Cationic Carbonyl Complexes of Platinum and Iridium

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THE recent synthesis of cationic carbonyl complexes of palladium[1] and platinum[1,2] prompts us to report a more convenient reaction which we have used to prepare a wide range of cationic carbonyl complexes of platinum and iridium. In the presence of sodium perchlorate, *cis-* or *trans-*$PtCl_2(PEt_3)_2$ react immediately with one mole of CO under ambient conditions in acetone solution to give *trans*-$PtCl(CO)(PEt_3)_2^+ ClO_4^-$ in quantitative yield. Cationic hydrido- and aryl-platinum carbonyl complexes may be similarly prepared. The reaction of *trans*-$PtHCl(PEt_3)_2$ to yield *trans*-$PtH(CO)(PEt_3)_2^+ClO_4^-$ may be contrasted with its reaction with CO under pressure in the presence of aqueous tetrafluoroboric acid to give the chlorocarbonyl cation.[2]

Many π-bonding ligands other than CO are equally effective in displacing halogen under these conditions. For example, Me_3CNC reacts with *trans*-$PtHCl(PEt_3)_2$ to yield *trans*-$PtH(CNCMe_3)(PEt_3)_2^+ ClO_4^-$, the first reported complex containing both isocyanide and hydride ligands.

Under the same conditions as for the platinum complexes, iridium compounds behave rather differently and *e.g.*, $IrCl(CO)(PPh_3)_2$ takes up *two* moles of CO giving $Ir(CO)_3(PPh_3)_2^+$. The n.m.r. spectrum of the analogous diphenylmethylphosphine complex indicates that the phosphines are *trans*; although ideally the triphenylphosphine cation has D_{3h} symmetry, the appearance of three CO frequencies in the i.r. spectrum implies some slight distortion due to interaction with the anion or

TABLE

Complex[a]	ν_{CO}[a] (cm.$^{-1}$)	ν_{M-H}[b] (cm.$^{-1}$)	τ_{MH}[b]
trans-$PtCl(CO)(PEt_3)_2^+$	2109s	—	—
trans-$PtH(CO)(PEt_3)_2^+$	2064s	2167s[c]	14·78
trans-$Pt(p\text{-}FC_6H_4)(CO)(PEt_3)_2^+$	2098s	—	—
trans-$PtH(CNCMe_3)(PEt_3)_2^+$	2203s (NC)	[d]	17·09
$Ir(CO)_3(PPh_3)_2^+$	2010s, 2018s, 2080w	—	—
$Co(CO)_3(PPh_3)_2^+$	2006s, 2013s, 2073w	—	—
$Ir(CO)[P(OMe)_3]_2(PPh_2Me)_2^+$	1953s	—	—

[a] Satisfactory analyses have been obtained for all complexes as their perchlorate salts.
[b] In $CHCl_3$ solution.
[c] Deuteriation studies indicate strong coupling of the CO and MH vibrations.
[d] Not observed. In the deuteride ν_{NC} is at 2194 cm.$^{-1}$.

solvent. (We have prepared the analogous cobalt complex[3] as its perchlorate salt, and this has an i.r. spectrum in chloroform solution almost identical with that of the iridium complex.) Again, other π-bonding ligands are effective in the reaction, *e.g.*, reaction of $IrCl(CO)(PPh_2Me)_2$ with $P(OMe)_3$ gives $Ir[P(OMe)_3]_2(PPh_2Me)_2(CO)^+$ ClO_4^-. A representative list of the complexes we have prepared is given in the Table.

The five co-ordinate iridium complexes are of interest as potential hydroformylation catalysts, although preliminary studies indicate that the tricarbonyl complex is less effective than the known catalyst $Ru(CO)_3(PPh_3)_2$.[4] This is probably due to the ease with which the iridium complex undergoes oxidative addition reactions to give stable six-co-ordinate products. Thus hydrogen at pressures of less than one atmosphere displaces CO from $Ir(CO)_3(PPh_2Me)_2^+$ giving $IrH_2(CO)_2(PPh_2Me_2)_2^+$ (τ_{MH}, 20·4 p.p.m.; J_{PH} 15·0 c./sec.).

Analogous chloro-complexes of palladium(II), nickel(II), and rhodium(I) do not react with CO at atmospheric pressure in the presence of sodium perchlorate.

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