Fluoro Ketone Adducts of Platinum(II) with Four-, Five-, and Seven-Membered Cyclic Structures

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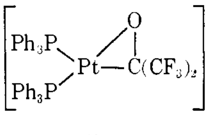
Abstract: Peroxobis(triphenylphosphine)platinum(II) reacts with hexafluoroacetone (HFA) to form novel cyclic adducts. With excess ligand, a product, $[(Ph_3P)_2PtO_2 \cdot 2HFA]$ (I), in which the metal and the peroxo group form part of a seven-membered ring, is obtained. With stoichiometric amounts of reactants (or, on recrystallization of I), a compound, $[(Ph_3P)_2PtO_2 \cdot HFA]$ (II), is formed, in which the peroxo group forms part of a five-membered ring. This, in turn, may be converted to a compound, $[(Ph_3P)_2PtO \cdot HFA]$ (III), which contains a four-membered ring, by reduction with triphenylphosphine, *i.e.*, I → II → III. The compounds have been characterized from their ^{19}F nmr and ir spectra. A compound analogous to II has been prepared by the reaction of $[(Ph_3P)_2PtO_2]$ with trifluoroacetone (TFA).

The reaction of tetrakis(triphenylphosphine)platinum(0) with oxygen has been shown to give an adduct, $[(Ph_3P)_2PtO_2]$,[1] the properties of which are such that it is probably best regarded as a peroxoplatinum(II) species rather than a π-bonded Pt(0) compound.[2] For example, the compound has a near-planar arrangement around the metal atom, typical of Pt(II) and contrasting with the usual tetrahedral environment about Pt(0).[3] Reactions of this compound may be classified into three main types: displacement, for example, by acetylenes;[2] addition with breaking of the peroxo bond, *e.g.*[4]

$$[(Ph_3P)_2PtO_2] + 2NO_2 \longrightarrow [(Ph_3P)_2Pt(NO_3)_2]$$

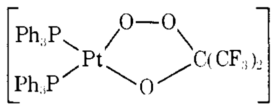
or addition with retention of the peroxo link and consequent ring expansion. We have previously reported that, with CO_2, ketones, and related unsaturated ligands, the reaction proceeds by the latter route to give products containing a five-membered ring.[2] Subsequent reduction of the peroxocarbonate (the CO_2 adduct) leads to a bidentate carbonato complex, but similar reduction and ring contraction of adducts formed with ketones proceeds only with difficulty and gives somewhat unstable products. It is generally found though, that transition-metal fluorocarbons are more stable than their hydrocarbon analogs.[5] In this context, the adduct with hexafluoroacetone is known,[6] whereas the



acetone analog is not readily obtained.[2] We therefore investigated the reactions of hexafluoroacetone and trifluoroacetone with $[(Ph_3P)_2PtO_2]$ in an attempt to form stable adducts with varying ring size. The series of complexes reported is probably without precedent in this type of system.

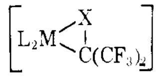
Adducts with Hexafluoroacetone

The reaction between hexafluoroacetone and peroxobis(triphenylphosphine)platinum(II) in a 1:1 mole ratio gave pale green crystals of the product



II

analogous to the compound formed with acetone. The infrared spectrum of this complex shows no bands attributable to ν(C=O), but a weak band at 790 cm⁻¹ due to ν(O—O). The spectrum showed many similarities to those of $[(Ph_3P)_2PtO_2 \cdot (CH_3)_2CO]$ and $[(Ph_3P)_2PtOCO_3]$, which are included in Table I for comparison purposes. The ^{19}F nmr spectrum in CH_2Cl_2 shows a resonance, centered on 77.0 ppm upfield from the external $CFCl_3$ standard, which is observed as a 1:4:1 triplet due to $^{195}Pt-^{19}F$ coupling ($J_{Pt-F} = 6.1 \pm 0.2$ cps). The magnitude of the coupling and the absence of any observable $^{31}P-^{19}F$ coupling indicate that the $C(CF_3)_2$ group is not directly attached to the metal atom. Furthermore, the shift of the ^{19}F resonance signal to higher field on complex formation (the signal due to free hexafluoroacetone was observed at 75.5 ppm) is in line with that of the ^1H resonance signal in the acetone analog. By contrast, it has been shown that in a wide variety of compounds with the structure



(L = phosphine; X = O, S, NH, NMe; M = Pt, Pd, Ni),[6-8] the fluorine resonance position is shifted downfield by about 10 ppm.

The adduct, $[(Ph_3P)_2PtO_2 \cdot HFA]$, unlike the acetone analog, may readily be reduced with triphenylphosphine

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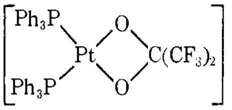
Table I. Infrared Spectra (2000–150 cm^{-1})[a]

Complex	Ref	ν_{as}(C—O) + ligand vib	ν_s-(C—O)	π def	ν(O—O)	δ(C—C) or δ(C=O) + ν(C—O)	ν(M—O)	ν(M—P)	Other
$(Ph_3P)_2PtO_2 \cdot (CH_3)_2CO$	2	1214 (m), 1180 (vs), 1140 (m)	965 (vs)	845 (m)	808 (w)	656 (s), 579 (s)	378 (vs), 298 (vs)	428 (m), 421 (m)	
$(Ph_3P)_2PtO_2 \cdot TFA$		1365 (m), 1210 (sh), 1155 (vs), 1125 (s), 980 (w)	950 (s)	850 (m)	795 (w)	638 (m), 569 (m)	394 (vs), 298 (vs)	427 (sh), 421 (m)	358 (m)
$(Ph_3P)_2PtO_2 \cdot HFA$		1300 (vs),[b] 1285 (m), 1215 (vs), 1195 (vs) 1155 (vs), 1140 (s), 1055 (vs)	975 (vs)	815 (vw)	790 (vw)	637 (w), 570 (sh)	392 (vs), 316 (sh)	428 (w), 420 (m)	326 (m)
$(Ph_3P)_2PtO \cdot HFA$		1310 (s),[b] 1185 (vs), 1130 (m), 1100 (vs)[b]	955 (vs)	785 (m)		637 (w), 596 (s)	436 (s),[c] 356 (vs)	417 (s)[c]	322 (m)
$(Ph_3P)_2PtOCO_3$	2	1678 (vs),[d] 1243 (vs)	978 (s)	836 (sh)	780 (m)	585 (m), 555 (s)	387 (s), 305 (vs)	429 (w)	
$(Ph_3P)_2PtCO_3$	2	1685 (vs),[d] 1185 (s)	980 (s)	815 (s)		675 (sh)	409 (m), 363 (vs)	409 (m)	
$(Ph_3P)_2PtO_2 \cdot 2HFA$		1355 (s), 1285 (s), 1200 (vs, br), 970 (vs), 900 (w), 775 (m),[e] 641 (w), 574 (w), 428 (m), 420 (w), 390 (vs),[f] 367 (sh), 347 (vw), 327 (m), 320 (w), 302 (m),[f] 150 (vs)							

[a] Assignments are based on those of K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," Wiley, New York, N. Y., 1963, p 163, for bidentate carbonate complexes. Bands here were identified by comparison with the spectrum of *cis*-[$(Ph_3P)_2PtCl_2$]. Phosphine bands are not included. [b] Band contains phosphine component. [c] Assignments may be reversed. [d] ν(C=O). [e] Probably ν(O—O). [f] Probably metal–oxygen stretches.

to give a new complex

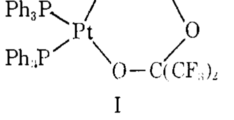


III

as green-yellow crystals in good yield. On conversion of [$(Ph_3P)_2PtO_2 \cdot HFA$] to [$(Ph_3P)_2PtO \cdot HFA$], the ir spectral changes followed the same trends as did those in the peroxocarbonate–carbonate system[2] (included in Table I).

The ^{19}F nmr spectrum again consists of the expected triplet, but it is shifted upfield to be centered at 84.0 ppm (J_{Pt-F} = 6.8 ± 0.2 cps). This shift to still higher field is the same as that observed in the ^1H resonances of the acetone analogs (acetone, 2.17; [$(Ph_3P)_2PtO_2 \cdot (CH_3)_2CO$], 1.60; [$(Ph_3P)_2PtO \cdot (CH_3)_2CO$], 1.30 ppm downfield from TMS).

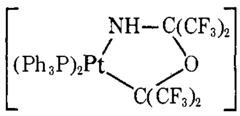
The reaction of an excess (twofold or more) of hexafluoroacetone with [$(Ph_3P)_2PtO_2$] gives white crystals of a new compound, [$(Ph_3P)_2PtO_2 \cdot 2HFA$], which has a novel seven-membered ring structure incorporating a peroxo group



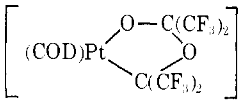
I

Several pieces of evidence are consistent with this formation.

Firstly, the presence of two nonequivalent $C(CF_3)_2$ groups is indicated by the ^{19}F nmr spectrum which consists of two complex multiplets of equal intensity, probably due to both Pt–F and F–F coupling, centered at 76.8 and 78.2 ppm above $CFCl_3$. The upfield shift of the resonance positions (from that of the free ligand) indicates that the $C(CF_3)_2$ groups are not directly attached to the metal, since it has been shown that the ^{19}F nmr spectra of



(or the isomer with a Pt–O bond) and



(COD = cyclooctadiene), consist of two signals, at 64.1 and 81.0 and at 68.1 and 81.4 ppm, respectively.[8] In the former case, it has been shown that the lower field band is due to the $C(CF_3)_2$ group directly attached to the metal. Concerning the spectrum of [$(Ph_3P)_2PtO_2 \cdot 2HFA$], one might speculate that, by analogy with the results obtained for the complexes [$(Ph_3P)_2PtO_2 \cdot HFA$] and [$(Ph_3P)_2PtO \cdot HFA$], the higher field line is due to the group closest to the metal and the lower field line to the group directly attached to the peroxo group.

Secondly, the infrared spectrum of [$(Ph_3P)_2PtO_2 \cdot 2HFA$] (Table I) shows no band attributable to ν(C=O) (highest energy band is at 1355 cm^{-1}), precluding any structures of the type $>C{=}O{\rightarrow}Pt$, but a band of medium intensity at 775 cm^{-1} is observed which is probably ν(O-O). A detailed analysis of the spectrum has not been attempted, but the complexity of the spectrum in the low-energy region (below 400 cm^{-1}) is consistent with the large "floppy" ring structure.

Thirdly, on standing in or recrystallizing from CH_2Cl_2, the complex loses one molecule of ligand and [$(Ph_3P)_2PtO_2 \cdot HFA$] is formed. This decomposition may be followed by ^{19}F nmr which shows a decrease in intensity of the bands associated with the initial complex, and growth of new bands at 77.0 and 75.5 ppm. The former was a triplet associated with the platinum complex, the latter a sharp singlet due to free ligand. On prolonged standing of this solution, the free ligand reacts further to give unidentified species with ^{19}F nmr lines at 80.7 and 83.3 ppm, both of which are sharp singlets. Intensity studies show that these new species are not formed at the expense of the platinum complex, $[(Ph_3P)_2PtO_2\cdot HFA]$, so we conclude that the compounds contain no platinum.

The reverse of this reaction, the ring expansion

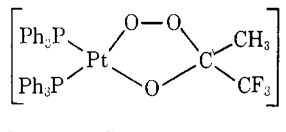
$$\underset{\text{II}}{[(Ph_3P)_2PtO_2\cdot HFA]} + HFA \longrightarrow \underset{\text{I}}{[(Ph_3P)_2PtO_2\cdot 2HFA]}$$

does not take place, even in the presence of a large excess of hexafluoroacetone under moderate pressure (2–3 atm). Only the starting materials could be isolated from the reaction mixture, even after several months. This is relevant to the mechanism of formation of the complexes, since it indicates that II is not an intermediate in the formation of I. The evidence further suggests that I and II are formed by two separate reaction paths which, in the former case, would require either some prior association of the ligand or the formation of some 2:1 transition species which may then rearrange to give I. There is no published evidence for dimerization of the ligand in the gas phase or in solution,[9] but dimerization may be promoted by the presence of the platinum complex. Low-temperature nmr studies (*ca.* $-80°$) showed no evidence for the formation of analogs of I with either trifluoroacetone or acetone.

Both $[(Ph_3P)_2PtO_2\cdot 2HFA]$ and $[(Ph_3P)_2PtO_2\cdot HFA]$ will liberate iodine from acidified iodide solution (though as noted previously,[2] the reaction is not strictly quantitative), but the complex $[(Ph_3P)_2PtO\cdot HFA]$, which has no peroxo group, does not.

Adducts with Trifluoroacetone

Trifluoroacetone reacts rapidly with $[(Ph_3P)_2PtO_2]$ to give the complex



analogous to the hexafluoroacetone and acetone adducts. The ^{19}F nmr spectrum consists of an ill-resolved quartet centered at 78.2 ppm. J_{F-H} was estimated at 1.7 cps, but the spectrum was not sufficiently resolved to enable an accurate determination of J_{Pt-F}. The ^1H nmr spectrum (in $CDCl_3$) consisted of two bands, intensities 30 H:3 H, at 7.24 and 1.48 ppm downfield from TMS, corresponding to the phenyl and methyl protons, respectively. The latter band was likewise split by H–F coupling into a quartet. Corresponding values for the free ligand are: ^{19}F, 80.8 ppm; ^1H, 2.40 ppm; $J_{H-F} = 1.0$ cps. No $^{195}Pt-^1H$ coupling was observed in this or any other adducts of this type.

Attempts to reduce $[(Ph_3P)_2PtO_2\cdot TFA]$ to the complex containing a four-membered ring were unsuccessful. This is surprising, since the properties of the trifluoroacetone adduct might be expected to be intermediate between those of hexafluoroacetone and acetone. This is true to some extent, in that both hexafluoroacetone and trifluoroacetone will displace acetone from the complex $[(Ph_3P)_2PtO_2\cdot(CH_3)_2CO]$ and that hexafluoroacetone will displace trifluoroacetone from $[(Ph_3P)_2PtO_2\cdot TFA]$, but in general, trifluoroacetone seems to resemble acetone much more closely than the perfluoro derivative. Thus, neither of the former will react with $[(Ph_3P)_4Pt]$ in the absence of oxygen, and neither will add more than one molecule to $[(Ph_3P)_2PtO_2]$, in contrast to the reactions of hexafluoroacetone. There was no evidence for the formation of any "mixed" complexes of the type $[(Ph_3P)_2PtO_2\cdot HFA\cdot TFA]$.

Experimental Section

Materials. Hexafluoroacetone (cylinder) was obtained from Matheson Co. and trifluoroacetone from Peninsular Chemresearch Inc. Both were used without further purification. $[(Ph_3P)_2PtO_2]$ was prepared from $[K_2PtCl_4]$ (Engelhard) *via* the tetrakis(triphenylphosphine)platinum(0) intermediate.[1,10] Triphenylphosphine (Cincinnati Malacron) was recrystallized from ethanol before use.

Preparation of the Complexes. $[(Ph_3P)_2PtO_2\cdot 2HFA]$ could be isolated in almost quantitative yield from the reaction of an excess (usually about sixfold) of hexafluoroacetone with a solution of $[(Ph_3P)_2PtO_2]$ (0.75 g, 1 mmol) in the minimum of methylene chloride (*ca.* 5 ml). The solution was frozen in liquid nitrogen and evacuated, and the ligand was distilled into the reaction vessel. The vessel was then sealed and allowed to stand at room temperature overnight. The yellow-orange solution slowly turned colorless, and well-formed white crystals separated. These were filtered off, washed with ether, and dried *in vacuo*, mp 215–216° dec (complex probably decomposes below melting point to $[(Ph_3P)_2PtO_2\cdot HFA]$; see below).

Anal. Calcd for $C_{42}H_{30}F_{12}O_4P_2Pt$: C, 46.5; H, 2.8; F, 21.0; P, 5.7. Found: C, 46.8; H, 2.8; F, 20.4; P, 5.7.

$[(Ph_3P)_2PtO_2\cdot HFA]$ was obtained in good yield as very pale green crystals by a procedure analogous to that described above, but using a 1:1 ratio of the reactants. This complex could also be obtained by recrystallizing the above adduct from CH_2Cl_2; mp 215–216° dec.

Anal. Calcd for $C_{39}H_{30}F_6O_3P_2Pt$: C, 51.0; H, 3.3; F, 12.4; P, 6.8; Pt, 21.3. Found: C, 51.1; H, 3.3; F, 12.2; P, 6.8; Pt, 21.5.

$[(Ph_3P)_2PtO\cdot HFA]$ was prepared by refluxing $[(Ph_3P)_2PtO_2\cdot HFA]$ (0.92 g, 1 mmol) for 2 days in methylene chloride solution (25 ml) under nitrogen and in the presence of an excess of triphenylphosphine (*ca.* 2 g). The product was separated by addition of ether and recrystallized from methylene chloride: yield, 75%; mp, 221–223° dec.

Anal. Calcd for $C_{39}H_{30}F_6O_2P_2Pt$: C, 51.9; H, 3.4; F, 12.6. Found: C, 51.6; H, 3.4; F, 12.3.

$[(Ph_3P)_2PtO_2\cdot TFA]$. Addition of trifluoroacetone dropwise to a solution of $[(Ph_3P)_2PtO_2]$ (0.75 g, 1 mmol) in methylene chloride (10 ml) caused the orange solution to turn pale green. When ether was added, the pale green crystalline complex precipitated. The complex was filtered off, washed with ether, and dried *in vacuo*: yield, 0.75 g, *ca.* 80%; mp, 175–177° dec.

Anal. Calcd for $C_{39}H_{33}F_3O_2P_2Pt$: C, 54.2; H, 3.8; P, 7.2. Found: C, 54.1; H, 3.8; P, 7.4.

Physical Measurements. Infrared spectra were recorded on a Perkin-Elmer 700 (2000–650 cm^{-1}), a Beckman IR4 (2000–350 cm^{-1}), and a Perkin-Elmer FIS-3 (400–150 cm^{-1}). Instruments were calibrated with a polystyrene film (2000–650 cm^{-1}) and atmospheric water vapor (650–150 cm^{-1}), and results reported are generally correct to $\pm 2\ cm^{-1}$ (except $\pm 5\ cm^{-1}$ on the P-E 700). Mulls were prepared in Nujol and run between NaCl and CsBr windows (2000–350 cm^{-1}) and in Vaseline between polyethylene plates (400–150 cm^{-1}).

Proton nmr spectra were recorded on a Varian A60 instrument using an internal TMS standard, and ^{19}F nmr spectra were obtained on a Varian DP60 operating at 56.4 mcps using an external $CFCl_3$ standard.

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