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Selective Formation of Cyclometallated Iridium(I) and Iridium(III) Complexes from $[(C_6H_5)_3P]_3IrCl$

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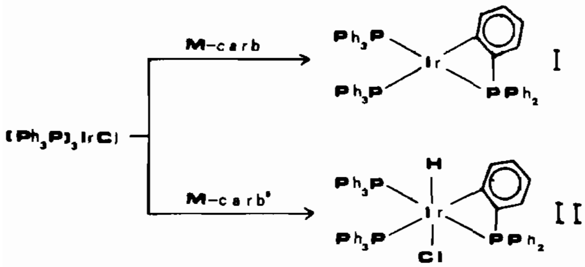
In previous papers [1, 2] we have reported the facile formation of the internally metallated tris(triphenylphosphine)iridium(I) complex, I, by reacting $(Ph_3P)_3IrCl$ with 1-Li-2-R-1,2-$B_{10}C_2H_{10}$ (R = CH_3, C_6H_5) in diethyl ether solution under very mild conditions. In this note we now wish to report the results of further investigations on the reactions between $(Ph_3P)_3IrCl$ and C(1)-lithium or -chloromagnesium derivatives of both 2-R-1,2- and 7-R-1,7-$B_{10}C_2H_{11}$ (R = H, CH_3, C_6H_5) in a number of solvents such as diethyl ether, tetrahydrofuran (THF) and benzene. Thus we found that the formation of the internally metallated iridium(I) complex, I, occurs only when $(Ph_3P)_3IrCl$ is reacted with lithium or chloromagnesium derivatives of the C(2)-methyl or -phenyl substituted 1,2-carborane. On the other hand, the cyclometallated chlorohydridoiridium(III) complex, II, is always formed when $(Ph_3P)_3IrCl$ is treated with the organometallic derivatives of either the unsubstituted 1,2- and 1,7-carborane or the C(7)-methyl and -phenyl substituted 1,7-carborane (Scheme 1).



Scheme 1. M = Li, ClMg. carb = -2-R-1,2-$B_{10}C_2H_{10}$ (R = CH_3, C_6H_5). carb$'$ = -2-H-1,2-$B_{10}C_2H_{10}$, -7-R-1,7-$B_{10}C_2H_{10}$ (R = H, CH_3, C_6H_5).

Complex II was fully characterized by ir and ^1H nmr spectroscopies which provide evidence that the hydrogen is *trans* to the chlorine atom and mutually *cis* to three non-equivalent phosphorus nuclei. Consequently the latter complex appears to be identical to that previously obtained by Bennett and Milner [3] by prolonged heating of the parent complex $(Ph_3P)_3IrCl$ in solution. These results confirm that C–Metal carborane derivatives are able to induce in $(Ph_3P)_3IrCl$ facile cyclometallation reactions through hydrogen abstraction from one phenyl group of the coordinated phosphines. In addition, the type of the carborane moiety, as shown in the reaction scheme 1, appears to be peculiar for the formation of the complexes I or II. In fact, while the reaction with the carborane having the highest steric hindrance (carb = -2-R-1,2-$B_{10}C_2H_{10}$, with R = CH_3, C_6H_5) gives the cyclometallated iridium(I) derivative, I, the reaction with the less bulky carboranes forms the cyclometallated chlorohydrido derivative of iridium(III), II.

At this time no satisfactory explanations can be suggested for the observed reaction behaviours. However, on considering that the complex II is obtained in the reaction of $(Ph_3P)_3IrCl$ with the organometallic derivatives of both unsubstituted 1,2- and 1,7-carborane, electronic arguments, such as the difference between the electron-withdrawing power of the carborane moieties [4], may be discounted. Hence, the most compelling explanation is likely to lie in the different steric requirements of the entering carboranyl ligands. Thus, we think that the reaction of $(Ph_3P)_3IrCl$ with the lithium- or chloromagnesium-carborane derivatives in any case proceeds through initial formation of a carborane–iridium(I) complex which undergoes rapid intramolecular oxidative addition of one *ortho* C–H bond of the phenyl groups of the coordinated phosphines, yielding a cyclometallated hydridocarboranyliridium(III) intermediate. In fact, the steric requirements of the bulky carboranyl group bonded to the iridium atom promote rapid *o*-metallation reaction by forcing the metal atom and the phosphine phenyl groups closer together [5]. But the different bulkiness of the carboranyl ligands may also determine the stereochemical course of the intramolecular metallation reaction giving hydridocarboranyl intermediates having different configurations. Therefore intermediates with suitable configurations might originate either the iridium(I) derivative, I, by reductive elimination of a carborane molecule or the sparingly soluble chlorohydridoiridium(III) derivative, complex II, through carborane–chloro exchange reaction.

Investigations are now in progress in order to confirm these suggested reaction routes.

Experimental

Complex I was obtained as previously described [2] starting from $(Ph_3P)_3IrCl$ and 1-M-2-R-1,2-

$B_{10}C_2H_{10}$ (M = Li, ClMg; R = CH_3, C_6H_5) in diethyl ether, THF or benzene solution at 0 °C (yield: 70–80%).

Complex II was prepared by adding a solution (diethyl ether, THF or benzene) of 0.5 mmol of Li- or ClMg-carb′ (carb′ = -2-H-1,2-$B_{10}C_2H_{10}$ or -7-R-1,7-$B_{10}C_2H_{10}$ with R = H, CH_3, C_6H_5) [6] to a stirred suspension of 0.50 g (0.49 mmol) of $(Ph_3P)_3$-IrCl under argon at 0 °C. After stirring for 1 h, the cream precipitate formed was separated by filtration and recrystallized from dichloromethane–diethyl ether to give white crystals of II (yield: 80–85%), mp 226–228 °C, dec.. Typical anal. Calcd. for $C_{54}H_{45}ClP_3Ir$: C, 63.93; H, 4.47. Found: C, 63.45; H, 4.45%.

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