SHORT COMMUNICATIONS

Platinum(II) Grignard and lithio derivatives

Lithio derivatives of many non-transition organometallic compounds are known (*e.g.* Ph_3SnLi) and have been used extensively in preparative chemistry. Analogous Grignard derivatives also exist: for example, $(aryl)_3GeMgX$ compounds are formed from $(aryl)_3GeX$ and magnesium, or by halogen–metal exchange[1]. As far as we are aware, however, lithio and Grignard transition metal derivatives have not previously been proposed.

Chatt and Shaw[2] reported that *cis*-bis(triethylphosphine)platinum(II) bromide and cyclohexylmagnesium bromide react to form the hydrido bromide, $(Et_3P)_2Pt(H)Br$ in 22 % yield. They suggested a mechanism (*reaction 1*) which is independent of subsequent hydrolysis and involves the formation of cyclohexene (which was not detected). Re-examination of this reaction, using 10 mols of a filtered ethereal solution of $C_6H_{11}MgBr$ per mol of *cis*-$(Et_3P)_2PtBr_2$ at room temperature for 2½ hours, gave the hydrido bromide complex in 50 % yield, and we conclude that two competing reaction paths are involved:

Reaction 1 accounts for about 30 % of the hydrido-platinum complex.

$$cis\text{-}(Et_3P)_2PtBr_2 + C_6H_{11}MgBr \longrightarrow (Et_3P)_2Pt(H)Br + C_6H_{10} + MgBr_2 \qquad (1)$$

Reaction 2, which accounts for the remaining 70 % of the hydrido-platinum complex is considered to proceed *via* the hydrolysis of an intermediate platinum-Grignard reagent.

$$\begin{tikzcd}[row sep=small] & & (Et_3P)_2Pt(H)Br \\ cis\text{-}(Et_3P)_2PtBr_2 + C_6H_{11}MgBr \arrow[r] & (Et_3P)_2Pt(MgBr)Br \arrow[ur, "H_2O"] \arrow[dr, "D_2O"'] & & (2) \\ & & (Et_3P)_2Pt(D)Br \end{tikzcd}$$

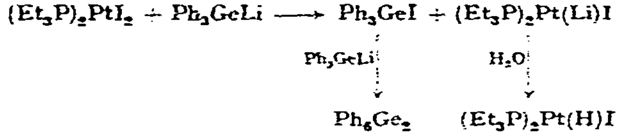
The evidence for *reaction 2* is based on the observation that deuterolysis gives a mixture of the hydrido- and deutero-platinum complexes [ν(PtH), 2217; δ(PtH), 812; ν(PtD), 1592; δ(PtD), 577 cm^{-1}; m.p. 99–100° *ex* methanol], together with bicyclohexyl. The deuteride is not produced by H–D exchange since deuterolysis of $C_6H_{11}MgBr$ followed by the addition of $(Et_3P)_2Pt(H)Br$ produces no infrared absorption due to PtD. *Reaction 2* involves halogen–metal exchange and must produce cyclohexyl bromide which, by reaction with the excess Grignard reagent gives bicyclohexyl. Separate experiments established that this reaction does occur at 20°, although the original Grignard solution was free from bicyclohexyl.

Two observations support *reaction 1*: deuterolysis gives the hydrido complex in 15 % yield, and cyclohexene is detectable (by vapour phase chromatography) after hydrolysis of the reaction mixture. (The original $C_6H_{11}MgBr$ solution gave cyclohexane and no cyclohexene on hydrolysis.) Other products from the overall reaction include intractable tarry material and the yellow *trans*-$(Et_3P)_2PtBr_2$ which is evidently unreactive towards cyclohexylmagnesium bromide.

We had earlier obtained evidence for the existence of a lithio-platinum(II) complex as a reactive intermediate in the reaction between triphenylgermyl-lithium and bis(triethylphosphine)platinum(II) iodide[3]. Metal iodides are well recognised as showing a greater tendency than other halides to undergo halogen–metal exchange reactions and, if rather less than two equivalents of triphenylgermyl-lithium are employed, the products isolated after hydrolysis are explicable in terms of (*a*) direct substitution:

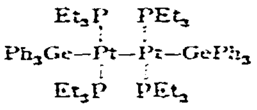
$$(Et_3P)_2PtI_2 + Ph_3GeLi \longrightarrow (Et_3P)_2Pt(GePh_3)_2 + (Et_3P)_2Pt(I)GePh_3$$

and (*b*) halogen–metal exchange, leading to at least one lithio-platinum complex:



$$\begin{tikzcd}(Et_3P)_2PtI_2 + Ph_3GeLi \arrow[r] & Ph_3GeI \arrow[d, dashed, "Ph_3GeLi"'] & + (Et_3P)_2Pt(Li)I \arrow[d, dashed, "H_2O"'] \\ & Ph_6Ge_2 & (Et_3P)_2Pt(H)I\end{tikzcd}$$

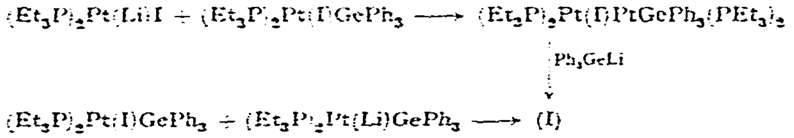
Some polymeric material is also formed together with the highly novel compound, (I), containing a platinum–platinum bond*. [Found: C, 48·9; H, 6·4; P, 7·8; mol. wt. (X-ray), 1476[4]. $C_{60}H_{90}Ge_2P_4Pt_2$ calcd.: C, 49·0; H, 6·2; P, 8·4%; mol. wt., 1470.]



$$\begin{array}{ccccc} & Et_3P & & PEt_3 & \\ Ph_3Ge- & Pt & - & Pt & -GePh_3 \\ & Et_3P & & PEt_3 & \end{array}$$

(I)

This complex can arise in several possible ways, each involving a lithio-platinum(II) intermediate.



$$\begin{tikzcd}(Et_3P)_2Pt(Li)I + (Et_3P)_2Pt(I)GePh_3 \arrow[r] & (Et_3P)_2Pt(I)PtGePh_3(PEt_3)_2 \arrow[d, dashed, "Ph_3GeLi"] \\ (Et_3P)_2Pt(I)GePh_3 + (Et_3P)_2Pt(Li)GePh_3 \arrow[r] & (I)\end{tikzcd}$$

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1 F. GLOCKLING AND K. A. HOOTON, *J. Chem. Soc.*, (1962) 3509.
2 J. CHATT AND B. L. SHAW, *J. Chem. Soc.*, (1959) 4020.
3 R. J. CROSS AND F. GLOCKLING, *Proc. Chem. Soc.*, (1964) 143.
4 H. M. M. SHEARER AND C. B. SPENCER, private communication.

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* *Added in proof.* More detailed X-ray study[4] is incompatible with (I) since the Pt–Pt distance is greater than 7 Å. Details will be reported shortly.