Platinum(IV) Complexes with π-Acceptor Ligands

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Summary Complexes of the type $[NBu^n_4][PtX_5(PY_3)]$ (X = Cl or Br; Y = F, Cl, Br, or OMe) have been prepared, and the anions $[PtX_5(CO)]^-$ identified in solution; the relationship between Pt–donor atom n.m.r. couplings of these and corresponding Pt^{II} complexes is discussed.

Carbon monoxide and phosphorus trifluoride are classical examples of π-acceptor ligands, and as such have the characteristic of forming stable complexes with electron-rich transition elements in low oxidation states. Thus, reports of their complexes with metals in high (formal) oxidation states are rare, especially it appears for PF_3. There are several examples of stable CO complexes of trivalent metals, *e.g.* $[MCl_5(CO)]^{2-}$ and $[MCl_3(CO)(PR_3)_2]$ (M = Rh or Ir[1,2]) but only one for PF_3, $[RhCl_3(PF_3)(PPh_3)_2]$.[3] We can find no record of such complexes with metals in a higher oxidation state than +3.

We find that the salts $[NBu^n_4][PtX_3(PF_3)]$ (X = Cl or Br)[4] in dichloromethane solution are readily oxidised by dihalogen to give $[NBu^n_4][PtX_5(PF_3)]$ which are easily isolated as stable solids (in absence of moisture) having satisfactory elemental analyses. The related Pt^{IV} complex anions, $[PtX_5\{P(OMe)_3\}]^-$, $[PtX_5(PCl_3)]^-$, and $[PtBr_5(PBr_3)]^-$ were formed similarly (the bromo complexes were isolated and characterised).

Although the formation of the corresponding CO complexes seemed unlikely, we attempted the oxidation of $[PtCl_3(CO)]^-$ with an almost stoicheiometric amount of dichlorine. The dichloromethane solution immediately became golden yellow in colour, characteristic of Pt^{IV} chloro-complexes, and in the i.r. spectrum, ν_{CO} of $[PtCl_3(CO)]^-$ (2 098 cm^{-1})[5] was largely replaced by a band at 2 184 cm^{-1}. Even when dihalogen is in excess, some of the Pt^{II} anion remains (*ca.* 5%); periodic re-measurement of the i.r. spectrum shows that after an induction period, which seems to be related to the amount of excess dihalogen, the new complex is gradually transformed back to $[PtCl_3(CO)]^-$. We presume that this platinum system acts as a catalyst for the chlorination of the solvent. The bromo-anion behaves similarly with Br_2 and using *ca.* 70% ^{13}CO enriched $[PtBr_3(CO)]^-$ we have obtained the ^{13}C n.m.r. parameters of the new complex {The central feature of $[PtBr_3(CO)]^-$ was also visible in the spectrum showing that interconversion is not rapid}. Because of the equilibrium with and reversion to $[PtX_3(CO)]^-$, we have not been able to isolate these new carbonyl complexes but in view of the increase of ν_{CO} and reduction of $^1J(PtC)$ (Table), there can be little doubt that they are the Pt^{IV} derivatives $[PtX_5(CO)]^-$.

The CO stretching frequency of $[PtCl_5(CO)]^-$ is the highest reported for a metal carbonyl complex in solution. The values for the complexes with both halides indicate an increase of *ca.* 8% in the CO force constant on oxidation of the metal which must be largely due to the loss of π-donation from the metal. The PF_3 complexes should also suffer some loss of π-back donation on oxidation and we

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TABLE. Effect of oxidation state on ^{195}Pt–donor atom spin–spin coupling constants

	^1J(PtA)[a]/Hz			^1J(PtA)[a]/Hz		
L	$[PtCl_3L]^-$	$[PtCl_5L]^-$	$^1J(Pt^{IV}A)/^1J(Pt^{II}A)$	$[PtBr_3L]^-$	$[PtBr_5L]^-$	$^1J(Pt^{IV}A)/^1J(Pt^{II}A)$
PF_3	7 464[b,c]	4 400[b]	0·589	7 257[b,c]	4 368[b]	0·602
PCl_3	6 182[c,d]	3 135[b]	0·507	5 869[c,d]	2 900[b]	0·494
PBr_3				5 214[c,d]	2 306[e]	0·442
$P(OMe)_3$	6 020[b,c]	3 630[d]	0·603	5 932[b,c]	3 707[d]	0·625
PMe_3	3 675[b,f]	2 119[b,f]	0·577	3 542[b,f]	2 095[b,f]	0·594
CO				1 720[b]	1 225[b]	0·712

[a] A = ^{31}P or ^{13}C, respectively. [b] In CH_2Cl_2 or CH_2Cl_2–CD_2Cl_2. [c] Ref. 4. [d] In $CDCl_3$. [e] In CH_2Cl_2–$CDCl_3$. [f] P. L. Goggin, R. J. Goodfellow, S. R. Haddock, J. R. Knight, F. J. S. Reed, and B. F. Taylor, *J.C.S. Dalton*, 1974, 523.

were interested to see what effect this might have on ^1J(PtP).

Venanzi[6] has argued that if π-bonding is significant in the stability of a Pt–P bond then this will produce a synergic enhancement of the σ-bond which in turn should have a noticeable effect on ^1J(PtP). As π-bonding is unlikely to be significant for any Pt^{IV} complex, the decrease in ^1J(PtP) that occurs on oxidation should be greater if π-bonding was present in the Pt^{II} species. For trialkylphosphines the ratio $^1J(Pt^{IV}P):{}^1J(Pt^{II}P)$ is close to 0·6:1 and it is clear from the results in the Table that PF_3 and $P(OMe)_3$ do not show any different behaviour. Whilst it might be inferred that there is no π-bonding even in $[PtX_3(PF_3)]^-$ we prefer the explanation that π-bonding does not necessarily result in a lower ratio of $^1J(Pt^{IV}P):{}^1J(Pt^{II}P)$. The latter view is supported by the ratio of $^1J(Pt^{IV}C):{}^1J(Pt^{II}C)$ found for the carbonyl system which is actually significantly higher than 0·6:1. Much lower ratios of $^1J(Pt^{IV}P):{}^1J(Pt^{II}P)$ are found for the complexes of PCl_3 and especially PBr_3 but here the cause is clearly not π-bonding but steric hindrance between these bulky ligands and the *cis* halides on the metal[4] which double in number on oxidation.

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