Hydrostannation of Some Iridium(I) Complexes

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Hydrometallation of unsaturated molecules provides an important method for the preparation of organometallic compounds (*e.g.* from olefins or isocyanates of compounds having M–C or M–N bonds). By analogy, hydrometallation of co-ordinatively-unsaturated inorganic complexes should afford a general method for the synthesis of compounds which have metal–metal bonds. Hitherto, this has been investigated for hydrosilation;[1–3] but the sole adducts stable in solution were those formed from chloro- or ethoxy-silanes and $RhCl(PPh_3)_3$.[2,3] There is evidence of $HGeX_3$ addition to Pt^{II}, but six-co-ordinate $L_4Pt(GeX_3)H$ complexes have not been isolated.[4]

We now report the hydrostannation of some d^8 Ir^I complexes (I) (L = PPh_3, PPh_2Me, or $PPhEt_2$; X = Cl, Br, or I; and R = Ph, Me, or Et) to give the stable d^6 species (II) or, in two cases, (III) [the yellow complexes, with L = PPh_3, X = Cl or Br, and R = Me, obtained by use of benzene as the reaction medium; the white isomers (II) were obtained when Me_3SnH also served as solvent].

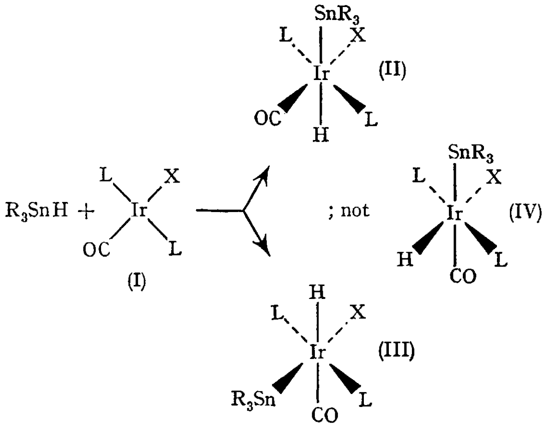
It is interesting that (i) hydrostannation of *trans*-$IrClCO(PPh_3)_2$ by Ph_3SnH was not effected in tetrahydrofuran, but was readily accomplished at *ca.* 20° in benzene, diethyl ether, or R_3SnH as solvent; and (ii) the reactions proceed equally readily with protic (Ar_3SnH) or hydridic (Alk_3SnH) stannanes. Instability in air, and solubility in organic solvents of (II) and (III) increased in

Spectral data for R_3Sn(H *or* D)$IrXCOL_2$

R, H or D, X, and L in R_3Sn(H or D)$IrXCOL_2$	ν(IrH) or ν(IrD) (cm.$^{-1}$)	ν(CO) (cm.$^{-1}$)	ν(IrCl) (cm.$^{-1}$)
Me, H, Cl, PPh_3[a,e]	2080[c]	1963[c]	290
Me, D, Cl, PPh_3[a]	1508[c]	1993[c]	290
Me, H, Br, PPh_3[a,f]	2080	1963	
Me, H, Cl, PPh_3[b]	2093[c]	1998[c]	299
Me, D, Cl, PPh_3[b]	1503[c]	1998[c]	297
Me, H, Cl, PPh_2Me[b]	2065	1980	297
Ph, H, Cl, PPh_3[b,d]	2138	1998	300
Ph. D, Cl, PPh_3[b,d]	1530	1998	300
Ph, H, Br, PPh_3[b,d]	2138	1998	
Ph, D, Br, PPh_3[b,d]	1530	1998	
Ph, H, I, PPh_3[b,d]	2140	1997	
Ph, H, Cl, PPh_2Me[b,d] ..	2073[c]	2005[c]	305
Ph, D, Cl, PPh_2Me[b,d] ..	1483[c]	2005[c]	307

[a] Assigned structure (III); [b] Assigned structure (II); [c] KBr disc; all other i.r. data are on Nujol mulls; [d] $\nu_{sym.}$ ($SnPh_3$), 247—248 cm.$^{-1}$; [e] ^1H n.m.r. signals (rel. intensity) (assignment) in $CDCl_3$: τ 10·01(9) Me_3Sn), τ 2·61(33) (Ph_3P), τ 20 (IrH); [f] ^1H n.m.r. signals (rel. intensity) (assignment) in $CDCl_3$: τ 10·03(9) (Me_3Sn), τ 2·6(34) (Ph_3P).

the series: L/R = PPh_3/Ph < PPh_2Me/Ph < PPh_3/Me < PPh_3/Et < PPh_2Me/Me. Thirteen of the complexes (II) and (III) (*cf.* ref. 5 for other compounds with R_3Sn–Ir bonds) have been characterised by (i) elemental analyses, (ii) molecular weights (isopiestic in benzene for five of the soluble compounds), and (iii) spectral data (see Table).



In order to assign configurations, the simplifying assumption was made that the phosphine ligands are *trans* [*i.e.*, the possible structures are now (II)—(IV)];[6] this was proved for $Ph_3SnIrHClCO(PPh_2Me)_2$ by the observation (in the n.m.r. spectrum) of virtual coupling[7] between the PPh_2Me ligands (P–Me triplet; τ 8·2; apparent coupling constant = 9 c,/sec.). The configuration of the complexes (II) is now assigned on the following basis. (*a*) The Ir–H stretching frequency in related (Cl, Br, or I) complexes is independent of X; this makes (IV) unlikely.[8] (*b*) The position of ν(Ir–Cl) for (III) [CO < R_3Sn ≃ Me < H in *trans* influence in Pt^{II} complexes][9] or (IV) would be expected[10] at 260—290 cm.$^{-1}$. (*c*) There is no significant ν(IrH)–ν(CO) vibrational interaction (as shown by comparing hydrides and deuterides) as would have been expected[11] from (III).

Similar arguments, and especially the evidence of strong ν(IrH)–ν(CO) interaction, served for the assignment of the yellow halogenohydrido(trimethylstannyl)carbonylbis(triphenylphosphine) complexes (III).

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