Formation of Germyliridium Hydrides

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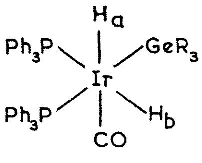
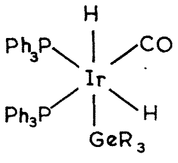
THE addition of trimethyl- or triethyl-germane to *trans*-$(Ph_3P)_2Ir(CO)Cl$ unexpectedly produces the 6-co-ordinate dihydrido-complex (1; R = Me or Et). This contrasts strikingly with analogous hydrosilation[1,2] and hydrostannation[3] reactions where addition of R_3MH occurs to yield $(Ph_3P)_2(R_3M)(CO)Ir(H)Cl$ (M = Si or Sn; R = alkyl, alkoxy, or halide).

$$\begin{aligned}&\textit{trans}\text{-}(Ph_3P)_2Ir(CO)Cl + 2R_3GeH \rightarrow\\ &\qquad R_3GeCl + \underset{(1)}{(Ph_3P)_2Ir(CO)(H)_2GeR_3}\\ &\qquad + (H_2 + R_6Ge_2)\end{aligned}$$

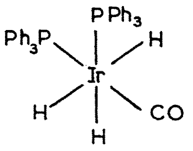
The trialkylgermane reactions require several weeks at 20° or 12 hr. in benzene under reflux; the trialkylchlorogermane is isolated together with traces of hydrogen and hexa-alkyldigermane. The complexes (1) are cream crystalline solids, stable to air and not decomposed or dissociated in solution, unlike the silicon– and tin–iridium compounds. The ^1H n.m.r. spectra are consistent only with structures (1) or (2), and the absence of long-range coupling, *trans*-^1H-Ir-Ge-CH_2, tends to eliminate (2). The non-equivalence of the two P atoms is clear from the spectra at 220 Mc./sec. (Figure). I.r. data (Table) substantiate (1)† since, if R_3Ge



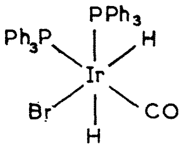
(1)



(2)



(3)



(4)

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† A crystal structure analysis of (1; R = Me) by Mr. M. L. Schneider and Dr. H. M. M. Shearer is in progress.

were *trans* to H, a low Ir–H stretching frequency would be expected, due to the extremely high *trans* effect of the R_3Ge group.[4] Moreover the closeness of ν(Ir–H) and ν(C≡O) for the two complexes (R = Me and Et) suggests that the R_3Ge group is *cis* to both metal–hydrogen atoms.

Spectroscopic data for $(Ph_3P)_2Ir(CO)(H)_2(GeR_3)$

R	^1H n.m.r. τ(CH_2)	^1H n.m.r. τ(CH_3)	ν(Ir–H), ν(C≡O) (cm.$^{-1}$)	
Me		9·20	2123, 2071, 1956	(KBr)
			2114(sh), 2076, 1969	(C_6H_{12})
Et	8·89	8·72	2119, 2081, 1953	(KBr)
			2124, 2077, 1966	(C_6H_{12})

The mechanism of the reaction may involve addition of R_3GeH to the iridium complex followed by a *cis*-elimination of R_3GeCl, yielding as intermediate the known[5] compound *cis*-$(Ph_3P)_2Ir(CO)H$.

$$trans\text{-}(Ph_3P)_2Ir(CO)Cl + R_3GeH \rightarrow cis\text{-}(Ph_3P)_2Ir(CO)H + R_3GeCl$$

$$cis\text{-}(Ph_3P)_2Ir(CO)H + R_3GeH \rightarrow (1)$$

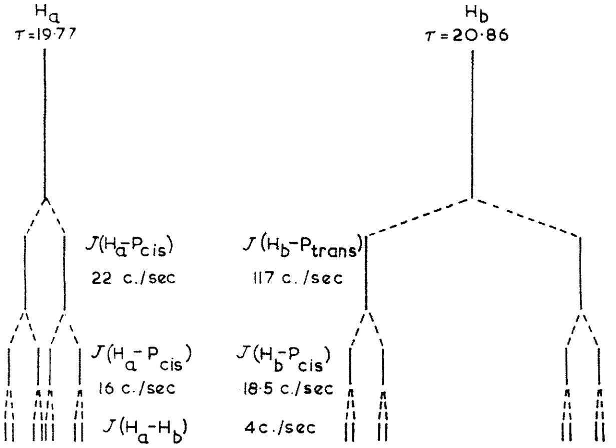

FIGURE. *High field* ^1H *n.m.r. spectrum of* $(Ph_3P)_2Ir(CO)(H)_2GeEt_3$ (1).

A reaction in which equimolar ratios of reactants were used gave (1) and unchanged $(Ph_3P)_2Ir(CO)Cl$, and the presence of a base (Et_3N) did not affect the reaction. Triphenylgermane combines with $(Ph_3P)_2Ir(CO)Cl$ only under more forcing conditions, and tri-isopropylgermane does not react, possibly for steric reasons. The triethylphosphine-iridium complex $(Et_3P)_2Ir(CO)Cl$ and trimethylgermane react differently from the triphenylphosphine analogue:

$$2Me_3GeH + cis\text{-},trans\text{-}(Et_3P)_2Ir(CO)Cl \downarrow Me_6Ge_2 + (Et_3P)_2Ir(CO)(H)_2Cl$$

The Ir–Ge bond in (1) is cleaved by hydrogen chloride and by 1,2-dibromoethane.

$$(1;R = Me) \xrightarrow{HCl} (Ph_3P)_2Ir(CO)Cl + (3) + Me_3GeCl + (\text{some } Me_6Ge_2 + Me_3GeH + H_2)$$

$$(1;R = Me) \xrightarrow{C_2H_4Br_2} (Ph_3P)_2Ir(CO)Br + (4) + Me_3GeBr + C_2H_4 + H_2$$

Complex (3) is known;[5] (4) was characterised by elemental analysis and comparative i.r. spectra[6] [ν(IrH) and ν(CO)(KBr) 2232, 2073, and 2028 cm.$^{-1}$].

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