A New Synthesis of Silyliridium Hydrides

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Summary Silyliridium hydrides may be prepared by the reaction: $IrCl(CO)(PPh_3)_2 + R_3SiH \rightleftharpoons IrHCl(SiR_3)(CO)(PPh_3)_2 \xrightarrow{R_3SiH} IrH_2(SiR_3)(CO)(PPh_3)_2 + R_3SiCl$.

IT was shown[1] that trialkylgermanium hydrides react irreversibly with *trans*-$IrCl(CO)(PPh_3)_2$.

$$IrCl(CO)(PPh_3)_2 + 2R_3GeH \rightarrow R_3GeCl + IrH_2(GeR_3)(CO)PPh_3)_2 \qquad (1)$$

This was contrasted with the analogous reactions with silicon hydrides[2] and tin hydrides.[3]

$$IrCl(CO)(PPh_3)_2 + R_3MH \rightarrow IrHCl(MR_3)(CO)(PPh_3)_2 \quad (2)$$

One would not expect such completely different behaviour on substituting germanium for silicon so we have re-examined our results[2] for the latter element. We find that the following reactions occur for silicon, which reconcile apparently conflicting earlier reports.

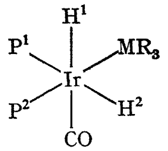
$$\begin{tikzcd}[column sep=small] \underset{\text{(I)}}{IrCl(CO)(PPh_3)_2} + R_3SiH \arrow[r, phantom, "\rightleftharpoons"] & \underset{\text{(II)}}{IrHCl(SiR_3)(CO)(PPh_3)_2} \arrow[d] & & (3) \\ \text{(III)} \quad IrH(CO)(PPh_3)_3 + R_3SiH \arrow[r, shift left, "25^\circ"] & IrH_2(SiR_3)(CO)(PPh_3)_2 + PPh_3 \arrow[l, shift left, "C_6H_6"] & \text{(IV)} & (4) \end{tikzcd}$$

Our earlier results reported the reversible formation of (II) when R was an electronegative group such as OEt or Cl. When R is alkyl, there is no obvious reaction, presumably because the adduct (II) is less stable and the equilibrium greatly favours (I). Evidence of a reaction comes from the report that the exchange reaction

$$R^1{}_3SiH + R^2{}_3SiD \rightleftharpoons R^1{}_3SiD + R^2{}_3SiH \qquad (5)$$

is catalysed by (I).[4] Further, if a suspension of (I) is heated under reflux overnight in triethylsilane or for 3 days in a mixture of triethylsilane and benzene, a clear solution is formed containing the adduct (IV). Adducts such as (IV) have also been reported by the reaction of silicon hydrides with (III)[5] so we have used both methods of preparation. We find that for R = Et, compounds having identical n.m.r. spectra (τ 19—22) are formed by the two methods, further, variation of the concentration of triethylsilane or triphenylphosphine altered the ratio of (III) to (IV), clearly indicating the equilibrium depicted. That oxidative addition to (III) should occur more readily than to (I) is to be expected in view of the greater electron-releasing properties of H as compared with Cl.[5] The adducts (IV) for M=Si[5] and Ge[1] have previously been identified as having the stereochemistry of (IV′). In view of the closely similar n.m.r. spectrum found for the triethylsilane adduct, the latter is assigned the same structure.

The adduct (II) was re-examined for triethoxysilane. Previous attempts to characterize it by n.m.r. failed because of its lack of solubility.[2] It was expected, though, that in view of the results with tin hydrides,[3] a number of isomeric adducts might be formed. A saturated solution of (I) in benzene was treated with a large excess of triethoxysilane and the solution was gradually concentrated by distillation *in vacuo*. When precipitation began, the mixture was centrifuged and the saturated solution examined by n.m.r.



(P=PPh$_3$)

(IV′)

A triplet centred at τ 16·1 was clearly discernible. Such a low chemical shift suggests a group *trans* to hydrogen with an extremely large *trans*-effect such as $Si(OEt)_3$. Silicon hydrides add *cis* to (III)[5] but addition to (I) could be accompanied by isomerization of (II). Tin hydrides also form *trans*-adducts with (I).[3] After 12 hr. the signal at τ 16·1 was no longer evident. A similar experiment in chloroform gave rise to a similar triplet at τ 16·34. The expected adduct should have two phosphines *cis* to hydrogen in which case *J*(P–H) is 14Hz. in both solvents, which is in the expected range. As in benzene, however, further reaction occurs since the signal decreased in size until after 2 hr. it was replaced by what appeared to be two overlapping triplets at τ 17·3.

Saturated solutions of the triethoxysilane adduct (II), free from excess of silane, were also examined in a variety of solvents. Signals similar to that found in chloroform at τ17·3 were found in pyridine, 1,2-dichloroethane, and dichloromethane. In the latter solvent the signal, which appeared at τ 17·0, decreased slowly in intensity, to be replaced after 3 hr. by a complex signal at τ 20 closely similar to that observed for a solution of the adduct (IV) prepared from (III).[5] The conversion of (II) into (IV) therefore appears to occur more readily for triethoxysilane than triethylsilane. When (I) was heated under reflux in a mixture of benzene and triethoxysilane (50/50 v/v) overnight, a clear solution was obtained which gave a complex signal centred at τ 21·5. This was not the adduct (IV), but was presumably a mixture of products of its further reaction.

Conversion of (I) into (IV) must occur by the elimination of the chlorosilane from (II). A similar reaction occurs with Pt^{II}.[2]

$$PtCl_2(PBu_3)_2 + R_3SiH \rightarrow PtHCl(PBu_3)_2 + R_3SiCl \quad (6)$$

Addition of R_3SiH to $IrH(CO)(PPh_3)_2$, as suggested by Glockling and Wilbey,[1] would then account for the formation of (IV).

Since the adduct (IV) is formed, by this route, free of triphenylphosphine, the less stable adducts (R = alkyl) are formed more quantitatively than from (III). In the preparation of (IV; R = Et) from (I) the solvents were removed on a vaccuum transfer line while heating to 60°. No decomposition of (IV) occurred until temperatures of 100—120° were used, when triethylsilane distilled off and n.m.r. examination of the product revealed the formation of some (III). No evidence for the formation of $IrH(CO)(PPh_3)_2$ was found, probably because of its disproportionation to (III).[6]

Reactions similar to (3) are to be expected for germanium when R is sufficiently electronegative. Presumably conversion of the germanium and tin analogues of (II) into (IV) could also be effected.

Catalysis of reaction 5 by (I)[4] could involve (IV) as the catalytic intermediate *e.g.*

$$IrH(CO)(PPh_3)_2 + R_3SiD \rightleftharpoons$$
$$IrHD(SiR_3)(CO)(PPh_3)_2 \rightleftharpoons IrD(CO)(PPh_3)_2 + R_3SiH$$

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