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PRELIMINARY COMMUNICATION

PHOSPHINE AND ARSINE COMPLEXES OF METHINYLTRICOBALT ENNEACARBONYLS

B.H. ROBINSON and W.S. THAM
Chemistry Department, University of Otago, P.O. Box 56, Dunedin (New Zealand)

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Few stable phosphone and arsine derivatives of first-row transition metal carbonyl clusters are known since Lewis bases show a tendency to split metal–metal bonds. Thus, although $Fe_3(CO)_{11}(C_6H_5)_3P$ is known as an unstable intermediate the major products from the reaction of $Fe_3(CO)_{12}$ and $(C_6H_5)_3P$ are $Fe(CO)_4P(C_6H_5)_3$ and $Fe(CO)_3[P(C_6H_5)_3]_2$ [1].

We have found that the trimeric clusters methinyltricobalt enneacarbonyls [2,3,4], $YCCo_3(CO)_9$ where Y = Cl,Br,CH_3,C_6H_5 etc., react reversibly with alkyl and aryl phosphines and arsines to give a range of new complexes, $YCCo_3(CO)_8L$ and $YCCo_3(CO)_7L_2$ (Table 1).

$$YCCo_3(CO)_9 + xL \underset{CO}{\overset{60^\circ}{\rightleftharpoons}} YCCo_3(CO)_{9-x}L_x + xCO \qquad (x = 1 \text{ or } 2)$$

These air-stable, volatile complexes, soluble in non-polar solvents without decomposition, were characterised by elemental analysis, infrared, NMR and mass spectrometry.

TABLE 1

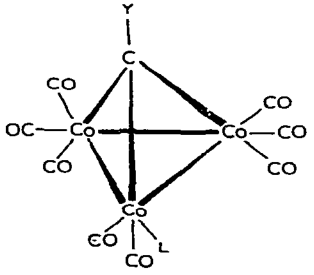
SOME PRODUCTS OBTAINED IN THE REACTION OF $YCCo_3(CO)_9$ WITH R_3P AND R_3As

Compound	Structural type in crystal	^1H NMR signal ($C{-}CH_3$)
$CH_3CCo_3(CO)_8L$:		
L = CO	I	6.83 τ
$(C_6H_5)_3P$	I	6.84
$(C_6H_5)_3As$	I	6.90
$(C_6H_{11})_3P$	II	
$(C_4H_9)_3P$	II	6.99
$(C_4H_9)_3As$	II	7.19
$CH_3CCo_3(CO)_7[(C_6H_5)_3P]_2$	II	7.35
$CH_3CCo_3(CO)_7[(C_4H_9)_3As]_2$	II	7.44
$ClCCo_3(CO)_8(C_6H_5)_3P$	I	-

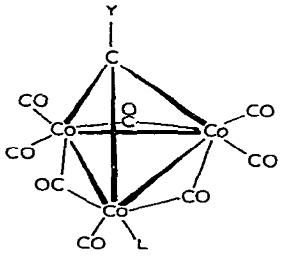
Similar products were obtained with phosphines under more vigorous reaction conditions. With $ClCCo_3(CO)_9$ and arsines an unusual dehalogenation occurred to give $[Co_3(CO)_9C]_2$ in 90% yield.

$$2ClCCo_3(CO)_9 + R_3As \xrightarrow{100^\circ \text{ in vacuo}} [Co_3(CO)_9C]_2 + R_3AsCl_2$$

An interesting feature is the structural isomerism displayed by the compounds, $CH_3CCo_3(CO)_8L$. Two structural types are possible differing only in the presence of bridging CO groups in (II).



(I)



(II)

The structure adopted in the crystal, as determined from IR and X-ray data, apparently varies irregularly with the Lewis base (Table 1). An X-ray investigation of $CH_3CCo_3(CO)_8P(C_6H_5)_3$ has shown that the ligand is equatorial not axial as would be expected on steric grounds. There is evidence of considerable steric congestion in this molecule; for example, the methyl group is bent away from the ligand[5]

TABLE 2

CO STRETCHING FREQUENCIES OF SOME $CH_3CCo_3(CO)_8L$ COMPOUNDS

L = $(C_6H_{11})_3P$		L = $(C_6H_5)_3P$	
Mull	Hexane	Mull	Hexane
-	2075 m	2074 s	2077 vs
2068 s	2065 m	-	2072 s
2034 vs	2037 vs	2033 vs	2033 vs
-	2029 s	-	-
-	2019 s	2018 vs	2020 vs
2008 vs	2011 vs	2010 vs	2011 vs
1997 ms	1999 s	-	1992 m
1983 m	1982 (sh) m	1989 m	1988 m
-	1977 m	1978 mw	-
-	1959 m	1960 m	1968 m
1889 mw	1894 m	-	1890 w
1869 ms	1871 s	-	1878 m
1847 ms	1859 s	-	1860 m

However the solution spectrum of $CH_3CCo_3(CO)_8P(C_6H_5)_3$ is inconsistent with this crystal structure because it contains additional bands in the C—O terminal and bridging region. Indeed the extra bands correspond closely to those of crystalline $CH_3CCo_3(CO)_8P(C_6H_{11})_3$ (Table 2). Likewise the extra bands in the solution spectrum of $CH_3CCo_3(CO)_8P(C_6H_{11})_3$ correspond to those of crystalline $CH_3CCo_3(CO)_8P(C_6H_5)_3$. This suggests that *both* isomers exist in solutions of these complexes as has been found in the case of $Co_2(CO)_8$[6]. All mono-derivatives of $CH_3CCo_3(CO)_9$ show similar behaviour although the bis-compounds, *e.q.* $CH_3CCo_3(CO)_7[P(C_6H_5)_3]_2$, apparently adopt a bridging CO structure exclusively in solution and in the crystal.

Unlike the parent clusters[2] these complexes do not undergo secondary fragmentation on electron impact by the loss of cobalt. This could indicate an increase in Co—Co bond strength brought about by σ electron donation by the ligand to the cluster. In agreement with this suggestion is the progressive shielding of the CH_3 protons as the donor power of the Lewis base and the number of ligands increases (Table 1). A reverse trend has been noted with π donors, for example, arenes[7].

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