Magnetic Double Resonance Studies of Some *trans*-Bis(triethylphosphine) Complexes of Platinum

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The ^1H n.m.r. spectra of 44 platinum complexes containing *trans*-triethylphosphine ligands, with halide, hydride, and silyl or germyl ligands, have been recorded. Heteronuclear double resonance experiments have been used to determine ^{31}P and ^{195}Pt chemical shifts, as well as the signs of coupling constants, and the magnitudes of coupling constants not observed in the ^1H spectra. Systematic trends in some of the parameters enable estimates of these parameters to be made for some complexes that have not been studied.

IN recent years we have been interested in silyl and germyl derivatives of four- and six-co-ordinated platinum.[1,2] These compounds, when they have two triethylphosphine groups that are mutually *trans*, and SiH or GeH bonds, are very easily studied by ^1H n.m.r. spectroscopy, usually having first-order spectra, with couplings to phosphorus and to the 33% abundant ^{195}Pt being observed. The spectra of hydride[3] or methyl[4] complexes of platinum show the same features. However, the spectra of many of these compounds are very similar, and it is often impossible to be sure, from the ^1H spectrum alone, what the products of a reaction may be. By investigating ^{31}P and ^{195}Pt spectra also, by double resonance methods, we have obtained information which greatly facilitates the identification of unknown compounds, as well as giving an insight into the nature of the platinum–silicon or platinum–germanium bonds. The methods have also proved invaluable to us in a study of some six-co-ordinate platinum hydrides, many of which could not have been identified by other means.[5] It is also of great importance in the study of complexes which may have no protons other than those in the triethylphosphine ligands.[6-8]

We report here the results of our studies of silyl- and germyl-platinum compounds, of platinum hydrides, and of some simple bis(phosphine)platinum halides.

EXPERIMENTAL

Platinum complexes were prepared by standard methods referenced in Table 1. *trans*-$[Pt(CN)I(PEt_3)_2]$ was prepared by reaction of equimolar quantities of HCN and *trans*-$[PtHI(PEt_3)_2$ in CH_2Cl_2 at 293 K.

Solvents used were benzene (AnalaR, dried over sodium wire) or methylene dichloride (dried over molecular sieve).

N.m.r. spectra were recorded on a Varian Associates HA 100 spectrometer operating at 100 MHz. The probe of this instrument was double tuned to accept a second radio frequency, provided by a Schlumberger FS 30 frequency synthesizer. The double-resonance technique used has been described fully elsewhere.[9]

RESULTS AND DISCUSSION

In all the compounds studied the ^{31}P and ^{195}Pt spectra are complicated by coupling with protons in the triethylphosphine groups. Nevertheless, couplings of ^{31}P and ^{195}Pt with other protons can usually be evaluated directly on a first-order basis from the ^1H spectra. For the double-resonance experiments it is necessary to assume that the ^{31}P and ^{195}Pt spectra consist of a number of complex sub-spectra, the relative positions of which are governed by first-order rules. Because of the complexity of the sub-spectra, it is often difficult to locate the exact centre of a group of lines, and so the estimated errors quoted in the tables of chemical shifts (Table 2) and coupling constants (Table 3) are quite large.

TABLE 1

Preparation of complexes

General formula	Complexes (see Table 2)	Ref. to preparation
trans-$[PtX_4(PEt_3)_2]$	1, 2	8
trans-$[PtHXYZ(PEt_3)_2]$	3—8	5
trans-$[PtX_2(PEt_3)_2]$	18, 20, 21	6, 7
cis-trans-$[PtH_2XY(PEt_3)_2]$	9—14	5
cis-$[PtX_2(PEt_3)_2]$	19	6
trans-$[PtHX(PEt_3)_2]$	23—26	3
trans-$[Pt(CH_3)I(PEt_3)_2]$	36	4
trans-$[Pt(MHYZ)X(PEt_3)_2]$	27—35, 37—44	1, 2
cis-trans-$[PtH(SiH_2Y)X_2(PEt_3)_2]$	15—17	1, 2

^{195}Pt *Chemical Shifts*.—Although the ^{195}Pt chemical shifts of a number of platinum complexes, determined both by direct observation[10] or from double-resonance experiments,[11,12] have been reported, no satisfactory explanation of the observed results has yet been put forward. Ramsey's equation[13] has been applied to some planar platinum(II) complexes,[10] but the observed chemical shifts do not correlate well with the parameters derived from electronic absorption spectra. Nevertheless, there are certain systematic trends that can be used

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to predict chemical shifts for complexes, the ^{195}Pt spectra of which have not been studied.

The first point to note is that there are no simple additivity rules. A consequence of this is that ^{195}Pt chemical shifts for different isomers of the same compound are different. This may be seen from Table 2 to be so for the *cis*- and *trans*-forms of $PtCl_2(PEt_3)_2$, and for the two isomers of $PtBr_2HI(PEt_3)_2$.

TABLE 2

^{195}Pt and ^{31}P Chemical shifts

No.	Compound	$\Xi(^{195}Pt)$/Hz [a]	(^{195}Pt) p.p.m. [b]	$\Xi^{31}P$/Hz [a]	(^{31}P) p.p.m. [c]	Solvent	*T*/K
1.	*trans*-[$PtCl_4(PEt_3)_2$]	21 454 721 (10)	+2925	40 480 925 (5)	+4·4	C_6H_6–Me_4Si	300
2.	*trans*-[$PtBr_4(PEt_3)_2$]	21 424 410 (5)	+1508	40 480 354 (3)	−9·7	C_6H_6–Me_4Si	300
3.	*trans–trans*-[$PtBr_3H(PEt_3)_2$]	21 414 081 (10)	+1026	40 480 835 (5)	+2·2	CH_2Cl_2–Me_4Si	193
4.	*trans–trans*-[$PtHI_3(PEt_3)_2$]	21 377 980 (10)	−662	40 480 082 (3)	−16·4	CH_2Cl_2–Me_4Si	233
5.	*trans–trans*-[$PtCl_2HI(PEt_3)_2$]	21 424 984 (8)	+1535	40 480 923 (4)	4·4	CH_2Cl_2–Me_4Si	183
6.	*trans–trans*-[$PtBr_2HI(PEt_3)_2$]	21 408 032 (10)	+743	40 480 624 (5)	−3·0	CH_2Cl_2–Me_4Si	193
7.	*cis–trans*-[$PtBr_2HI(PEt_3)_2$]	21 398 838 (20)	+313	40 480 587 (8)	−3·9	CH_2Cl_2–Me_4Si	213
8.	*trans–trans*-[$PtBrHI_2(PEt_3)_2$]	21 385 293 (10)	−320	40 480 316 (5)	−10·6	CH_2Cl_2–Me_4Si	193
9.	*cis–cis–trans*-[$PtCl_2H_2(PEt_3)_2$]	21 410 997 (10)	+881	40 481 241 (5)	+12·2	CH_2Cl_2–Me_4Si	293
10.	*cis–cis–trans*-[$PtBr_2H_2(PEt_3)_2$]	21 403 575 (10)	+534 [d]	40 481 037 (5)	+7·2	CH_2Cl_2–Me_4Si	253
11.	*cis–cis–trans*-[$PtH_2I_2(PEt_3)_2$]	21 389 020 (7)	−146 [e]	40 480 689 (3)	−1·4	CH_2Cl_2–Me_4Si	253
12.	*cis–trans*-[$PtClBrH_2(PEt_3)_2$]	21 407 284 (30)	+708	40 481 144 (5)	+9·8	CH_2Cl_2–Me_4Si	253
13.	*cis–trans*-[$PtClH_2I(PEt_3)_2$]	21 400 586 (30)	+395	40 480 976 (5)	+5·7	CH_2Cl_2–Me_4Si	253
14.	*cis–trans*-[$PtBrH_2I(PEt_3)$]	21 396 569 (15)	+207	40 480 872 (5)	+3·1	CH_2Cl_2–Me_4Si	253
15.	*cis–trans*-[$PtHI_2(SiH_2I)(PEt_3)_2$]	21 385 708 (25)	−301	40 480 077 (5)	−16·5	C_6H_6–Me_4Si	253
16.	*cis–trans*-[$PtHI_2(SiH_2CCH)(PEt_3)_2$]	21 384 253 (10)	−369	40 480 180 (5)	−14·1	C_6H_6–Me_4Si	243
17.	*cis–trans*-[$PtHI_2(SiH_2CCCF_3)(PEt_3)_2$]	21 383 008 (10)	−427	40 480 161 (8)	−14·5	C_6H_6–Me_4Si	243
18.	*trans*-[$PtCl_2(PEt_3)_2$] [g]	21 412 376 (15)	+946 [f]	40 481 244 (5)	+12·3	C_6H_6–Me_4Si	300
19.	*cis*-[$PtCl_2(PEt_3)_2$] [g]	21 401 000 (30)	+414	40 481 097 (5)	+8·7	CH_2Cl_2	300
20.	*trans*-[$PtBr_2(PEt_3)_2$]	21 400 386 (5)	+384	40 481 054 (3)	+7·6	C_6H_6–Me_4Si	300
21.	*trans*-[$PtI_2(PEt_3)_2$]	21 377 753 (10)	−673 [h]	40 480 754 (3)	+0·2	C_6H_6–Me_4Si	300
22.	*trans*-[$Pt(CN)I(PEt_3)_2$]	21 391 667 (5)	−22	40 481 132 (3)	+9·5	CH_2Cl_2–Me_4Si	300
23.	*trans*-[$PtClH(PEt_3)_2$] [i]	21 392 145 (5)	0 [j]	40 481 670 (3)	+22·8	CH_2Cl_2	293
24.	*trans*-[$PtBrH(PEt_3)_2$] [i]	21 389 444 (10)	−126	40 481 635 (3)	+22·0	C_6H_6–Me_4Si	293
25.	*trans*-[$PtHI(PEt_3)_2$] [i]	21 385 195 (10)	−325	40 481 527 (3)	+19·3	C_6H_6–Me_4Si	293
26.	*trans*-[$Pt(CN)H(PEt_3)_2$] [i]	21 386 100 (10)	−283	40 481 541 (5)	+19·6	CH_2Cl_2–Me_4Si	300
27.	*trans*-[$PtCl(SiH_3)(PEt_3)_2$]	21 387 770 (10)	−205	40 481 450 (5)	+17·4	C_6H_6–Me_4Si	273
28.	*trans*-[$PtCl(SiH_2F)(PEt_3)_2$] [k]	21 390 593 (10)	−73	40 481 554 (3)	+20·0	C_6H_6–Me_4Si	233
29.	*trans*-[$PtCl(SiH_2Cl)(PEt_3)_2$] [l]	21 389 360 (5)	−130	40 481 428 (3)	+16·8	C_6H_6–Me_4Si	273
30.	*trans*-[$PtCl(SiHCl_2)(PEt_3)_2$]	21 392 342 (5)	+9	40 481 468 (3)	+17·8	C_6H_6–Me_4Si	300
31.	*trans*-[$PtCl(SiH_2CCH)(PEt_3)_2$]	21 388 141 (10)	−187	40 481 420 (3)	+16·6	C_6H_6–Me_4Si	300
32.	*trans*-[$PtCl(SiH_2CCCF_3)(PEt_3)_2$] [m]	21 388 442 (4)	−173	40 481 399 (5)	+16·1	C_6H_6–Me_4Si	300
33.	*trans*-[$PtCl(GeH_2Cl)(PEt_3)_2$]	21 391 250 (10)	−42	40 481 293 (5)	+13·5	C_6H_6–Me_4Si	300
34.	*trans*-[$PtBr(SiH_2Br)(PEt_3)_2$]	21 387 898 (10)	−199	40 481 296 (3)	+13·6	C_6H_6–Me_4Si	300
35.	*trans*-[$PtBr(SiHBr_2)(PEt_3)_2$]	21 391 291 (5)	−40	40 481 313 (3)	+14·0	C_6H_6–Me_4Si	300
36.	*trans*-[$Pt(CH_3)I(PEt_3)_2$]	21 392 931 (10)	+37	40 481 164 (3)	+10·3	C_6H_6–Me_4Si	300
37.	*trans*-[$PtI(SiH_3)(PEt_3)_2$]	21 383 421 (6)	−408	40 481 217 (3)	+11·6	C_6H_6–Me_4Si	273
38.	*trans*-[$PtI(SiH_2Cl)(PEt_3)_2$]	21 384 950 (10)	−336	40 481 143 (5)	+9·8	C_6H_6–Me_4Si	300
39.	*trans*-[$PtI(SiH_2I)(PEt_3)_2$]	21 385 685 (5)	−302	40 481 028 (10)	+7·0	C_6H_6–Me_4Si	300
40.	*trans*-[$PtI(SiH_2\text{-})(PEt_3)_2]_2S$	21 385 320 (10)	−319	40 481 199 (5)	+11·2	C_6H_6–Me_4Si	263
41.	*trans*-[$PtI(SiH_2\text{-})(PEt_3)_2]_2Se$	21 385 591 (10)	−306	40 481 132 (5)	+9·5	C_6H_6–Me_4Si	263
42.	*trans*-[$PtI(SiH_2SeSiH_3)(PEt_3)_2$]	21 385 381 (20)	−316	40 481 113 (10)	+9·1	C_6H_6–Me_4Si	263
43.	*trans*-[$PtI(SiHICCH)(PEt_3)_2$]	21 386 830 (10)	−248	40 481 039 (7)	+7·2	C_6H_6–Me_4Si	300
44.	*trans*-[$Pt(GeH_3)I(PEt_3)_2$]	21 382 411 (10)	−455	40 481 058 (5)	+7·7	C_6H_6–Me_4Si	273

Estimated standard deviations are quoted in parentheses. These do not include a possible error in the determination of absolute frequencies of at most 4 Hz.

[a] Resonant frequency at a polarising field strength such that the Me_4Si proton resonance is at exactly 100 MHz. [b] To high frequency of 0·5M-$PtClH(PEt_3)_2$ in CH_2Cl_2 at 293 K [$\Xi(^{195}Pt)$ = 21 392 145 (5) Hz]. [c] To high frequency of 85% H_3PO_4 [$\Xi(^{31}P)$ = 40 480 746 (3) Hz]. [d] 56 p.p.m. lower in C_6H_6–Me_4Si. [e] 57 p.p.m. lower in C_6H_6–Me_4Si. [f] 21 p.p.m. higher in CH_2Cl_2–Me_4Si. [g] See also ref. 21. [h] 23 p.p.m. higher in CH_2Cl_2–Me_4Si. [i] See also ref. 12. [j] 36 p.p.m. lower in C_6H_6. [k] (^{19}F) = 94 077 089 (3) Hz; $\delta(^{19}F)$ = 179·7 p.p.m. to high frequency of CCl_3F $\Xi(^{19}F)$ = 94 093 963 (3) Hz. [l] $\Xi(^{29}Si)$ = 19 866 685 (10) Hz; $\delta(^{29}Si)$ = − 25·0 p.p.m. to high frequency of internal Me_4Si. [m] $\Xi(^{19}F)$ = 94 089 130 (1) Hz; $\delta(^{19}F)$ = − 51·3 p.p.m. to high frequency of CCl_3F.

It does however appear that in any complex containing the grouping *trans*-[X–Pt–X] (X = Cl, Br, or I), the effect of replacing one of the X ligands by H depends on X, but is independent of the nature of the *cis*-ligands, or indeed of whether there are two or four of them. This is expressed graphically in the Figure for some complexes containing halide and hydride ligands. Observed chemical shifts (marked +) are linked by continuous lines, representing changes of mutually *trans* (X,X) (X = Cl, Br, or I) ligand pairs by (X,H). These lines are of three different gradients only, corresponding to the three different halogens. The dashed lines are extrapolations to unknown or unstudied compounds such as $PtI_4(PEt_3)_2$ or $PtBrCl_2H(PEt_3)_2$; these extrapolations may not predict chemical shifts exactly, but in view of the wide range of ^{195}Pt shifts, they should be close enough to the true values to be useful.

We also note that for both the six-co-ordinate and the four-co-ordinate complexes, the three lines corresponding to the three different halides meet at a common point (marked *) when extrapolated (dotted line in Figure). This observation is not necessarily of physical significance. However, if the ratios of the changes in chemical shifts for replacement of an (X,X) ligand pair by (X,H), and replacement of (X,H) by (H,H), is the same for each different X, then these two points represent the complexes $PtH_4(PEt_3)_2$ and $PtH_2(PEt_3)_2$. Other similar extrapolations would give chemical shifts for $PtH_2X_2(PEt_3)_2$ and $PtH_3X(PEt_3)_2$.

The influence of ligands other than halides on the ^{195}Pt chemical shifts can be seen from the series of complexes $PtIL(PEt_3)_2$, where the values change with the ligand L in the order $CH_3 > CN \gg H > SiH_3 > GeH_3 > I$. The relative positions of CH_3, H, and SiH_3 in this series is of interest, as silyl or, to a lesser extent, hydrido-groups lead to low-frequency resonances for ^{15}N,[9] ^{19}F,[14] ^{31}P,[15] and ^{77}Se [16] compounds, when compared with the resonances for equivalent organo-derivatives.

The effects on the ^{195}Pt chemical shifts of changing substituents on silicon or germanium are, of course, relatively small. Nevertheless, the changes are suffi-

TABLE 3

Coupling constants/Hz

No.	Compound	^1J(PtP)	^1J(PtH)	^2J(PH)	^2J(PtH)	^3J(PH)	Notes
1.	*trans*-[$PtCl_4(PEt_3)_2$]	+1488(10)	—	—	—	—	—
2.	*trans*-[$PtBr_4(PEt_3)_2$]	+1480(15)	—	—	—	—	—
3.	*trans–trans*-[$PtBr_3H(PEt_3)_2$]	+1578(20)	+845(2)	−5·0(0·5)	—	—	—
4.	*trans–trans*-[$PtHI_3(PEt_3)_2$]	+1590(20)	+784(2)	−5·5(0·5)	—	—	—
5.	*trans–trans*-[$PtCl_2HI(PEt_3)_2$]	+1675(20)	+942(2)	−4·0(0·5)	—	—	—
6.	*trans–trans*-[$PtBr_2HI(PEt_3)_2$]	+1590(20)	+870(2)	−4·5(0·5)	—	—	—
7.	*cis–trans*-[$PtBr_2HI(PEt_3)_2$]	n.o.	+831(2)	−5·3(0·5)	—	—	—
8.	*trans–trans*-[$PtBrHI_2(PEt_3)_2$]	+1600(20)	+794(2)	−5·3(0·5)	—	—	—
9.	*cis–cis–trans*-[$PtCl_2H_2(PEt_3)_2$]	+1775(20)	+1178(2)	−6·5(0·5)	—	—	—
10.	*cis–cis–trans*-[$PtBr_2H_2(PEt_3)_2$]	+1730(20)	+1202(2)	−6·3(0·5)	—	—	—
11.	*cis–cis–trans*-[$PtH_2I_2(PEt_3)_2$]	+1728(20)	+1186(2)	−5·8(0·5)	—	—	—
12.	*cis–trans*-[$PtClBrH_2(PEt_3)_2$]	+1770(20)	+1233(2)	−7·0(0·5)	—	—	—
		—	+1168(2)	−7·0(0·5)	—	—	—
13.	*cis–trans*-[$PtClH_2I(PEt_3)_2$]	+1729(20)	+1240(2)	−7·0(0·5)	—	—	—
		—	+1132(2)	−6·0(0·5)	—	—	—
14.	*cis–trans*-[$PtBrH_2I(PEt_3)_2$]	+1710(20)	+1220(2)	−6·0(0·5)	—	—	—
		—	+1176(2)	−6·0(0·5)	—	—	—
15.	*cis–trans*-[$PtHI_2(SiH_2I)(PEt_3)_2$]	+1700(25)	+1160(2)	−6·0(0·5)	+59·2(0·8)	+7·6(0·5)	—
16.	*cis–trans*-[$PtHI_2(SiH_2CCH')(PEt_3)_2$]	+1690(15)	+1126(2)	−5·5(0·5)	+19·0(1)	+8·6(0·5)	^4J(HH′) n.o.
17.	*cis–trans*-[$PtHI_2(SiH_2CCCF_3)(PEt_3)_2$]	n.o.	+1113(2)	−5·8(0·3)	n.o. [a]	+7·7(0·5)	Coupling with ^{19}F n.o.
18.	*trans*-[$PtCl_2(PEt_3)_2$]	+2457(30)	—	—	—	—	—
19.	*cis*-[$PtCl_2(PEt_3)_2$] [b]	+3560(40)	—	—	—	—	—
20.	*trans*-[$PtBr_2(PEt_3)_2$]	+2368(15)	—	—	—	—	—
21.	*trans*-[$PtI_2(PEt_3)_2$]	+2272(20)	—	—	—	—	—
22.	*trans*-[$Pt(CN)I(PEt_3)_2$]	+2202(15)	—	—	—	—	—
23.	*trans*-[$PtClH(PEt_3)_2$]	+2730(15)	+1275(2)	−14·5(0·3)	—	—	—
24.	*trans*-[$PtBrH(PEt_3)_2$]	+2736(20)	+1331(2)	−13·7(0·3)	—	—	—
25.	*trans*-[$PtHI(PEt_3)_2$]	+2660(20)	+1369(2)	−13·3(0·3)	—	—	—
26.	*trans*-[$Pt(CN)H(PEt_3)_2$]	+2546(25)	+807(2)	−15·5(0·5)	—	—	—
27.	*trans*-[$PtCl(SiH_3)(PEt_3)_2$]	+2465(20)	—	—	+36·5(0·5)	+6·5(0·5)	—
28.	*trans*-[$PtCl(SiH_2F)(PEt_3)_2$]	+2515(20)	—	—	+123·6(0·5)	+5·0(0·5)	^2J(FH+52·2(0·5), ^2J(PtF)+358·5(0·5), ^3J(PF)+9·5(0·5)
29.	*trans*-[$PtCl(SiH_2Cl)(PEt_3)_2$]	+2470(15)	—	—	+117·6(0·5)	+8·8(0·3)	^1J(SiH)−204(2), ^1J(PtSi)−1600(100), ^2J(PSi)+18(3)
30.	*trans*-[$PtCl(SiHCl_2)(PEt_3)_2$]	+2400(15)	—	—	+245 0(0·5)	+10·4(0·3)	—
31.	*trans*-[$PtCl(SiH_2CCH')(PEt_3)_2$]	+2480(20)	—	—	+43·5(0·5)	+8·8(0·3)	^4J(PtH)−15·4(0·7), ^4J(HH′)−1·4(0·3), ^5J(PH′) n.o.
32.	*trans*-[$PtCl(SiH_2CCCF_3)(PEt_3)_2$]	+2420(10)	—	—	+45·0(0·5)	+8·8(0·3)	^5J(PtF+23·7(0·8), ^5J(HF) ± 2·2(0·3), ^6J(PF) n.o.
33.	*trans*-[$PtCl(GeH_2Cl)(PEt_3)_2$]	+2410(20)	—	—	+218·0(0·5)	+7·4(0·3)	—
34.	*trans*-[$PtBr(SiH_2Br)(PEt_3)_2$]	+2440(40)	—	—	+125·2(0·5)	+9·4(0·3)	—
35.	*trans*-[$PtBr(SiHBr_2)(PEt_3)_2$]	+2380(20)	—	—	+244·4(0·5)	+11·2(0·3)	
36.	*trans*-[$Pt(CH_3)I(PEt_3)_2$]	+2750(20)	—	—	−80·6(0·5)	+6·2(0·3)	—
37.	*trans*-[$PtI(SiH_3)(PEt_3)_2$]	+2465(15)	—	—	+36·5(0·5)	+6·5(0·5)	—
38.	*trans*-[$PtI(SiH_2Cl)(PEt_3)_2$]	+2430(20)	—	—	+123·8(0·5)	+9·6(0·3)	—
39.	*trans*-[$PtI(SiH_2I)(PEt_3)_2$]	+2390(10)	—	—	+127·1(0·5)	+9·6(0·3)	—
40.	*trans*-[$PtI(SiH_2\text{-})(PEt_3)_2]_2S$	+2542(40)	—	—	+83·5(0·5)	+9·5(0·5)	—
41.	*trans*-[$PtI(SiH_2\text{-})(PEt_3)_2]_2Se$	+2512(20)	—	—	+85·5(0·5)	+9·5(0·5)	—
42.	*trans*-[$PtI(SiH_2SeSiH_3)(PEt_3)_2$]	n.o.	—	—	+91(1)	+9·5(0·5)	—
43.	*trans*-[$PtI(SiHICCH')(PEt_3)_2$]	+2380(20)	—	—	+131·2(0·5)	+12·7(0·3)	^4J(HH′)(−)1·3(0·4)
44.	*trans*-[$Pt(GeH_3)I(PEt_3)_2$]	+2440(20)	—	—	+87·8(0·5)	+5·9(0·3)	—

Estimated errors are noted in parentheses. n.o. = not observed. [a] <14. [b] Ref. 21.

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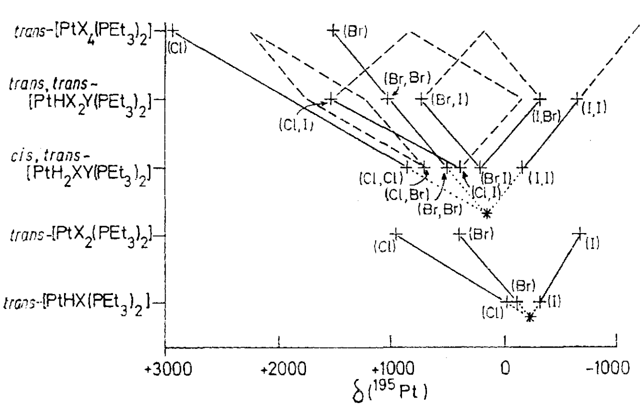
ciently great to be useful diagnostically, as in general, replacement of one group by a more electronegative one leads to a high-frequency shift. However, accurate prediction is difficult for unknown compounds, as the changes are certainly not additive, and sometimes vary in unexpected ways. The relative resonant frequencies of the four- and six-co-ordinate complexes with $-SiH_2C\equiv CH$ and $-SiH_2C\equiv CCF_3$ ligands exemplify this.

^{31}P *Chemical Shifts*.—As in all the complexes studied here except one the two triethylphosphine groups are mutually *trans*, any variations in ^{31}P chemical shift must be due to the influence of the two or four *cis*-ligands. That the number of other ligands co-ordinated to platinum is important is immediately evident from Table 2, for nearly all of the six-co-ordinate complexes resonate at lower frequencies than 85% H_3PO_4, whereas all the four-co-ordinate complexes resonate at higher frequencies. It should be noted that free triethylphosphine resonates at $-20{\cdot}4$ p.p.m.,[17] lower than any of the complexes studied here.



^{195}Pt chemical shifts of some *trans*-$[Pt(PEt_3)_2]$ complexes containing halogen and hydride ligands. For interpretation, see text.

The relative effects of *cis*-ligands in raising the ^{31}P chemical shifts is $H > CH_3 \sim SiR_3 > GeR_3 > Cl > Br > I$, and within the SiR_3 group the order is $SiH_2F > SiHCl_2 > SiH_3 > SiH_2C\equiv CR \sim SiH_2Cl > SiH_2I$, although the changes within the latter series are relatively small. However, as with ^{195}Pt chemical shifts, the changes are sufficiently great for the ^{31}P shifts to be useful for identification purposes.

The relative arrangement, as well as number and type, of the *cis*-ligands is of some importance in determining the ^{31}P chemical shift. This is demonstrated by the two isomers of $PtBr_2HI(PEt_3)_2$, which have a small, but significant, difference in shift.

^{29}Si *Chemical Shifts*.—The ^{29}Si chemical shift has been determined for only one platinum complex, $PtCl(SiH_2Cl)(PEt_3)_2$. The value found ($-25{\cdot}0$ p.p.m. relative to tetramethylsilane) is *ca.* 12 p.p.m. higher than that for free silyl chloride.

Coupling Constants.—Although the investigation of platinum–phosphorus coupling constants was not one of the main aims of this work, the values found confirm the observations made previously.[18,19] In particular a wide range of six-co-ordinate complexes is included here, and it can be seen that this coupling constant is larger in complexes with less halide and more hydride ligands, as was found for the four-co-ordinate complexes. In contrast, the values of $^1J(^{195}Pt^1H)$ are not dependent primarily on the co-ordination number of platinum, for the values are small for the six-co-ordinate monohydride complexes, but larger for the dihydride six-co-ordinate and nearly all the four-co-ordinate complexes. Both $^1J(^{195}Pt^1H)$ and $^1J(^{195}Pt^{31}P)$ have been taken to be positive in all the compounds studied,[20,21] and the signs of other coupling constants have been related to these.

Only one other one-bond coupling constant was determined: $^1J(^{195}Pt^{29}Si)$ in $PtCl(SiH_2Cl)(PEt_3)_2$ was found to be -1600 Hz. The reduced coupling constant, $^1K(PtSi)$, is therefore $+3120 \times 10^{19}$ N A^{-2} m^{-3}, compared with 2330×10^{19} N A^{-2} m^{-3} in *cis*-$[PtCl_2(PEt_3)_2]$, where the ligand *trans* to the phosphine is also a chloride.

Most of the other reduced coupling constants in the compounds studied are positive over odd numbers of bonds, and negative over even numbers; this is consistent with a mechanism for coupling that is dominated by Fermi contact terms. There is however, one important exception. It has been noted that in the complexes $PtX(MHYZ)(PEt_3)_2$ the magnitude of $^2J(^{195}Pt^1H)$ is greater with increasing substitution of halides for hydrides at M, and is much larger for M = Ge than for M = Si.[1] Values range from 434 Hz for a $GeHCl_2$ complex to less than 20 Hz in six-co-ordinate silyl acetylene complexes.[2] With such a wide range of values, it was quite possible that the coupling constant would be found not to be always of the same sign. However, in every silyl or germyl complex the sign was found by ^1H-{^{31}P} double resonance experiments to be the same as that of $^1J(^{195}Pt^{31}P)$, and therefore positive, although in $Pt(Me)I(PEt_3)_2$ the equivalent coupling constant is negative. It would seem, therefore, that in the silyl and germyl complexes there is a positive contribution to the coupling constant which is greater than the negative Fermi contact term. This positive term is much larger when electron-withdrawing groups are attached to the silicon or germanium atom, larger for germanium than for silicon, and must also be smaller for six-co-ordinate complexes than for the corresponding four-co-ordinate complexes.

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