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Preliminary communication

INTERNALLY METALLATED TRIS(TRIPHENYLPHOSPHINE)-IRIDIUM(I)

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Summary

Treatment of $(Ph_3P)_3IrCl$ with 1-Li-2-R-1,2-$B_{10}C_2H_{10}$ in ether gives the internally metallated complex $(PPh_3)_2\overline{Ir(PC}_6H_4Ph_2)$.

Transition metal complexes incorporating 1,2- and 1,7-dicarba-*closo*-dodecaborane(12) (carb) ligands linked by metal—carbon σ bonds of the types $(PPh_3)_2Rh(\sigma\text{-carb})$ and $(PPh_3)_2Ir(CO)(\sigma\text{-carb})$, were recently made by reactions of lithium—carborane derivatives with $(PPh_3)_3RhCl$ and $(PPh_3)_2Ir(CO)Cl$ [1,2]. We find in contrast that the reaction between $(PPh_3)_3IrCl$ and 1-Li-2-R-1,2-$B_{10}C_2H_{10}$ ($R = CH_3$ and C_6H_5) does not give iridium—carborane complexes, and the internally metallated complex III is the final product.

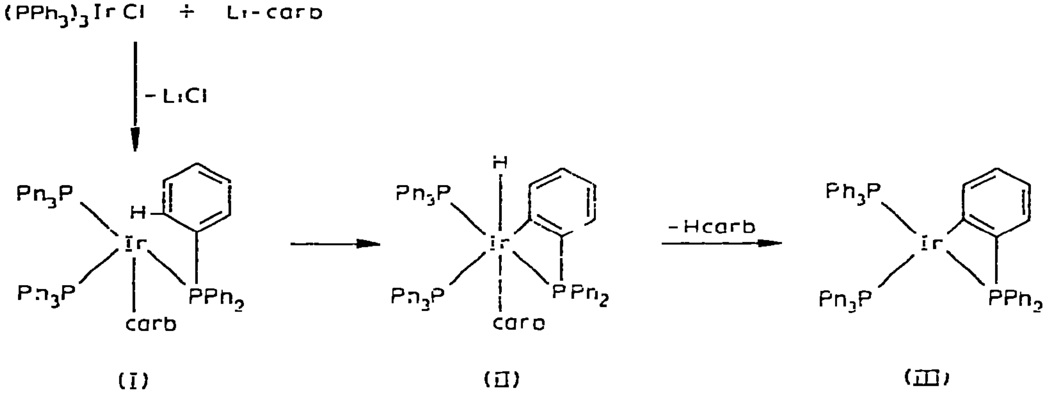
Typically, an ethereal solution of 2.26 mmol of lithium—carborane [1] was added dropwise to a stirred suspension of 0.20 g (0.19 mmol) of $(PPh_3)_3IrCl$ [3] in 15 ml of diethyl ether, under argon at 0 °C. The mixture was stirred for 1 h, during which red-orange crystalline material was formed. This was filtered off and dissolved in CH_2Cl_2 and the solution was filtered. Addition of n-hexane gave bright orange crystals of $(PPh_3)_2\overline{Ir(PC}_6H_4Ph_2)$ (III) (70-80% yield based on $(PPh_3)_3IrCl$), m.p. 185-187 °C, dec.). Anal. Found: C, 66.05; H, 4.74; P, 9.38. $IrP_3C_{54}H_{44}$ calcd.: C, 66.31; H, 4.53; P, 9.50%.

The IR spectrum (Nujol mull) of III shows no bands in the region 2800-1600 cm^{-1}. The weak bands at 1565 and 1570 cm^{-1} attributed to $\nu(CC)$ in the spectrum of $(PPh_3)_3IrCl$ are replaced by bands centered at 1558 m, 1570 w and 1585 m cm^{-1} in the spectrum of III. The spectrum of III also exhibits a strong band at 725 cm^{-1} which is in the range characteristic of C—H out-of-plane deformations for *ortho* disubstituted phenyl rings [4].

Complex III is stable in an inert atmosphere, but reacts rapidly with oxygen and moisture. The formation of III was recently postulated in the thermal decomposition of $(PPh_3)_3IrCH_3$ [5], but the complex was not fully characterized, since it was not satisfactorily purified by recrystallization. On the other hand, a well defined rhodium analog of III was isolated as a product of the thermal decomposition of $(PPh_3)_3RhCH_3$ [6].

We suggest that the reaction with lithium—carborane proceeds by initial formation of a carborane—iridium(I) complex (I), which is transformed to III through the intermediate II, by rapid intramolecular oxidative-addition and reductive elimination, as shown in Scheme 1.

SCHEME 1



Li carb = 1-Li-2-R-1,2-$B_{10}C_2H_{10}$ (R = CH_3, C_6H_5)

A similar sequence of reactions was suggested for the thermal decomposition of the analogous d^8 complexes such as $(PPh_3)_3RhR$ with R = CH_3, $(CH_3)_3SiCH_2$, $(CH_3)_3CCH_2$ [6,7] and $(PPh_3)_3IrCH_3$ [5].

Our unability to isolate complex I is probably due to the high rate of the conversion I→III [7]. The steric requirements of the carboranyl group bonded to the iridium atom increase the rate of *o*-metallation by forcing the metal atom and the phenyl groups of the phosphine ligands closer together [8].

It is noteworthy that complex III reacts rapidly with methanol in CH_2Cl_2 solution at room temperature, showing it to be an efficient decarbonylating agent. The product (yellow crystals, m.p. 149 °, dec.) appears to contain terminal and acyclic CO groups, as shown by its IR spectrum (ν(CO), 1942 and 1735 cm^{-1}). We shall describe our studies of this decarbonylation reaction elsewhere in the near future.

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