Magnetic Double-resonance Studies of Platinum-195 Chemical Shifts in Organoplatinum Compounds

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Platinum-195 chemical shifts and coupling constants obtained by ^{1}H-$\{^{31}$P$\}$ and ^{1}H-$\{^{195}$Pt$\}$ double resonance are reported for 78 platinum compounds, of which most have direct platinum–carbon bonds. Empirical trends are noted and where possible assessed in terms of current theories. Electronic excitation energy, interbond angle, and substituent bulk and/or polarizability all appear to make significant contributions to the ^{195}Pt nuclear shielding.

IN order to assess and develop theories which attempt to describe the magnetic shielding of the heavier nuclei, and to facilitate the use of measured shieldings in the identification and structural elucidation of new species, it is important to have data on closely related series of compounds. In the case of ^{195}Pt shielding, major studies have been concerned with platinum hydrides,[1,2] Group 5 and Group 6 donor compounds of platinum halides,[3,4] and an extensive series of *trans*-bis(triethylphosphine) compounds of platinum.[5] Organoplatinum compounds, however, have not been systematically investigated, and in this paper we therefore present ^{195}Pt chemical shifts determined by ^{1}H-$\{^{195}$Pt$\}$ multiple resonance for compounds containing platinum–carbon bonds. Other ^{195}Pt and ^{31}P data, not directly accessible from ^{1}H spectra, are also reported.

EXPERIMENTAL

Compounds were prepared by methods previously reported,[6-10] and examined at 24 °C as $\leqslant 20\%$ w/v solutions in benzene, dichloromethane, or deuteriochloroform. N.m.r. measurements [except for compounds (57) and (73)—(75)] were carried out as described previously,[4,11,12] using a JEOL C60-H spectrometer modified for double resonance with an additional coil in the probe.[13] Frequencies of 12.8 and 24.28 MHz for ^{1}H-$\{^{195}$Pt$\}$ and ^{1}H-$\{^{31}$P$\}$ experiments were supplied by a Schlumberger FS-30 frequency synthesizer, which was also used to drive the spectrometer main oscillator at 60 MHz. Data for compounds (57) and (73)—(75) were obtained by double resonance on a Varian XL 100 spectrometer; more accurate ^{195}Pt chemical-shift values than those previously reported [14] are given for compounds (72)—(75).

RESULTS

In most of the compounds studied in this work satellites due to ^{195}Pt (natural abundance 33.7%) were clearly resolved in the proton spectra [$|^{2}J(^{195}\text{Pt–C–}^{1}\text{H})|$ 39—84; $|^{3}J(^{195}\text{Pt–X–C–}^{1}\text{H})|$ 10—74 Hz (X = C, N, S, P, or As)] and the ^{1}H-$\{^{195}$Pt$\}$ experiments used to give the platinum resonance frequencies were straightforward. In compounds containing phosphorus ligands the spectra were often complex and care was taken to ensure that the frequency obtained was that of the centre of the platinum spectrum and not for example $\nu(^{195}\text{Pt}) \pm \frac{n}{2}\,^{1}J(^{195}\text{Pt–}^{31}\text{P})$. In these cases the ^{1}H-$\{^{195}$Pt$\}$ experiments also gave a value for $^{1}J(^{195}\text{Pt–}^{31}\text{P})$. However, because of the relative sizes of the various ^{1}H-^{195}Pt and ^{1}H-^{31}P couplings, a more accurate estimate of this was generally obtained by ^{1}H-$\{^{31}$P$\}$ experiments which additionally yielded values for the ^{31}P chemical shifts. These chemical shifts and coupling constants are given in the Table. In conformity with previous reports from these laboratories,[4,11] platinum chemical shifts are given relative to *cis*-[PtCl$_2$(SMe$_2$)$_2$] in deuteriochloroform, for which Ξ is taken as 21 420 980 Hz.[‡] In accordance

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[‡] Ξ Is the ^{195}Pt resonance frequency corrected to the field strength at which the protons in tetramethylsilane resonate at *exactly* 100 MHz.

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with practice now becoming standard, positive shieldings are given a negative sign. Since no standard reference compound has yet been agreed upon for ^{195}Pt chemical shifts, Ξ values for each compound are also given. No large variation of platinum chemical shifts with solvent was observed among the solvents used in this work, but it is not expected that this is the general case. Platinum-195 shieldings exhibit [4] variations with temperature of from 0.1 to 1.0 p.p.m. per degree which may lead to differences outside the areas quoted in the Table; all our results were obtained at 24 °C.

The ^{1}H-{^{31}P} and ^{1}H-{^{195}Pt} experiments on the ^{195}Pt

Platinum-195 and ^{31}P n.m.r. data for organoplatinum compounds

	Compound	Ξ (Pt) [a]	δ(Pt) [b]	δ(P) [c]	^1J(Pt–P) [a]	^2J(PP) [a]
1	*cis*-$[\mathrm{PtCl_2(SMe_2)_2}]$	21 420 980 ± 10	0			
2	*cis*-$[\mathrm{PtMe_2(PMe_2Ph)_2}]$	21 398 645 ± 70	−1 043	−12.5 ± 0.2	1 820 ± 10	*d*, *e*
3	*cis*-$[\mathrm{PtMe_2(PMePh_2)_2}]$	21 397 460 ± 150	−1 098	5.3 ± 0.2	1 852 ± 10	*d*, *e*
4	*cis*-$[\mathrm{Pt(AsEt_3)_2Ph_2}]$	21 398 835 ± 70	−1 034			
5	*trans*-$[\mathrm{Pt(AsEt_3)_2Ph_2}]$	21 401 180 ± 70	−924			
6	*trans*-$[\mathrm{Pt(Me)I(PMe_2Ph)_2}]$	21 390 735 ± 70	−1 412	−9.7 ± 0.1	2 810 ± 10	464 ± 5
7	*trans*-$[\mathrm{Pt(Br)Me(PMe_2Ph)_2}]$	21 396 990 ± 70	−1 120	−5.5 ± 0.2	2 587 ± 10	457 ± 10
8	*trans*-$[\mathrm{Pt(Me)Cl(PMe_2Ph)_2}]$	21 399 710 ± 70	−933	−2.95 ± 0.1	2 889 ± 4	473 ± 4
9	*trans*-$[\mathrm{Pt(Me)I(PMePh_2)_2}]$	21 390 685 ± 150	−1 414	7.9 ± 0.2	2 942 ± 15	452 ± 15
10	*trans*-$[\mathrm{PtMe(PMe_2Ph)_2(SePh)}]$	21 393 520 ± 70	−1 282	−2.9 ± 0.2	2 813 ± 10	481 ± 5
11	*cis*-$[\mathrm{Pt(Me)Cl(PMe_2Ph)_2}]$	21 400 185 ± 150	−971	−15.0 ± 0.8 [f]	4 250 ± 20 [f]	
				−6.3 ± 0.8 [g]	1 730 ± 20 [g]	−17 ± 5
12	*trans*-$[\mathrm{Pt(CF_3)I(PMe_2Ph)_2}]$	21 397 885 ± 70	−1 078	−10.2 ± 0.4	2 670 ± 15	435 ± 20
13	*trans*-$[\mathrm{Pt(Me)I(PEt_3)_2}]$	21 392 995 ± 70	−1 306	9.4 ± 0.4	2 754 ± 20	425 ± 20
14	*trans*-$[\mathrm{Pt(Me)Cl(PEt_3)_2}]$	21 400 465 ± 70	−958	14.5 ± 0.2	2 816 ± 15	*e*
15	*trans*-$[\mathrm{Pt(AsMe_3)_2IMe}]$	21 392 970 ± 70	−1 308			
16	*trans*-$[\mathrm{Pt(AsMe_3)_2(Br)Me}]$	21 398 170 ± 70	−1 065			
17	*trans*-$[\mathrm{Pt(AsMe_3)_2(Me)Cl}]$	21 401 215 ± 70	−923			
18	*trans*-$[\mathrm{Pt(AsMe_3)_2(Br)Ph}]$	21 402 695 ± 70	−854			
19	*trans*-$[\mathrm{Pt(AsMe_2Ph)_2(Me)I}]$	21 391 460 ± 150	−1 378			
20	*trans*-$[\mathrm{Pt(AsMe_2Ph)_2(Br)Me}]$	21 396 775 ± 150	−1 130			
21	*trans*-$[\mathrm{Pt(AsMe_2Ph)_2(Me)Cl}]$	21 399 970 ± 60	−981			
22	*cis*-$[\mathrm{PtI_2(PMePh_2)_2}]$ [h]	21 385 090 ± 150	−1 675	−5.1 ± 0.4	3 394 ± 30	*d*, *e*
23	*cis*-$[\mathrm{PtI_2(PMe_2Ph)_2}]$ [h]	21 386 800 ± 150	−1 596	−18.2 ± 0.2	3 364 ± 10	*d*, *i*
24	*trans*-$[\mathrm{PtI_2(PMePh_2)_2}]$ [h]	21 375 515 ± 150	−2 122	−8.0 ± 0.4	2 400 ± 100	*e*
25	*trans*-$[\mathrm{PtI_2(PMe_2Ph)_2}]$ [h]	21 377 155 ± 30	−2 046	−24.0 ± 0.2	2 312 ± 10	488 ± 5
26	*cis*-$[\mathrm{PtBr_2(PMe_2Ph)_2}]$	21 397 550 ± 80	−1 094	−16.1 ± 0.8	3 515 ± 20	*d*, *e*
27	*cis*-$[\mathrm{PtCl_2(PMe_2Ph)_2}]$	21 402 710 ± 15	−853	−16.2 ± 0.2	3 548 ± 10	*d*, *i*
28	*cis*-$[\mathrm{PtCl_2(PMePh_2)_2}]$	21 401 995 ± 45	−886	−2.2 ± 0.2	3 622 ± 15	*d*, *e*
29	*cis*-$[\mathrm{Pt(AsMe_2Ph)_2Cl_2}]$	21 404 700 ± 70	−757			
30	*trans*-$[\mathrm{Pt(PMe_2Ph)_2(SPh)_2}]$	21 396 015 ± 50	−1 165	−7.5 ± 0.2	2 570 ± 10	510 ± 5
31	*trans*-$[\mathrm{Pt(PMe_2Ph)_2(SePh)_2}]$	21 389 710 ± 70	−1 460	−12.5 ± 0.2	2 565 ± 5	497 ± 5
32	*trans*-$[\mathrm{Pt(PBu^n{}_3)_2(SPh)_2}]$	21 396 525 ± 30	−1 142	*e*	2 480 ± 40	*e*
33	$[\mathrm{Pt(cod)Cl_2}]$ [j]	21 425 050 ± 200	190			
34	$[\mathrm{Pt(cod)Me_2}]$ [j]	21 420 060 ± 50	− 43			
35	$[\mathrm{Pt(cod)Ph_2}]$ [j]	21 419 415 ± 70	−73			
36	$[\mathrm{Pt(cod)(C_6H_4Cl\text{-}}p\mathrm{)_2}]$ [j]	21 419 375 ± 70	−75			
37	$[\mathrm{Pt(cod)(C_6H_4Ph\text{-}}p\mathrm{)_2}]$ [j]	21 419 415 ± 150	−73			
38	$[\mathrm{Pt(cod)(C_6H_4Me\text{-}}p\mathrm{)_2}]$ [j]	21 419 540 ± 150	−67			
39	$[\mathrm{Pt(cod)(C_6H_4F\text{-}}p\mathrm{)_2}]$	21 419 625 ± 150	−63			
40	$[\mathrm{Pt(cod)(C_6H_4F\text{-}}m\mathrm{)_2}]$	21 419 465 ± 150	−71			
41	$[\mathrm{Pt(cod)(C_6H_4Me\text{-}}o\mathrm{)_2}]$	21 421 290 ± 70	15			
42	$[\{\mathrm{PtCl(}\mu\mathrm{\text{-}Cl)(PMe_2Ph)}\}_2]$	21 424 630 ± 30	170	−19.6 ± 0.4	3 900 ± 20	
43	$[\{\mathrm{PtCl(PMe_2Ph)(}\mu\mathrm{\text{-}SEt)}\}_2]$	21 415 485 ± 70	−257	*e*	3 220 ± 50	
44	$[\{\mathrm{PtMe(PMe_2Ph)(}\mu\mathrm{\text{-}SMe)}\}_2]$	21 407 730 ± 70	−619	−13.2 ± 0.4	3 750 ± 15	
45	$[\{\mathrm{PtCl(PMe_2Ph)(}\mu\mathrm{\text{-}SPh)}\}_2]$	21 410 965 ± 70	−467	−12.6 ± 0.2	3 347 ± 10	
46	$[\{\mathrm{PtCl(PMe_2Ph)(}\mu\mathrm{\text{-}SMe)}\}_2]$	21 415 565 ± 70	−253	−14.8 ± 0.2	3 260 ± 10	
47	$[\{\mathrm{PtMe_3(}\mu_3\mathrm{\text{-}I)}\}_4]$	21 437 742 ± 15	782			
48	*fac*-$[\mathrm{PtMe_3I(tmen)}]$ [k]	21 445 360 ± 100	1 138			
49	*fac*-$[\mathrm{PtMe_3I(py)_2}]$ [l]	21 443 170 ± 15	1 036			
50	*fac*-$[\mathrm{Pt(AsMe_2Ph)_2(Br)Me_3}]$	21 415 315 ± 50	−264			
51	*fac*-$[\mathrm{PtMe_3I(PMe_2Ph)_2}]$	21 405 175 ± 70	−738	−46.1 ± 0.2	1 182 ± 5	*d*, *e*
52	*fac*-$[\mathrm{PtBrMe_3(PMe_2Ph)_2}]$	21 411 590 ± 70	−438	−40.5 ± 0.1	1 182 ± 5	*d*, *e*
53	*fac*-$[\mathrm{PtMe_3Cl(PMe_2Ph)_2}]$	21 414 970 ± 70	−280	−37.2 ± 0.4	1 180 ± 10	*d*, *e*
54	*fac*-$[\mathrm{PtMe_3I(PMePh_2)_2}]$	21 406 235 ± 90	−688	−36.3 ± 0.2	1 080 ± 15	*d*, *i*
55	*fac*-$[\mathrm{PtMe_3I(PMe_3)_2}]$	21 403 790 ± 80	−802	−54.4 ± 0.2	1 230 ± 20	*d*, *e*
56	*fac*-$[\mathrm{PtMe_3I(dppe)}]$ [m]	21 400 290 ± 150	−966	2.3 ± 0.2	1 100 ± 50	*e*
57	$[\mathrm{PtBr_2{}^{\mathit{ce}}Me_2{}^{\mathit{ab}}(py)_2{}^{\mathit{df}}}]$	21 448 827 ± 20	1 300			
58	$[\mathrm{PtMe_2{}^{\mathit{ab}}I_2{}^{\mathit{ce}}(py)_2{}^{\mathit{df}}}]$	21 425 350 ± 50	204			
59	$[\mathrm{PtMe_2{}^{\mathit{ab}}I_2{}^{\mathit{df}}(PMe_2Ph)_2{}^{\mathit{ce}}}]$	21 403 070 ± 70	−836	−30.5 ± 0.2	1 956 ± 10	542 ± 10
60	$[\mathrm{PtMe_2{}^{\mathit{ab}}I_2{}^{\mathit{df}}(PEt_3)_2{}^{\mathit{ce}}}]$	21 405 190 ± 70	−737	−23.4 ± 0.4	1 880 ± 30	515 ± 20
61	$[\mathrm{PtBr_2{}^{\mathit{df}}Me_2{}^{\mathit{ab}}(PMe_2Ph)_2{}^{\mathit{ce}}}]$	21 415 300 ± 70	−265	−20.0 ± 0.2	1 970 ± 10	540 ± 5
62	$[\mathrm{PtMe_2{}^{\mathit{ab}}Cl_2{}^{\mathit{df}}(PMe_2Ph)_2{}^{\mathit{ce}}}]$ [h]	21 421 760 ± 150	36	−13.8 ± 0.4	2 012 ± 20	551 ± 10
63	$[\mathrm{PtMe_2{}^{\mathit{ab}}Cl_2{}^{\mathit{ce}}(PMe_2Ph)_2{}^{\mathit{df}}}]$ [h]	21 430 460 ± 150	442	−39.5 ± 0.4	1 190 ± 20	*d*, *e*
64	$[\mathrm{PtBr_3{}^{\mathit{bdf}}Me^{\mathit{a}}(PMe_2Ph)_2{}^{\mathit{ce}}}]$	21 417 090 ± 70	−181	−23.8 ± 0.1	1 710 ± 10	580 ± 5
65	$[\mathrm{PtMe_2{}^{\mathit{ab}}(CF_3)^{\mathit{c}}I^{\mathit{f}}(PMe_2Ph)_2{}^{\mathit{de}}}]$	21 411 415 ± 150	−446	−45.9 ± 0.8 [n,o]	*ca.* 1 200 [n,p]	*d*, *e*
66	$[\mathrm{PtMe_2{}^{\mathit{ab}}(CF_3)^{\mathit{c}}I^{\mathit{e}}(PMe_2Ph)_2{}^{\mathit{df}}}]$	21 413 100 ± 300	−368	−44.6 ± 0.4	1 086 ± 20	*d*, *e*
67	$[\mathrm{PtBr^{\mathit{f}}Me_2{}^{\mathit{ab}}(C_3H_5)^{\mathit{c}}(PMe_2Ph)_2{}^{\mathit{de}}}]$	21 412 890 ± 70	−378	−40.3 ± 0.8 [q]	1 160 ± 100 [n]	15 ± 5[r]
				−36.8 ± 0.8 [q]		

TABLE (*Continued*)

	Compound	Ξ (Pt) [a]	δ(Pt) [b]	δ(P) [c]	^1J(Pt–P) [a]	^2J(PP) [a]
68	$[PtMe_2{}^{ab}(C_3H_5)^{c}Cl^{f}(PMe_2Ph)_2{}^{de}]$	21 415 790 ± 70	−242	−38.2 ± 0.4 [q] −34.9 ± 0.4 [q]	1 230 ± 10 [n]	<5 [i]
69	$[PtBr^{f}Me_2{}^{ab}(CH_2Ph)^{c}(PMe_2Ph)_2{}^{de}]$	21 413 640 ± 70	−343	−37.2 ± 0.8 [n]	1 300 ± 200 [n]	*d*, *e*
70	$[PtMe_2{}^{ab}(COMe)^{c}Cl^{f}(PMe_2Ph)_2{}^{de}]$	21 399 500 ± 150	−1 003	*e*	*e*	*e*
71	$[PtBr^{f}Me_2{}^{ab}(COMe)^{c}(PMe_2Ph)_2{}^{de}]$	21 396 875 ± 75	−1 125	*e*	*e*	*e*
72	$[Pt\{(CH_2)_3\}^{ab}Cl_2{}^{ce}(4Me\text{-}py)_2{}^{df}]$	21 467 303 ± 15	2 162			
73	$[PtBr_2{}^{ce}\{(CH_2)_3\}^{ab}(4Me\text{-}py)_2{}^{df}]$	21 457 096 ± 20	1 686			
74	$[Pt\{(CH_2)_3\}^{ab}Cl_2{}^{ce}(py)_2{}^{df}]$	21 467 935 ± 20	2 192			
75	$[PtBr_2{}^{ce}\{(CH_2)_3\}^{ab}(py)_2{}^{df}]$	21 456 903 ± 20	1 677			
76	*cis*-$[Pt\{(CH_2)_4\}(PMe_2Ph)_2]$	21 396 870 ± 150	−1 126	−11.6 ± 0.2	1 763 ± 5	*e*
77	$[Pt(CF_3C{\equiv}CCF_3)(PPh_3)_2]$	21 397 550 ± 15	−1 094	19.7 ± 0.4	3 590 ± 10	
78	$[Pt(CF_2{=}CF_2)(PPh_3)_2]$	21 394 430 ± 300	−1 240	25.7 ± 0.2	2 545 ± 30	
79	$[Pt(CH_2{=}CH_2)(PPh_3)_2]$	21 388 550 ± 70	−1 514	*e*	*e*	*e*

[a] In Hz. [b] In p.p.m. relative to *cis*-$[PtCl_2(SMe_2)_2]$ (1); δ 0. [c] In p.p.m. relative to 85% H_2PO_4 (Ξ 40 480 790 Hz), δ 0. [d] ^2J-(^{31}P–^{31}P) small. [e] Not measured. [f] *cis* to methyl. [g] *trans* to methyl. [h] Pairs of isomers were present in the same solution. [i] Probably negative. [j] cod = Cyclo-octa-1,5-diene. [k] tmen ≡ *NNNN*-Tetramethylethylenediamine. [l] py = Pyridine. [m] dppe = 1,2-Bis(diphenylphosphino)ethane. [n] Mean value. [o] ^{31}P chemical shifts were nearly identical. [p] Values differed by several hundred Hz. [q] Assignments uncertain. [r] Sign not determined.

satellites in the proton spectra [15–18] also gave information on the signs of platinum–proton and phosphorus–proton couplings respectively relative to $^1J(^{195}Pt–^{31}P)$ which can be taken to be positive. In these experiments $^2J(^{195}Pt–C–^1H)$ and $^2J(^{31}P–C–^1H)$ were always negative, whereas $^3J(^{31}P–Pt–C–^1H)$ in methylplatinum phosphine compounds was positive when the coupling path was *cis*, but negative when the path was *trans*. The latter results support the suggestion [15,16] that these two signs are specific for these two stereochemistries. It was generally found that the magnitudes of these two couplings were comparable; for example in *cis*-$[PtMeCl(PMe_2Ph)_2]$ [compound (11)] $^3J(^{31}P–^1H)$(*cis*) was 4.5 Hz and $^3J(^{31}P–^1H)$(*trans*) was −7.7 Hz. However, replacement of chloride in this compound by a group with a stronger *trans* influence can reverse the order of these magnitudes and in *cis*-$[PtMe_2(PMe_2Ph)_2]$ [compound (2)] [$^3J(^{31}P–^1H)$(*cis*) + $^3J(^{31}P–^1H)$(*trans*)] = 1.8 Hz. The magnitudes of these and of the other proton couplings mentioned above have largely been reported and discussed in the literature [15–17,19–24] and are therefore not included in the Table.

In compounds with two mutually *trans* methylphosphine ligands the central P–Me proton resonance was a 'deceptively simple' triplet,[25] and ^1H-{^{31}P} experiments on the outer components of this [26] gave the magnitude of $^2J(^{31}P–^{31}P)$ and showed that its sign was positive relative to negative $^2J(^{31}P–^1H)$. These results are also incorporated in the Table, and in appropriate cases [*e.g.* compounds (6)—(8) and (59)] they were confirmed by ^1H-{^{31}P} experiments on the Pt–Me proton resonances.[18] In principle, these methods can be extended [27] to the determination of $^2J(^{31}P–^{31}P)$ in symmetrical compounds with mutually *cis* phosphine ligands, in which it is close to zero, but in the compounds studied here small longer-range couplings $^nJ(^{31}P–^1H)$ due to protons in the P–Ph groups, *etc.*, generally had the effect of broadening the ^{31}P spectrum to such an extent that no significant asymmetry was detectable in the ^1H–{^{31}P} experiments under our conditions. An exception to this was *cis*-$[PtCl_2(PMe_2Ph)_2]$, (27), in which the sense of the asymmetry showed that $^2J(^{31}P–^{31}P)$ was negative relative to $(^2J + {}^4J)(^{31}P–^1H)$ taken as negative, although we were unable to make a reliable estimate of the magnitude.

It is of interest to note that, for a number of the platinum(IV) species [*e.g.* compounds (62), (63), and (67)] the proton spectrum on initial dissolution was complex and only after several minutes was it consistent with the structures given in the Table, indicating that the isomers occurring in the solid state differed from those occurring in the liquid phase. The process is reversible, and these and associated phenomena are currently under more detailed investigation.

DISCUSSION

It is usually convenient to discuss the magnetic shielding of the heavier nuclei principally in terms of local 'paramagnetic' and 'diamagnetic' contributions σ^p and σ^d.[28–30] The magnitude of the diamagnetic contribution, σ^d, depends on the density of the electrons circulating about the nucleus and is susceptible to factors which alter this density such as oxidation state, the nature of the co-ordination sphere, substituent inductive effects, *etc.* For electronic changes occurring within the valence shell, this contribution can be shown to lead to variations of at most a few tens of p.p.m.,[31] and can therefore be neglected in the interpretation of the ^{195}Pt chemical shifts reported here, which span ranges of 2 100 to −2 100 p.p.m. and 1 100 to −1 500 p.p.m. for the four-co-ordinate platinum(II) and six-co-ordinate platinum(IV) compounds respectively.

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The observed variations can therefore be ascribed to changes in the paramagnetic term, σ^p, which arises from the hindrance of the diamagnetic electronic circulation about the platinum nucleus due to the presence of covalent bonds and polar centres. This term depends upon (*a*) the asymmetry of the electronic distribution within the valence $5d$ and $6p$ orbitals of the platinum atom, (*b*) the mean inverse cube of the distance between these electrons and the platinum nucleus, and (*c*) the inverse of the energy separations between the ground and excited states for these electrons. All three factors will generally change with a given change in structure and their complex interaction hinders the assessment of their relative importance.

Correlations have been established between metal nuclear shielding and electronic excitation energies when the differences among the latter are large, *e.g.* for the shielding of ^{59}Co in series of compounds of cobalt,[32,33] but interpretations of ^{195}Pt chemical-shift variations on this basis have met with limited success.[3,4] The ^{195}Pt nucleus in *cis*-$[PtCl_2(PEt_3)_2]$ resonates at 560 p.p.m. to high field of the *trans* isomer, and the difference has been tentatively ascribed to the difference in σ^p due to the change in electronic excitation energy;[4] however, this chemical-shift difference is considerably reduced in analogous bromide compounds of Pt^{II}, and in corresponding iodides [compounds (22)—(25)] it is the *trans* isomer that resonates at 450 p.p.m. to high field. This may be taken to indicate that changes in the excitation energies of orbitals centred on the metal atom do not necessarily dominate changes in the ^{195}Pt magnetic shielding, even for closely related compounds, so that the differences in chemical shift noted for pairs of isomers [compounds (4), (5); (8), (11); (22)—(25); and (62), (63)] also depend on the differences in the asymmetry of electronic distribution about the central nucleus.

Electronic withdrawal by a substituent on platinum also modifies the electronic imbalance among its valence orbitals, and will result in a change in the paramagnetic contribution to the shielding. The chemical shifts for the *meta*- and *para*-substituted arylplatinum cyclooctadiene compounds, (35)—(40), however, are all similar and show no obvious correlation with substituent effect, indicating that the electronic changes at the platinum atom which affect its shielding are minimal. The *o*-tolyl compound, (41), on the other hand has a considerable shift to low field which can be ascribed to the proximity of the *o*-methyl group to the platinum atom, and may be due to induced dipole–induced dipole interactions. It is however significant in this context that the *o*-tolyl derivatives of Ni^{II}, Pd^{II}, and Pt^{II} are generally more stable than their *meta* and *para* isomers.[34,35] This has been ascribed to the steric effect of the *o*-methyl group which may prevent reagents gaining access to the metal centre or which may hold the aryl group perpendicular to the square plane and hence maximize π bonding between the metal and the aryl group. The shielding change may therefore also reflect the ability of the methyl hydrogens to impinge on the space formally occupied by the platinum $5d_{z^2}$ orbitals, although it cannot be excluded that the changes are due to steric crowding which results in interbond angle distortion at the platinum atom.

The last effect will alter the electronic asymmetry about the nucleus and produce concomitant changes in the shielding; data for the platinacycloalkane derivatives show that the chemical-shift variations arising from this effect can be large: compared to their acyclic analogues [compounds (2), (3), and (57)], incorporation of platinum into three-membered [(79)], four-membered [(72)—(75)], and five-membered [(76)] carbocyclic rings changes the chemical shift by −400, 400, and −100 p.p.m. respectively. It is reasonable to ascribe these differences to the deviation of the interbond angles at platinum from the idealized non-constrained formally right-angled square-planar or octahedral geometries, although it must be emphasized that other shielding effects due to the proximity of a small ring are difficult to assess. Similar effects have been observed for other heavier nuclei, for example ^{207}Pb, for which incorporation into five- and six-membered rings produces changes of 200 and −100 p.p.m. respectively:[36] in this case the deviations are from tetrahedral sp^3 geometry. It is important to recognize that a large change in chemical shift arising from abnormal interbond angles is not necessarily accompanied by a large degree of thermodynamic ring strain. This is because the shielding may be particularly sensitive to those aspects of electronic distribution which are affected by changes in molecular geometry about the nucleus in question. Nevertheless it is significant that the platinacyclopropane, (79), and the platinacyclobutanes, (72)—(75), show considerably enchanced chemical reactivities,[14,37-39] whereas the compound (76) with a five-membered ring exhibits similar behaviour to that of the dimethyl analogue [compound (2)][40] and is considerably more inert to thermolysis than is *cis*-$[PtEt_2(PMe_2Ph)_2]$.

Interbond angles also affect the n.m.r. parameters of the chelate compound (56), in which incorporation into the five-membered 1,3-diphospha-2-platinacyclopentane ring produces changes in both platinum and phosphorus chemical shifts, of −280 and 40 p.p.m. respectively.

Modifications of the substituents on unidentate ligands have less dramatic effects than either of the foregoing.

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The substitution of a phenyl group for methyl on P or As tends to increase the shielding of the platinum nucleus [compounds (2), (3); (15)—(17), (19)—(21); (22), (23); (24), (25); (27), (28); and (59), (60)], which is in accord with general trends noted for other heavier nuclei adjacent to unsaturated moieties.[41,42] However, the trend is less significant when the other ligands about platinum are of disparate size [compounds (51), (54), and (55)] which suggests that interbond angle differences may again be of significance.

The effect of replacement of a methyl group on Pt by phenyl is more difficult to assess with the limited data available. It results in an increase in shielding in the presence of a cyclo-octadiene ligand [compounds (34) and (35)] but with two mutually *trans* arsine ligands [compounds (16) and (18)] deshielding occurs which may result from conjugative interaction *via* the platinum atom.

Replacement of a methyl group on Pt by chloride reduces the ^{195}Pt shielding [*e.g.* compounds (2), (11), (27); (33), (34); (44), (46)] as is expected on the basis of electronegativity differences and changes in electronic asymmetry. The larger increases in shielding on replacement of chlorine by heavier halogens are however difficult to rationalize on this basis, and constitute further examples of the ' heavy-atom ' effect [4] which has also been observed in the shielding of other heavier elements.[43-46] For the platinum compounds studied here, the increases in ^{195}Pt shielding are as follows: replacement of Cl by Br, 120—150; replacement of Br by I, 240—300; and replacement of PhS by PhSe, *ca.* 150 p.p.m. These figures apply only to compounds with arsine or phosphine ligands; in the absence of these the increases are much greater [compounds (57), (58) and (72)—(75)].

Shielding contributions due to the diamagnetic circulation of electrons in these substituent atoms will increase with the atomic number of the substituent,[47,48] but estimates of the magnitudes of these effects for platinum-bonded moieties show that they are too small to account for the observed changes, which may therefore be related to the polarizability of the substituent.[4] It is pertinent in this respect that substitution by a heavier arsine ligand for the equivalent phosphorus one in the compounds examined here [(6)—(8), (19)—(21); (27), (29); and (50), (52)] generally produces a decrease in the shielding of the platinum nucleus. A similar situation obtains in the series of compounds [$MMe_3(SnMe_3)$] (M = Si, Sn, or Pb) in which the shielding of ^{119}Sn also decreases with increasing atomic number of the substituent metal atom M.[49] In both these examples, all the electrons in the valence shells of the atoms (As, P, and M) bonded to the nucleus in question are involved in bonding, and therefore the ' heavy-atom ' effect may have a substantial dependence on the availability, within the heavy atom, of non-bonding electrons (*i.e.* lone pairs in this instance) of energies comparable to those of the electrons used in bonding.

The trends observed in the ^{31}P chemical shifts are largely in accord with those noted elsewhere:[1,2,5,50-52] there are general increases in ^{31}P shielding associated with decreasing aromatic substitution on phosphorus and increasing halogen substitution on platinum. The increases in shielding with increasing atomic number of the halogen may be due to longer range ' heavy-atom ' effects. The anomalous shielding of the ^{31}P nuclei in compound (56) has been discussed above, and it is also of interest that the phosphorus nuclei in the platinum(II) compounds resonate 20—30 p.p.m. to lower field than those in platinum(IV) species.

The decrease in $^1J(^{195}Pt-^{31}P)$ in going from Pt^{II} to Pt^{IV} is also in accord with previously published and rationalized results,[2,5,19,24,51-54] as is the general increase with increased substitution of methyl for phenyl groups on P. The increase in this coupling constant with increased halogen substitution presumably results from an increase in *s*-electron density at the ^{195}Pt nucleus due to an increase in effective nuclear charge, and this is supported by the changes observed as the electronegativity of the halogen increases in the order $I < Br < Cl$. These increases are greatest when the phosphorus atom is *trans* to the halogen and presumably result from the diversion of *s* character away from the more electronegative substituent, *i.e.* into the Pt–P bond.

The high values of $^1J(^{195}Pt-^{31}P)$ in compounds (77) and (78) merit particular comment, and should be compared with those of species (2), (3), and (76). Similar large increases in $^1J(^{195}Pt-^{31}P)$ have been observed recently in some tetraphosphineplatinum(0) complexes,[55] and have been ascribed to the effects of constraint of the interbond angles at platinum; a decrease in the interbond angle has the effect of increasing the *s* character in the other platinum bonding orbitals. In the compounds described here, the P–Pt–P interbond angles are expected to be similar {[$Pt\{(CH_2)_4\}(PPh_3)_2$], 98.8;[56] [$Pt(CF_2{=}CClF)(PPh_3)_2$], 104.7;[57] and [$Pt(CF_3C{\equiv}CCF_3)(PPh_3)_2$], 100.2?[58]},

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but the C–Pt–C interbond angles are expected to decrease in the order *cis*-[PtMe$_2$(PMe$_2$Ph)$_2$] > [Pt(CF$_2$=CF$_2$)-(PPh$_3$)$_2$] > [Pt(CF$_3$C≡CCF$_3$)(PPh$_3$)$_2$]. This sequence will therefore correspond to the sequence of increasing diversion of *s* character into the Pt–P bond and may account for the observed increases in $^1J(^{195}Pt–^{31}P)$. The sensitivity of this coupling constant in the olefin and acetylene complexes suggests that it may be a useful probe in the assessment of the nature of the metal–carbon bond in these systems.

It may be noted that there is an increase in $^2J(^{31}P–^{31}P)$ (*trans*) of *ca.* 20% associated with a change in the platinum oxidation number from II to IV, and that there is also an increase associated with an increase in halogen substitution on platinum, but at present we have insufficient data for a meaningful discussion of these results.

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