$[Pt(MeSeCH_2CH_2SeMe)Cl_4]$[e]	−2070, −2078		249, 222	1342
$[Pt(MeSeCH_2CH_2SeMe)Br_4]$[e]	−2902, −2908		110, 116	917
$[Pt(MeSe(CH_2)_3SeMe)Cl_4]$[e]	−1816, −1848		201, 189	1398
$[Pt(MeSe(CH_2)_3SeMe)Br_4]$[e]	−2970, −3013		128, 103	646
$[Pt(PhSeCH_2CH_2SePh)Cl_4]$[e]	−2217, −2211		174, 154	1249
$[Pt(PhSeCH_2CH_2SePh)Br_4]$[e]	−3004, −3012		85, 90	901

[a] ^{195}Pt chemical shift relative to external 1 mol dm^{-3} Na_2PtCl_6 in H_2O (δ = 0) d = doublet, t = triplet, q = quintet, q,d = quartet of doublets, d,t = doublet of triplets. [b] ^{31}P chemical shift relative to external 85% H_3PO_4 (δ = 0). [c] ^1J(Pt–P) or ^1J(Pt–Se). [d] Oxidation shift, *i.e.* δ(Pt^{IV} complex) – δ(Pt^{II} complex). [e] Data from ref. 6. The corresponding data for the Pt(II) selenoether complexes in ref. 4. The two δ(Pt) values reflect the presence of *meso* and *DL* invertomers in the dithio- and diselenoether complexes. [f] CH_2Cl_2 solution all others in dmso. [g] *In situ* in dilute ~10 mol dm^{-3} HNO_3.

TABLE II. ^{195}Pt and ^{31}P NMR Data on some Platinum(II) Compounds

Complex	δ(Pt) (ppm)[a,b]	δ(P) (ppm)[a]	^1J(Pt–P)[a] (Hz)
$[Pt(Me_2NCH_2CH_2NMe_2)Cl_2]$[c]	−2258		
$[Pt(Me_2NCH_2CH_2NMe_2)Br_2]$	−2520		
[Pt(2,2′-bipyridyl)Cl_2]	−2315		
[Pt(2,2′-bipyridyl)Br_2]	−2544		
$[Pt(Ph_2PCH_2CH_2PPh_2)Cl_2]$	−4554(t)	43.8	3600
$[Pt(Ph_2PCH_2CH_2PPh_2)Br_2]$	−4821(t)	47.0	3553

(continued on facing page)

TABLE II *(continued)*

Complex	δ(Pt) (ppm)[a,b]	δ(P) (ppm)[a]	^1J(Pt–P)[a] (Hz)
$[Pt(Ph_2PCH_2CH_2PPh_2)I_2]$[d]	–5371(t)	47.4	3400
$[Pt(Ph_2PCH_2CH_2PPh_2)_2]Cl_2$[d]	–5294(q)	47.8	2370
$[Pt(Ph_2PCHCHPPh_2)Cl_2]$	–4467(t)	50.1	3623
$[Pt(Ph_2PCHCHPPh_2)Br_2]$	–4898(t)	54.0	3576
$[Pt(Ph_2PCHCHPPh_2)I_2]$[d]	–5431(t)	55.4	3409
$[Pt(o\text{-}C_6H_4(PPh_2)_2)Cl_2]$	–4525(t)	43.9	3607
$[Pt(P(CH_2CH_2PPh_2)_3)Cl]Cl$	–4372(q,d)	28.2, 121.9	2585, 2516
$[Pt(Me_2PCH_2CH_2PMe_2)_2]Cl_2$	–5312	33.2	2227
$[Pt(Me_2PCH_2CH_2PMe_2)_2]Br_2$	–5263	30.2	2280
$[Pt(PhP(CH_2CH_2PPh_2)_2)Cl]BF_4$[d]	–4859(d,t)	42.0, 85.6	3020, 2460
$[Pt(PhP(CH_2CH_2PPh_2)_2)Br]Br$[d]	–5008(d,t)	42.9, 89.5	3021, 2440
$[Pt(o\text{-}C_6H_4(AsMe_2)_2)Cl_2]$	–4556		
$[Pt(o\text{-}C_6H_4(AsMe_2)_2)Br_2]$	–4872		
$[Pt(Ph_2AsCH_2CH_2AsPh_2)Cl_2]$	–4550		
$[Pt(Ph_2AsCH_2CH_2AsPh_2)Br_2]$	–4912		
$[Pt(Me_2As(CH_2)_3AsMe_2)Cl_2]$	–4320		
$[Pt(o\text{-}C_6H_4(AsMe_2)_2)_2]Cl_2$	–5406		
$[Pt(o\text{-}C_6H_4(AsMe_2)_2)_2]Br_2$	–5604		
$[Pt(o\text{-}C_6H_4(AsMe_2)_2)_2]I_2$	–5597		
$[Pt(MeAs(CH_2CH_2CH_2AsMe_2)_2)Cl]Cl$	–4712		
$[Pt(As(CH_2CH_2CH_2AsMe_2)_3)Cl]Cl$	–4745		
$[Pt(Me_2SbCH_2CH_2CH_2SbMe_2)Cl_2]$[d]	–4553		
$[Pt(Me_2SbCH_2CH_2CH_2SbMe_2)Br_2]$[d]	–4952		
$[Pt(Me_2SbCH_2CH_2CH_2SbMe_2)I_2]$[d]	–5800		
$[Pt(Ph_2SbCH_2CH_2CH_2SbPh_2)Cl_2]$[d]	–4556		
$[Pt(Ph_2SbCH_2CH_2CH_2SbPh_2)Br_2]$[d]	–4833		
$[Pt(MeSCH_2CH_2SMe)Cl_2]$	–3763, –3777		
$[Pt(MeSCH_2CH_2SMe)Br_2]$	–4125, –4139		
$[Pt(MeS(CH_2)_3SMe)Cl_2]$	–3538, –3570		
$[Pt(MeS(CH_2)_3SMe)Br_2]$	–3893, –3922		
$[Pt(PhSCH_2CH_2SPh)Cl_2]$	–3796, –3823		
$[Pt(PhSCH_2CH_2SPh)Br_2]$	–4192, –4219		

[a] See footnotes to Table I. [b] Corresponding diselenoether data in ref. 4. [c] Samples dissolved in dmso except (d) CH_2Cl_2.

in solution with halogenation of the distibine [8]. Similarly although materials of composition $[Pt(L{-}L)I_4]$ have been obtained with diphosphines, diarsines or dithioethers [7, 8], these were poorly soluble in common solvents except for dmso, in which they gave identical ^{195}Pt spectra to $[Pt(L{-}L)I_2]$. Careful examination of higher frequency regions of the spectrum showed no platinum resonances attributable to platinum(IV) species, and the absence of the latter is clear from the ^{31}P NMR spectra of the diphosphines which show only signals characteristic of $[Pt(L{-}L)I_2]$. Even with a large excess (*ca.* 10 fold) of added I_2 only the platinum(II) complexes are evident in the NMR spectra, and thus it is possible that the $[Pt(L{-}L)I_4]$ [8] are really platinum(II) polyiodides [*cf.* $Pd(Ph_2PCHCHPPh_2)I_2{\cdot}I_2$] [10] and $[Pd(o\text{-}C_6H_4(SPh)_2)I_3]$ [11], although only an X-ray study will resolve the question for certain.

$[Pt(L{-}L)_2X_2]^{2+}$

It is not possible to prepare 2:1 $[Pt(L{-}L)_2X_2]^{2+}$ complexes of Pt(IV) with $Me_2NCH_2CH_2NMe_2$, 2,2'-bipyridyl or dithioethers [7, 8]. Halogen oxidation of $Pt(L{-}L)_2X_2$ ($L{-}L = o\text{-}C_6H_4(AsMe_2)_2$, $Me_2PCH_2CH_2PMe_2$; X = Cl, Br) gave the expected [8] *trans*-$[Pt(L{-}L)_2X_2]X_2$, but chlorination of $Pt(Ph_2PCH_2CH_2PPh_2)_2Cl_2$ gave a complex mixture of products. A comparison of the δ(Pt) shifts in $Pt(L{-}L)_2X_2$ with $[Pt(L{-}L)_2X_2]^{2+}$ (Tables I, II) reveals much smaller oxidation shifts (*ca.* 1000 ppm, X = Cl; *ca.* 400 ppm, X = Br) than between $[Pt(L{-}L)X_2]/[Pt(L{-}L)X_4]$. Harris *et al.* [12] isolated $[Pt(o\text{-}C_6H_4(AsMe_2)_2)_2I_2](NO_3)_2$ by oxidation of the $[Pt(o\text{-}C_6H_4(AsMe_2)_2)_2I_2]$ with 10 mol dm^{-3} nitric acid; we find *in situ* oxidation of $[Pt(o\text{-}C_6H_4(AsMe_2)_2)_2I_2]$ (δ(Pt) = –5597 ppm) with HNO_3 gave a reddish solution with δ(Pt) = –5406 ppm. Although the oxidation shift is small (191 ppm) it is in line with the decreasing oxidation shifts in this series (Cl = 950, Br = 402 ppm), and would seem to support the Pt(IV) formulation. Attempts to oxidise $[Pt(Me_2PCH_2CH_2PMe_2)_2I_2]$ similarly *in situ* resulted in a brown suspension which failed to give a ^{195}Pt NMR spectrum.

Multidentate Ligand Complexes

The ^{195}Pt spectra of *mer*-$[Pt(PhP(CH_2CH_2PPh_2)_2)X_3]X$ show the expected doublet of triplets coupling pattern, and oxidation shifts which lie between those of P_2X_4 and P_4X_2 donor sets. The ^{31}P NMR spectrum of $Pt(P(CH_2CH_2PPh_2)_3)Cl_2$ shows two resonances each with platinum satellites due to coordinated $P<$ and $-PPh_2$, whilst the ^{195}Pt NMR spectrum consists of a 1:3:3:1 quartet, each line split into a further doublet showing the presence of a trigonal bipyramidal $[PtP_4Cl]^+Cl^-$ cation. Although cautious chlorine oxidation of this produces (*cis*) pseudooctahedral $[Pt(P(CH_2CH_2PPh_2)_3)Cl_2]Cl_2$, this is unstable in solution and decomposes with displacement of coordinated phosphorus by Cl^- [8]. The addition of an excess of chlorine to $[Pt(P(CH_2CH_2PPh_2)_3)Cl]Cl$ in CH_2Cl_2 solution produces a yellow solution stable for some hours which has the ^{195}Pt and ^{31}P NMR spectra shown in Fig. 1. These are readily interpretable as due to a *mer*-$[PtP_3Cl_3]^+$ cation (**I**), the free arm of the tetraphosphine having being oxidised to P=O.

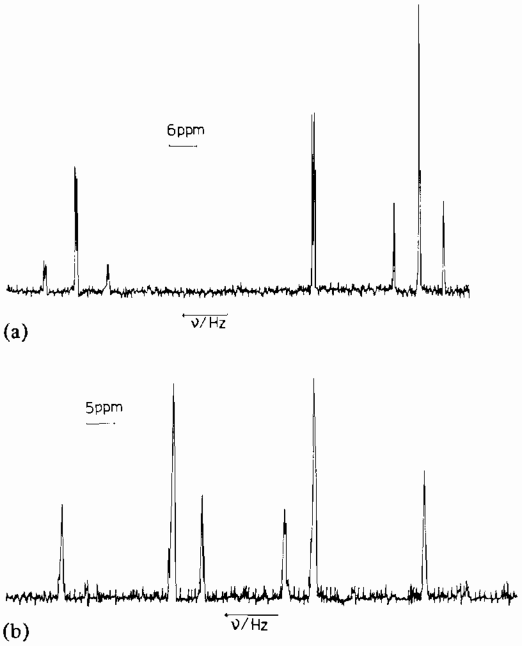
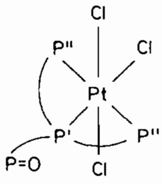


Fig. 1. (a) ^{31}P, and (b) ^{195}Pt NMR spectra of the product of the reaction $[Pt(P(CH_2CH_2PPh_2)_3)Cl]Cl + Cl_2$ in CH_2Cl_2.



I

The ^{31}P NMR resonances at 96.5, 24.9 and 47.0 ppm are assigned to $P'\,^1J(Pt-P) = 1910$, $P''\,^1J(Pt-P) = 1523$ Hz, and PO respectively. A small coupling between P′ and P of *ca.* 48 Hz is also observed. The δ(Pt) resonance of this solution is also consistent with a P_3Cl_3 donor set, rather than with P_4Cl_2 [−3509, *cf.* $[Pt(PhP(CH_2CH_2PPh_2)_2)Cl_3]^+$ −3546, $[Pt(Me_2PCH_2CH_2PMe_2)_2Cl_2]^{2+}$ −4161 ppm]. In the case of the complexes of the tripod tetrarsine $As(CH_2CH_2CH_2AsMe_2)_3$ the $[Pt(As(CH_2CH_2CH_2AsMe_2)_3)Cl]Cl$ is probably planar (As_3Cl) since it has δ(Pt) = −4745 ppm, similar to that of $[Pt(MeAs(CH_2CH_2CH_2AsMe_2)_2)Cl]Cl$ −4712 ppm and *mer*-$[Pt(AsMe_3)_3Cl]^+$ −4732 ppm [2]. The oxidation product $Pt(As(CH_2CH_2CH_2AsMe_2)_3)Cl_4$ has δ(Pt) = −4348 ppm, compared with $[Pt(AsMe_3)_3Cl_3]^+$ −3072 ppm [2] and $[Pt(o\text{-}C_6H_4(AsMe_2)_2)_2Cl_2]^{2+}$ −4456 ppm, which indicates an As_4Cl_2 donor set. It is likely that the differences between the tetraphosphine and tetraarsine result from the stronger donor and smaller steric properties of $-AsMe_2$ *versus* $-PPh_2$ substituents.

Discussion

The chemical shifts of metal nuclei are predominantly affected by the paramagnetic term σ_p [3], and for several metals a correlation of δ with the lowest energy electronic spectra absorptions has been established [2]. For platinum some qualitative success has been achieved by this approach [13, 14] but quantitative predictions of the chemical shifts have proved elusive.

One of the major problems is the difficulty of distinguishing satisfactorily the d–d transitions which lie to low energy of intense charge transfer bands, and are often partially obscured by the tails of these more intense bands [15]. The complexes studied in our work are of low symmetry which further complicates the interpretation.

Empirically we observe that a plot of δ[Pt(L–L)Cl$_4$] *versus* δ[Pt(L–L)Br$_4$] gives an approximate straight line, although the diselenoether ligands chemical shifts are in poorer agreement than the other donor types. Inclusion of P_3X_3, P_4X_2 and As_4X_2 donor sets results in a curved plot (Fig. 2). The theoretical justification of such a plot is weak, but empirically it is useful to confirm the presence of the same donor sets in chloride and bromide complexes. It is not however a sufficiently precise correlation to predict accurately chemical shifts.

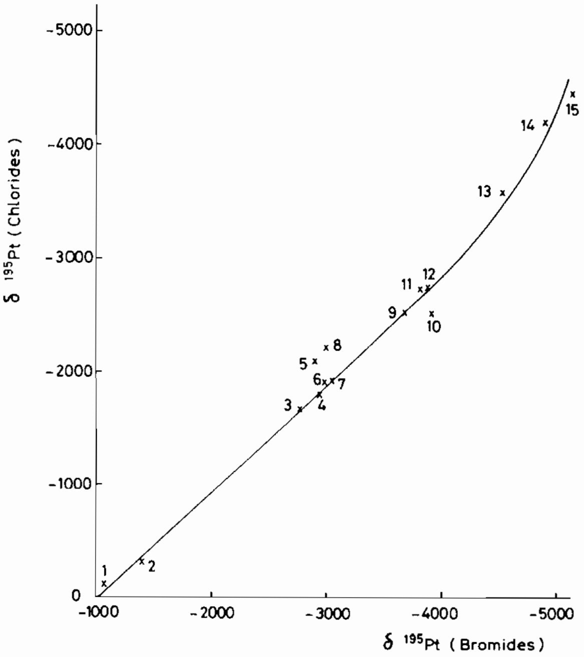


Fig. 2. 195-Pt chemical shifts in Pt(IV) complexes. Key: **1**, $[Pt(Me_2NCH_2CH_2NMe_2)X_4]$; **2**, [Pt(2,2′-bipyridyl)X_4]; **3**, $[Pt(MeS(CH_2)_3SMe)X_4]$; **4**, $[Pt(PhSCH_2CH_2SPh)X_4]$; **5**, $[Pt(MeSeCH_2CH_2SeMe)X_4]$; **6**, $[Pt(MeSe(CH_2)_3SeMe)X_4]$; **7**, $[Pt(MeSCH_2CH_2SMe)X_4]$; **8**, $[Pt(PhSeCH_2CH_2SePh)X_4]$; **9**, $[Pt(Ph_2AsCH_2CH_2AsPh_2)X_4]$; **10**, $[Pt(Ph_2PCHCHPPh_2)X_4]$; **11**, $[Pt(Ph_2PCH_2CH_2PPh_2)X_4]$; **12**, [Pt(*o*-$C_6H_4(AsMe_2)_2)X_4$]; **13**, $[Pt(PhP(CH_2CH_2PPh_2)_2)X_3]^+$; **14**, $[Pt(Me_2PCH_2CH_2PMe_2)_2X_2]^{2+}$; **15**, [Pt(*o*-$C_6H_4(AsMe_2)_2)_2X_2]^{2+}$.

The empirical correlation of δ(Pt) with donor set (and hence with coordination numbers) is particularly useful in complexes of multidentate ligands as the examples above demonstrate.

Experimental

195-Pt NMR spectra were recorded on a Bruker AM360 spectrometer. Samples were dissolved in the solvents indicated and spectra recorded immediately, using 10 mm external diameter tubes, containing a 5 mm co-axial tube filled with D_2O to provide the lock. A 1 M solution of Na_2PtCl_6 in H_2O was used as external reference (δ = 0) which has a frequency of 77.418 MHz.

Many of the platinum(IV) samples were those prepared previously [7, 8] or where necessary were made by the methods described therein, or by literature methods.

The $[Pt(Ph_2PCHCHPPh_2)X_2]$ (X = Cl, Br, I) were made by reaction of K_2PtCl_4 [with KX (X = Br, I)] and *cis*-$Ph_2PCHCHPPh_2$ in water–ethanol, followed by dissolution of the product in boiling *N,N*-dimethylformamide (dmf). After solution was complete the dmf solution was concentrated to small volume, cooled, and excess diethyl ether added to precipitate the products [8]. As prepared the products are the expected *cis* chelates with ^{31}P NMR shifts (Table II) indicative of a five-membered ring [δ(P) ~50–56 ppm). If the dmf dissolution stage is omitted the products have a $[Pt(Ph_2PCHCHPPh_2)X_2]_n$ composition, but are much less soluble in organic solvents. These materials dissolve poorly in dmso to give solutions with ^{31}P NMR shifts of 7.3 [^1J(Pt–P) = 3614 Hz] X = Br, and 8.7 [3536] X = Cl, and appear to be ligand bridged dimers [16, 17].

[Pt(o-$C_6H_4(AsMe_2)_2)_2Br_2]Br_2$

[Pt(*o*-$C_6H_4(AsMe_2)_2)_2]Br_2$ prepared by the literature method was suspended in CCl_4 and excess of a solution of bromine in CCl_4 was added. After stirring vigorously for 2 h, the product was filtered off, washed with dichloromethane/ethanol (1:1 *v/v*) and dried *in vacuo*. *Anal.* Found: C, 21.9; H, 3.0. Calc. for $C_{20}H_{32}As_4Br_4Pt$: C, 22.1; H, 2.9%. E_{max} (cm^{-1}) [ϵ_{mol} (dm^3 cm^{-1} mol^{-1})] 26 300 [4700].

$[Pt(Me_2PCH_2CH_2PMe_2)_2Br_2]Br_2$

The complex was prepared by an analogous method to that used in the preparation of [Pt(*o*-$C_6H_4(AsMe_2)_2)_2Br_2]Br_2$. *Anal.* Found: C, 17.6; H, 4.0. Calc. for $C_{12}H_{32}Br_4P_4Pt$: C, 17.7; H, 3.9%. E_{max} (ϵ_{mol}) = 27 800(2600).

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