Preliminary communication

Reversible addition of molecular hydrogen and conjugated dienes to Co^{I} complexes with 2,2' -bipyridine and 1,10-phenanthroline

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In a previous paper¹ we reported the synthesis of stable σ -alkyl and π -allyl derivatives of Co^{III} with 2,2'-bipyridine (Bipy) and 1,10-phenanthroline (Phen) and suggested the existence of unstable hydridic cobalt compounds. We now report the synthesis and reactivity of series of new hydride complexes of Co^{III} and diene complexes of Co^I with Bipy and Phen, stabilized by tertiary phosphines.

When Co^I derivatives such as $[Co(Chel)_3]$ *ClO₄ (Chel = Bipy or Phen)² are treated with molecular hydrogen in the presence of PR₃ at room temperature and atmospheric pressure, crystalline yellow-orange compounds of suggested structure (I) can be isolated.

$$\begin{bmatrix} PR_{3} \\ \downarrow \\ N \\ N \\ PR_{3} \end{bmatrix}^{+} Clo_{4}^{-}$$

(PR₃ = triethyl-, tri-n-propyl-, tri-n-butyl- and diethylphenyl-phosphine)

Elemental analysis and magnetic measurements are in agreement with the assigned formulae. NMR confirms the presence of two equivalent atoms of hydrogen $(\tau 32.4, J(\text{HP}) 65 \text{ cps})$. Models favour the *trans* position of the phosphines.

The reported reactions are reversible; in fact, with an excess of chelating ligand, molecular hydrogen is evolved and $[Co(Chel)_3]ClO_4$ is reformed.

In the presence of PR_3 and under similar conditions, $[Co(Chel)_3]^+$ complexes also react with butadiene and isoprene, giving deep red crystalline complexes $[Co(Chel)(PR_3)diene]ClO_4$ (II). These reactions are reversible in the presence of an excess of Bipy or Phen. Even in excess of PR_3 in atmosphere of hydrogen the π -bonded diene is displaced and (I) is formed.

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The inverse reaction $I \rightarrow II$ can also be brought about by treating (I) with butadiene in excess, according to the following scheme:

 $[Co(Chel)(PR_3)_2H_2]^+ + 2 C_4H_6 \rightarrow [Co(Chel)(PR_3)C_4H_6]^+ + butenes$

Complexes (I) can therefore be considered as potential catalysts for the hydrogenation of conjugated dienes to alkenes

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