Anions Derived from PH$_3$ Complexes: Deprotonation by PH$_2$

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The complexes (PH$_3$)$_2$Mo(CO)$_4$ and [P$_2$H$_4$Mo(CO)$_4$]$_2$ react with potassium in liquid ammonia, giving products which appear to contain anions of the type [(PH$_2$)$_2$Mo(CO)$_4$]$_2^-$, but in the former case at least the reactions are complicated and the products are difficult to characterize. We have found, however, that phosphane complexes can be deprotonated by potassium phosphide in dimethyl ether. The complex pentacarbonylphosphanemolybdenum(0), for example, reacts quantitatively with KPH$_2$ in (CH$_3$)$_2$O at 0 °C over a period of an hour; phosphane is evolved, and the salt K[PH$_2$Mo(CO)$_5$] can be isolated from the resulting solutions as a yellow solid.

\[ \text{PH}_3\text{Mo(CO)}_5 + \text{PH}_2^- \rightarrow [\text{PH}_2\text{Mo(CO)}_5]^+ + \text{PH}_3 \]

The compound has been characterized by its IR and NMR spectra \( \nu(\text{Mo} \equiv \text{C}) = 160.5 \text{ Hz; } \nu(\text{P} \equiv \text{P}) = 10.36 \text{ Hz in (CH}_3)_2\text{O} \) and by analysis. An excess of PH$_3$Mo(CO)$_5$ yields the binuclear anion complex \( \mu\text{-phosphido-bis(pentacarbonylmolybdate(0))} \)\( ^\text{[2]} \):

\[ \text{PH}_3\text{Mo(CO)}_5 + [\text{PH}_2\text{Mo(CO)}_5]^+ \rightarrow [\text{CO}_5\text{MoPH}_2\text{Mo(CO)}_5]^+ + \text{PH}_3 \]

The NMR spectrum of the dimeric anion has been recorded \( \nu(\text{Mo} \equiv \text{P}) = 249.3 \text{ Hz; } \nu(\text{P} \equiv \text{P}) = 8.69 \text{ Hz in [D}_6\text{]-acetone} \). Signals of minor intensity in the spectrum we assign to a compound like [PH$_3$Mo(CO)$_5$PH$_2$Mo(CO)$_5$]$^-$ which is formed with the evolution of a small amount of CO.

The salt K[PH$_2$Mo(CO)$_5$] reacts slowly with CH$_3$Cl, giving 50% of the expected yield of CH$_3$PH$_2$Mo(CO)$_5$ (characterized spectroscopically by comparison with spectra of authentic samples); reactions with trimethylchlorosilane and with acetyl chloride lead to the formation of a mixture of products \( \text{R}_2\text{PH}_2^-\mu\text{Mo(CO)}_3 \text{[R} = (\text{CH}_3)_2\text{Si- or CH}_3\text{CO}-] \).

An excess of CH$_3$PH$_2$Mo(CO)$_5$ yields the bridged anion \( [(\text{CO})_5\text{MoPH(}\text{CH}_3\text{)}\text{Mo(CO)}_5]^+ \). Similar results have been obtained with (PH$_3$)$_2$Mo(CO)$_4$ and KPH$_2$.

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