

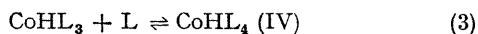
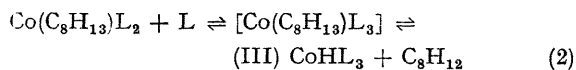
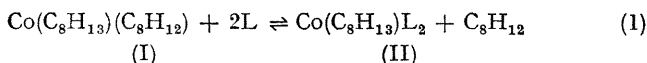
## A New Route to Hydrido- and Nitrogen Complexes of Cobalt

By M. ROSSI and A. SACCO\*

*(Istituto di Chimica Generale e Inorganica, Università di Bari, Italy)*

THE reactions of  $\pi$ -cyclo-octenyl- $\pi$ -cyclo-octa-1,5-diene-cobalt,  $\text{Co}(\text{C}_8\text{H}_{13})(\text{C}_8\text{H}_{12})$ , with carbon monoxide and subsequently with tertiary phosphines and phosphites have been described.<sup>1</sup> As an extension of our studies on the hydrido-complexes of transition metals and on the fixation of molecular nitrogen under mild conditions,<sup>2</sup> we report the reactions of  $\text{Co}(\text{C}_8\text{H}_{13})(\text{C}_8\text{H}_{12})$  with tertiary phosphines, arsines, and phosphites under argon, hydrogen, and nitrogen at room temperature and atmospheric pressure. These reactions furnish a new and more convenient method for the preparation of hydrido- and nitrogen complexes of cobalt, of formula  $\text{CoH}_3\text{L}_3$  and  $\text{CoHN}_2\text{L}_3$ , some of which have been described already,<sup>2</sup> and new complexes, of formulae  $\text{CoHL}_3$ ,  $\text{CoHL}_4$  and  $\text{Co}(\text{C}_8\text{H}_{13})\text{L}_2$ .

The reactions between  $\text{Co}(\text{C}_8\text{H}_{13})(\text{C}_8\text{H}_{12})$  and the ligand, in pentane or benzene solution and under argon, occur according to the following equilibria [ $\text{L} = \text{PPh}_3$ ,  $\text{PMePh}_2$ ,  $\text{PEtPh}_2$ ,  $\text{PBuPh}_2$ ,  $\text{PET}_2\text{Ph}$ ,  $\text{PBu}_2\text{Ph}$ ,  $\text{PBu}_3$ ,  $\text{PPh}(\text{OPh})_2$ ,  $\text{P}(\text{OPh})_3$ , or  $\text{AsPh}_3$ ]:



only with  $\text{PPh}_3$  and  $\text{PMePh}_2$ , in pentane solution and with a molar ratio ligand:cobalt 2:1. These compounds, slightly soluble in pentane, were characterised by means of their elemental analysis and n.m.r. spectra.

With the other ligands, in the same molar ratio, compounds (II) were detected in solution by means of their n.m.r. spectra ( $\text{C}_6\text{D}_6$ ), but could not be crystallised from benzene or pentane.

With an excess of ligand, under argon, reactions (1), (2), and (3) are quantitatively displaced to the right where  $\text{L} = \text{PMePh}_2$ ,  $\text{PPh}(\text{OPh})_2$ , and  $\text{P}(\text{OPh})_3$ . Compounds (IV) with these ligands were obtained in pure crystalline form and characterised by means of their elemental analysis, thermal decomposition, and i.r. spectra (Table).

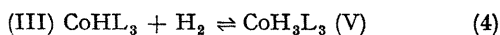
With an excess of ligand (ligand:cobalt >4:1), under hydrogen, reactions (1) and (2) are quantitatively displaced to the right with all the ligands used. However, under these conditions, both reactions (3) and (4) can occur. Reaction (3) is favoured with  $\text{PMePh}_2$ ,  $\text{PPh}(\text{OPh})_2$ ,  $\text{P}(\text{OPh})_3$ , and  $\text{AsPh}_2$ , which give compounds (IV), whereas reaction (4) is favoured with  $\text{PPh}_3$ ,  $\text{PEtPh}_2$ ,  $\text{PBuPh}_2$ ,  $\text{PET}_2\text{Ph}$ ,  $\text{PBu}_2\text{Ph}$ ,  $\text{PBu}_3$ , which give compounds (V). Compounds (V) with  $\text{PMePh}_2$  could be obtained under the same conditions, but with a molar ratio cobalt:ligand of 1:3.

With an excess of ligand in benzene solution and under nitrogen the reactions (1), (2), and (5) yield compounds

*I.r. absorption bands (cm.<sup>-1</sup>)*

L	Solvent	$\text{CoHL}_3$ $\nu_{\text{Co-H}}$	$\text{CoHL}_4$ $\nu_{\text{Co-H}}$	$\text{CoH}_3\text{L}_3$ $\nu_{\text{Co-H}}$	$\text{CoHN}_2\text{L}_3$ $\nu_{\text{N-N}}$
$\text{PPh}_3$	Benzene			1760s—1947m	2090vs
$\text{PMePh}_2$	Nujol		1958m		
$\text{PMePh}_2$	Benzene			1740s—1944m	2077vs
$\text{PEtPh}_2$	Benzene			1743s—1928m	2060vs
$\text{PBuPh}_2$	Benzene			1738s—1920m	2070vs
$\text{PET}_2\text{Ph}$	Nujol	1940s			
$\text{PET}_2\text{Ph}$	Benzene			1720s—1924m	2060vs
$\text{PBu}_2\text{Ph}$	Benzene			1722s—1922m	2060vs
$\text{PBu}_3$	Benzene			1720s—1920m	2050vs
$\text{AsPh}_3$	Nujol		1978w		

Reactions (2) and (3) are more or less displaced to the right according to the nature of the ligand. Under hydrogen, the reaction (2) is quantitatively displaced to the right, because of the hydrogenation of the cyclo-octadiene. Moreover, in competition with reaction (3), the following equilibrium occurs:



Under nitrogen, the following reaction, in competition with reactions (2) and (3), occurs:



Compounds (II) were obtained in pure crystalline form

<sup>1</sup> S. Ctsuka and M. Rossi, *J. Chem. Soc. (A)*, 1969, 497.

<sup>2</sup> A. Sacco and M. Rossi, *Chem. Comm.*, 1967, 316; *Inorg. Chim. Acta*, 1968, 2, 127; A. Sacco and M. Aresta, *Chem. Comm.*, 1968, 1223.

(VI) with the ligands  $\text{PPh}_3$ ,  $\text{PEtPh}_2$ ,  $\text{PBuPh}_2$ ,  $\text{PET}_2\text{Ph}$ ,  $\text{PBu}_2\text{Ph}$ , and  $\text{PBu}_3$  (Table).

Preliminary data on the equilibrium constants of equations (4) and (5) show that the equilibria are strongly dependent on the  $\pi$ -acceptor and  $\sigma$ -donor properties of the ligand; compounds (V) and (VI) are less stable with the more  $\pi$ -acid ligands. Compounds (III) can easily be obtained from compounds (V) and (VI) when the ligand is of the type  $\text{PR}_2\text{Ph}$  or  $\text{PR}_3$  ( $\text{R} = \text{alkyl}$ ).

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