Bistriphenylphosphineplatinum(0)

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IN their work on zerovalent platinum derivatives, Malatesta and Cariello pointed out[1] that these compounds dissociate easily in solution, and suggested the existence of a compound such as

$[Pt(PPh_3)_2]$ to explain the dissociation of $[Pt(PPh_3)_3]$. The same intermediate was suggested later[2] to account for the rate of exchange of the acetylene part of $[Pt(PPh_3)_2L]$, where L is acetylenic.

The compound bistriphenylphosphineplatinum-(0) has now been isolated in several ways.

(1) Potassium hydroxide in alcohol is slowly added to an alcoholic solution of $[PtH(PPh_3)_3]HSO_4$ through which a stream of oxygen is passing.

$$2[PtH(PPh_3)_3]HSO_4 + 2KOH + O_2 \rightarrow 2[Pt(PPh_3)_2] + 2Ph_3PO + 2KHSO_4$$

(2) A stoicheiometric amount of hydrogen peroxide and KOH in alcohol are slowly added to an alcoholic solution of $[PtH(PPh_3)_3]HSO_4$.

$$[PtH(PPh_3)_3]HSO_4 + KOH + H_2O_2 \rightarrow [Pt(PPh_3)_2] + Ph_3PO + KHSO_4 + 2H_2O$$

The yield in this case is 60%.

(3) The following reactions also give the desired product, in lower yields.

$$trans\text{-}[PtH(CN)(PPh_3)_2] + KOH \rightarrow [Pt(PPh_3)_2] + KCN + H_2O$$

$$trans\text{-}[PtHCl(PPh_3)_2] + LiC_4H_9 \rightarrow [Pt(PPh_3)_2] + LiCl + C_4H_{10}$$

In the latter case, the stoicheiometric amount of butyl-lithium is essential, and the reaction must be carried out under nitrogen.

$[Pt(PPh_3)_2]$ is a yellow compound, m.p. 157—160°, stable for a few hours in the solid state, but unstable in solution, where it seems to dissociate (M, found 464 in benzene, 395 in acetone; calc. 719). It behaves as an unsaturated compound, for example, $[Pt(PPh_3)_2] + L \rightarrow [Pt(PPh_3)_2L]$ (L = PPh_3, CO, PhC≡CPh, Ph–CH=CH–Ph) and in some reactions it shows a carbene-like reactivity: $[Pt(PPh_3)_2] + CH_3I \rightarrow [Pt(PPh_3)_2CH_3I]$. However, it does not catalyse the hydrogenation or the isomerisation of olefins and seems to be a very poor catalyst for the dimerisation or polymerisation of butadiene.

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[1] L. Malatesta and C. Cariello, *J. Chem. Soc.*, 1958, 2323.
[2] A. D. Allen and D. C. Cook, *Canad. J. Chem.*, 1964, **42**, 1063.