Some Binuclear Complexes of Platinum containing Single PF_2 Bridges

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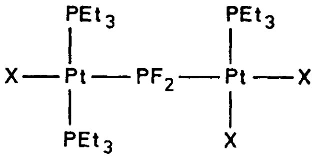
Reaction between $[PtH(X)(PEt_3)_2]$ and PF_2X (X = Cl, Br, or I) in CD_2Cl_2 at room temperature gives $[(Et_3P)_2XPt\text{-}PF_2Pt(PEt_3)X_2]$, which have been characterised by ^{31}P and ^{19}F n.m.r. spectroscopy and by analysis. At low temperatures the complexes $[PtH_2X_2(PEt_3)_2]$ and *trans*-$[PtX(PF_2H)(PEt_3)_2]$ have been detected as intermediates, and n.m.r. parameters for the latter are given. A mechanism for the reaction is suggested.

WE have recently reported the formation of binuclear platinum complexes containing PH_2 bridges.[1] They are among the few examples known where two platinum atoms are linked by a single monoatomic bridge. Recent studies have shown that similar complexes can be made containing a single PF_2-bridging unit. Although several examples have been reported where PF_2 acts as a bridging ligand, most of the complexes concerned are doubly bridged.[2-4] It is only relatively recently that Malisch and Panster [5] described the first example of a transition-metal complex in which two metal atoms are joined only by a single PF_2 group. In this paper we report the preparation of three binuclear platinum complexes containing single PF_2-bridging units.

RESULTS AND DISCUSSION

The reactions of $[PtH(X)(PEt_3)_2]$ with PF_2X (X = Cl, Br, or I) were allowed to occur at room temperature in CH_2Cl_2; crystalline solid products were obtained and characterised by C and H analysis and by ^{31}P and ^{19}F n.m.r. spectroscopy. The n.m.r. spectra were all first order, and could be interpreted in terms of the structure shown below.

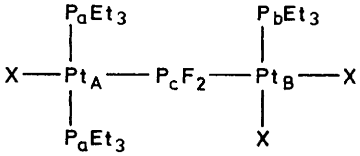


(1) X = Cl
(2) X = Br
(3) X = I

In the ^{31}P-$\{^1H\}$ n.m.r. spectra there were two distinct sets of resonances, one around $\delta = 0$—20 and the other at about $\delta = 200$ p.p.m. The resonances at 200 p.p.m. showed the wide triplet patterns ($J \approx 1\,100$ Hz) associated with a PF_2 group. Each was also associated with two sets of platinum satellites, showing that the PF_2 group concerned was bound to two different types of Pt atoms; when X was Br or I, the two sets of satellites were clearly separated from one another, but when X was Cl the couplings to Pt were so similar that the satellites overlapped, leading to peaks with complicated envelopes. Each line in the central triplet and in the satellites was split into a triplet of doublets; although the relative magnitudes of the couplings were sensitive to the halogen atoms in the complex, the chemical shifts of the PF_2-phosphorus nuclei were relatively constant. We deduce that the species concerned contain two Pt atoms linked by PF_2; one of the Pt atoms is bound to one other phosphorus ligand, and the other to two. These deductions are confirmed both by the details of the resonances at lower frequency in the ^{31}P-$\{^1H\}$ n.m.r. spectra and by the ^{19}F spectra.

TABLE 1

Phosphorus-31 and ^{19}F n.m.r. parameters



	(1; X = Cl)	(2; X = Br)	(3; X = I)
$\delta(P_a)$/p.p.m.	17.3	12.7	4.7
$\delta(P_b)$/p.p.m.	17.3	17.7	15.5
$\delta(P_c)$/p.p.m.	211.0	208.8	204.6
$\delta(F)$/p.p.m.	−30.9	−27.6	−27.5
$^1J(PtP_a)$/Hz	2 406	2 430	2 386
$^1J(PtP_b)$/Hz	3 479	3 470	3 330
$^1J(Pt_AP_c)$/Hz	4 519	4 578	4 501
$^1J(Pt_BP_c)$/Hz	4 452	4 288	3 869
$^2J(Pt_BF)$/Hz	541	512	453
$^2J(Pt_AF)$/Hz	551	566	570
$^2J(P_aP_c)$/Hz	19	15	14
$^2J(P_bP_c)$/Hz	10	8	n.r.
$^1J(P_cF)$/Hz	1 059	1 079	1 112
$^3J(P_aF)$/Hz	14	16	14
$^3J(P_bF)$/Hz	10	17	12

Measurements were made at room temperature in CD_2Cl_2. Values are considered accurate to ± 2 in the last figure quoted. Shifts are given as positive to high frequency of 85% H_3PO_4 (for ^{31}P) or CCl_3F (for ^{19}F). n.r. = Not resolved.

The peaks in the ^{31}P spectra between 0 and 20 p.p.m. are associated with PEt_3 groups; in each case they consisted of two sets of resonances, one twice as strong as the other and each with platinum satellites. Both central peaks appeared as doublets of triplets; the two doublet splittings corresponded to the smaller of the couplings in the PF_2 resonance, and confirm that only one PF_2 group is present. The ^{19}F resonances showed the expected wide doublet coupling with platinum satellites; each line was further split into a doublet of triplets. The absence of any large coupling assignable to $^2J(PP)$ between PF_2 and PEt_3 nuclei shows that all the PEt_3 groups are *cis* to PF_2; similarly, the PF_2 resonances were virtually unaffected when proton coupling was retained, so that there can be no hydride ligand *trans* to PF_2. The values of $^1J(PPt)$ are consistent with the structures proposed, being much larger for the resonances assigned to P *trans* to halogen.

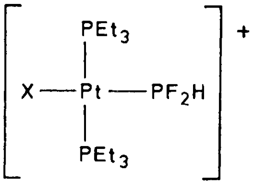
In comparing the n.m.r. parameters for the three complexes, it is a little surprising to find that the chemical shift of the P nuclei in the $PtX(PEt_3)_2$ residues is more sensitive to change in X than is the chemical shift of P in the $PtX_2(PEt_3)$ residue, but the relative intensities of the two resonances leave no doubt about the correctness of the assignment. Since we did not record ^{195}Pt n.m.r. spectra directly or do any experiments involving decoupling platinum, we cannot associate the different values of $^1J(PtP_c)$ with specific platinum atoms with any certainty. We know that $^1J(Pt_AP_a)$ changes with a change in halogen in much the same way as does the larger of the two sets of values of $^1J(PtP_c)$, and so we assign that coupling as $^1J(Pt_AP_c)$; by similar reasoning the other is assigned to $^1J(Pt_BP_c)$. Similarly, we know (see Table 2) that values of $^2J(PtF)$ in a series of PF_2H complexes decrease as the halogen changes from chloride to iodide. We therefore assign the set of PtF couplings in the bridging complexes that decrease in the same sense to $^2J(Pt_AF)$. These assignments are very tentative.

The i.r. spectra of the three species were not assigned in detail, but their general features were also consistent with the proposed structures. There were no peaks assignable to metal–hydride stretching frequencies, but strong bands were observed in the regions associated with PF_2 groups. We tried to determine the crystal structure of the chloride, but were frustrated by disorder in the crystal.

We have studied the n.m.r. spectra of the reaction systems at low temperatures to try to discover something about the mechanism of formation of the bridged complexes. The species detected at 190 K depended to some extent on the starting materials used and on their relative proportions. In every system one of the initial products was the complex $[PtH_2X_2(PEt_3)_2]$; these complexes are well known,[6] and were identified by their ^{31}P and ^1H n.m.r. parameters. In the reaction between $[PtBr(H)(PEt_3)_2]$ and $PBrF_2$, however, there were additional peaks in the ^{31}P-$\{^1H\}$ n.m.r. spectrum at 190 K: a wide triplet with ^{195}Pt satellites in the high-frequency region that we assign to a co-ordinated PF_2 group, and a doublet with ^{195}Pt satellites in the region associated with PEt_3 groups. Each line of the high-frequency triplet showed a small triplet coupling equal to the doublet splitting of the low-frequency peaks, and the satellites were roughly a quarter of the height of the main resonances. These observations suggest that we have detected the presence of a mononuclear platinum complex to which is bound a PF_2 group. In the spectrum with proton coupling retained, each line in the PF_2 resonance showed a doublet coupling of about 600 Hz. This is in principle consistent with the presence of a hydride ligand *trans* to PF_2, but the coupling would be unusually large for such a species; it would also be consistent with the presence of H bound to the PF_2 group. The ^1H n.m.r. spectrum confirmed the presence of co-ordinated PF_2H: there was a resonance at δ 9, with a doublet coupling of *ca.* 600 Hz and a narrow triplet coupling [which we assign to $^2J(HF)$], each line having platinum satellites. We therefore believe that the species we have observed is *trans*-$[PtX(PF_2H)(PEt_3)_2]^+$. The presence of the halide ligand is inferred. However, we were able to detect the presence of an analogous complex in the reaction between $[PtH(I)(PEt_3)_2]$ and PF_2I, and its n.m.r. parameters differed somewhat from those of the species formed in the reaction between the bromides. Finally, by using a four-fold initial excess of $PClF_2$ we were also able to detect the formation of the analogous chloride, whose n.m.r. parameters were again slightly different from those of the bromide and the iodide. The n.m.r. parameters for the complexes containing PF_2H are collected in Table 2.

TABLE 2

N.m.r. parameters for complexes (4)—(6)



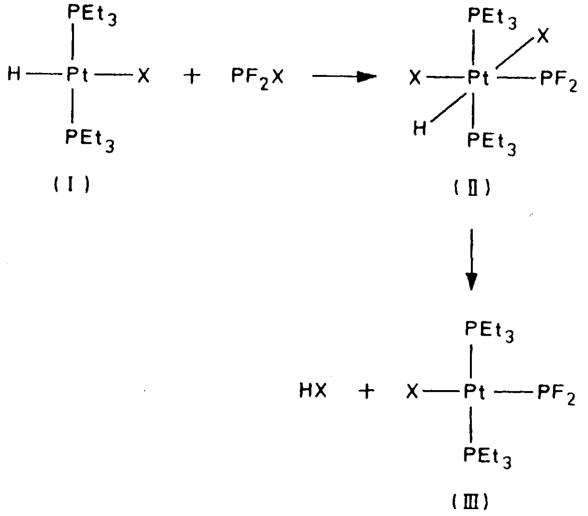
$$\left[X\text{—}Pt(PEt_3)_2\text{—}PF_2H\right]^+$$

Parameter	(4; X = Cl)	(5; X = Br)	(6; X = I)
δ(H)/p.p.m.	9.01	9.04	8.98
δ(*P*Et$_3$)/p.p.m.	14.4	13.3	3.2
δ(PF$_2$)/p.p.m.	101.8	110.0	107.2
δ(F)/p.p.m.	−71.7	−74.0	−74.2
$^1J(Pt\mathit{P}Et_3)$/Hz	2 119	2 057	2 052
$^1J(Pt\mathit{P}F_2)$/Hz	5 927	5 874	5 676
$^1J(PF)$/Hz	1 068	1 075	1 114
$^1J(PH)$/Hz	638	636	603
$^2J(FPt)$/Hz	515	493	488
$^2J(FH)$/Hz	60	61	60
$^2J(PP)$/Hz	24	22	19
$^2J(HPt)$/Hz	377	377	370
$^3J(PF)$/Hz	n.r.	n.r.	5

Parameters were measured in CD_2Cl_2 at *ca.* 213 K. Values are considered accurate to ±1 in the last figure quoted. Shifts are measured as positive to high frequency of 85% H_3PO_4 (for ^{31}P), CCl_3F (for ^{19}F), or $SiMe_4$ (for ^1H). n.r. = Not resolved.

As the solutions were allowed to warm, no other species were detected until the formation of the bridged complexes began.

Any mechanism proposed must explain the initial formation of $[PtH_2X_2(PEt_3)_2]$, the formation of complexes containing PF_2H ligands, and the ultimate production of the bridged complex with non-equivalent Pt atoms. The initial formation of the dihydride of six-co-ordinated Pt^{IV} in every case implies production of HX, which is known to give such compounds by reaction with the platinum starting materials.[6] The most obvious source of HX is the hydrolysis of PF_2X by traces of water, but we can discount this possibility since the other product of such hydrolysis, $O(PF_2)_2$, was not observed. An alternative possibility involves oxidative addition of P–X to Pt^{II}, giving a product (II) which could then eliminate HX, leaving a derivative with a terminal PF_2 group. We have no evidence for the formation of a complex containing a terminal PF_2 group. We know from work with other systems that oxidative addition of PF_2–X to Ir^I occurs readily, giving products with terminal PF_2 groups, and we found no resonances in the ^{31}P n.m.r. spectra of the systems described in this paper in the region where we expect peaks from such ligands.[7] We also know, however, that terminal PF_2 groups react readily with HX to give cationic complexes of PF_2H; this suggests a possible source of the PF_2H species observed.



We do not understand the mechanism by which the final binuclear product is formed. Its formation is associated with the production of PEt_3H^+, whose ^{31}P n.m.r. spectra show that H and not D is bound to P. The stoicheiometry appears to lead to the presence of one hydride ligand too many and one halide too few, and so it appears that some reduction of the solvent must occur (see equation). There are several possible mechanisms.

$$2[PtH(X)(PEt_3)_2] + PF_2X + CD_2Cl_2 \longrightarrow [(Et_3P)_2XPtPF_2Pt(PEt_3)X_2] + PEt_3H^+ + CHD_2Cl + Cl^-$$

The postulated species (III) might react with (I) to displace either PEt_3 or X^-, or the PF_2H complex whose presence we have detected might react with (I) by oxidative addition followed by elimination of PEt_3H^+. Further experiments are in hand to try to clarify the steps involved and the role played by the solvent.

EXPERIMENTAL

N.m.r. measurements were made on JEOL FX-60 (^{31}P), Varian XL100 (^{31}P and ^{19}F), and Brüker WH 360 (^1H) Fourier-transform spectrometers. Infrared spectra were recorded by means of a Perkin-Elmer 457 spectrometer (250—4 000 cm^{-1}). All manipulations were carried out either under vacuum or in an atmosphere of dry nitrogen gas. Platinum starting materials [8] and PF_2X (X = Cl, Br, or I) [9] were prepared by standard methods. Solvents were carefully dried and freshly distilled before use.

Preparation of Complexes (1)—(3).—Complex (1) was prepared by allowing $PClF_2$ (1 mmol) to react with $[PtCl(H)(PEt_3)_2]$ (1 mmol); the platinum complex was weighed into a Schlenk tube, pumped dry for 24 h, dissolved in CH_2Cl_2, and allowed to warm to room temperature with $PClF_2$. The white solid product was obtained by pumping away the solvent, washed with diethyl ether, and recrystallised as needles from methanol. Complexes (2) and (3) were prepared similarly from (1) by treatment with LiBr or NaI [Found: C, 23.4; H, 4.8. Calc. for $C_{18}H_{45}Cl_3F_2P_4Pt_2$ (1): C, 23.5; H, 4.9. Found: C, 22.0; H, 4.6. Calc. for $C_{18}H_{45}Br_3F_2P_4Pt_2$ (2): C, 22.0; H, 4.6. Found: C, 18.0; H, 3.8. Calc. for $C_{18}H_{45}F_2I_3P_4Pt_2$ (3): C, 18.1; H, 3.8%].

Identification of Unstable Species.—The complex *trans*-$[PtH(X)(PEt_3)_2]$ (0.1 mmol) was weighed into an n.m.r. tube, followed by CD_2Cl_2 (*ca.* 0.5 cm^3) and PF_2X (0.1 mmol). The tube was sealed and kept at 77 K; spectra were recorded without allowing reaction mixtures to warm above 190 K.

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