Polynuclear Phosphine- and Arsine-substituted Rhodium Carbonyls

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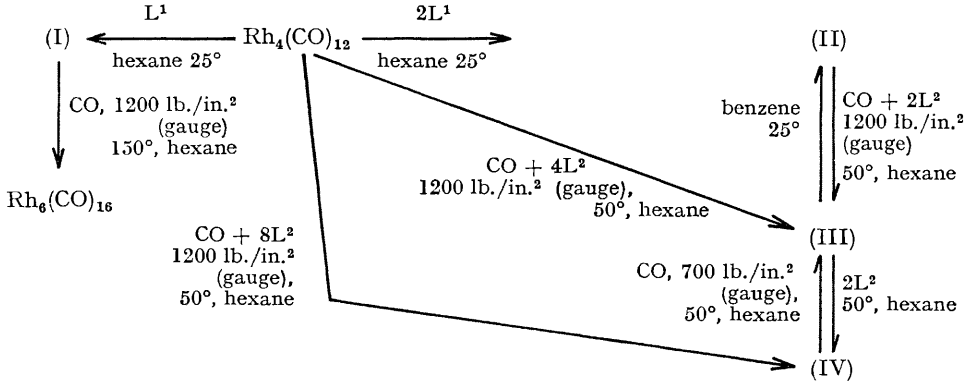
Summary Polynuclear phosphine- and arsine-substituted rhodium carbonyls of the types $\mathrm{Rh_4(CO)_{11}L}$, $\mathrm{Rh_4(CO)_{10}L_2}$, and $\mathrm{Rh_2(CO)_6L_2}$ are described.

FOLLOWING recent reports of the preparation of phosphine-substituted derivatives of cobalt[1] and iridium[2,3] dodecacarbonyls in which the basic structure of the parent cluster carbonyl is retained, the formation of analogous rhodium carbonyl complexes is described.

Phosphine and arsine ligands react readily at room temperature with hexane solutions of rhodium dodecacarbonyl to form $\mathrm{Rh_4(CO)_{11}L}$ (I) and $\mathrm{Rh_4(CO)_{10}L_2}$ (II), (see Scheme), where L = $\mathrm{PPh_3}$, $\mathrm{AsPh_3}$, $\mathrm{P(}p\mathrm{\text{-}MeC_6H_4)_3}$, and $\mathrm{P(}p\mathrm{\text{-}FC_6H_4)_3}$, and 2L = $\mathrm{Ph_2PCH_2CH_2PPh_2}$, with the evolution of one or two molecules of carbon monoxide respectively, as indicated by gas-burette measurements. The dark-red crystalline complexes are air-stable, sparingly soluble in inert solvents such as petroleum ethers and benzene, and non-electrolytes in nitrobenzene.



$\mathrm{L^1}$ = $\mathrm{PPh_3}$, $\mathrm{AsPh_3}$,$\mathrm{P(}p\mathrm{\text{-}MeC_6H_4)_3}$, $\mathrm{P(}p\mathrm{\text{-}FC_6H_4)_3}$, and $\frac{1}{2}\mathrm{Ph_2PCH_2CH_2PPh_2}$.
$\mathrm{L^2}$ = $\mathrm{PPh_3}$, $\mathrm{P(}p\mathrm{\text{-}MeC_6H_4)_3}$, and $\mathrm{P(}p\mathrm{\text{-}FC_6H_4)_3}$.

SCHEME

The similarity between the carbonyl stretching frequencies of the i.r. spectra of these complexes and those of $\mathrm{Rh_4(CO)_{12}}$ suggests that the structure of the parent carbonyl is retained (see Table). Also, the similarity between the spectra of $\mathrm{Rh_4(CO)_{10}(PPh_3)_2}$ and $\mathrm{Ir_4(CO)_{10}(PPh_3)_2}$ (whose crystal structure has been determined[3]) may imply the same stereochemical configuration.

In contrast to observations with the $\mathrm{Co_4(CO)_{11}XPh_3}$ systems (X = As and Sb),[1] there is no evidence to indicate that these reactions are reversible at atmospheric pressure and temperature. However, reaction of $\mathrm{Rh_4(CO)_{11}L}$ with carbon monoxide at 1200 lb/in.^{2} (gauge) and 150° does yield $\mathrm{Rh_6(CO)_{16}}$. Similar treatment of hexane suspensions of the disubstituted complexes at 50° in the presence of two equivalents of the ligand affords unstable yellow compounds of empirical formula $\mathrm{[Rh(CO)_3L]}$ (III), where L = $\mathrm{PPh_3}$, $\mathrm{P(}p\mathrm{\text{-}MeC_6H_4)_3}$, and $\mathrm{P(}p\mathrm{\text{-}FC_6H_4)_3}$. The i.r. spectra of these complexes in the carbonyl stretching region display one very strong band at *ca.* 1960 cm^{-1} together with a shoulder at *ca.* 1980 cm^{-1}, an absorption pattern which is very similar to that observed for the dimeric non-bridged phosphine-substituted complexes of cobalt octacarbonyl, $\mathrm{Co_2(CO)_6L_2}$.[4] The dimeric nature of these latter materials has been confirmed by *X*-ray analysis of $\mathrm{Co_2(CO)_6(PBu^n_3)_2}$.[5,6] The rhodium complexes described here are accordingly formulated as dimeric species. Consistent with this interpretation, reaction of the compounds with a further two equivalents of phosphine yields $\mathrm{Rh_2(CO)_4L_4}$ (IV), which, in the case of L = $\mathrm{PPh_3}$, has recently been described elsewhere.[7,8] This reaction may be reversed by treatment of $\mathrm{Rh_2(CO)_4(PPh_3)_4}$ with carbon monoxide at 700 lb./in.^{2} (gauge) and 50°. Both $\mathrm{Rh_2(CO)_6L_2}$ and $\mathrm{Rh_2(CO)_4L_4}$ are of considerable interest since they are among the few known formal substitution products of $\mathrm{Rh_2(CO)_8}$.

Mol. wt. and n.m.r. studies on the dimeric species (III) are unfortunately precluded since the compounds are either insoluble or react in the solvents examined. For example, suspensions of yellow $\mathrm{Rh_2(CO)_6(PPh_3)_2}$ in dry benzene saturated with carbon monoxide yield red solutions, the i.r. spectra of which suggest the presence of $\mathrm{Rh_4(CO)_{10}(PPh_3)_2}$. It appears likely that the reverse of the carbonylation reaction occurs in benzene, *i.e.*

$$\mathrm{2[Rh_2(CO)_6(PPh_3)_2]} \xrightarrow{\text{benzene}} \mathrm{Rh_4(CO)_{10}(PPh_3)_2 + 2PPh_3 + 2CO}.$$

A ready dimer–tetramer transformation of this sort with loss of carbon monoxide may well account for the difficulty experienced in characterising $\mathrm{Rh_2(CO)_8}$, first claimed by Hieber and Lagally in 1943.[9]

The presence of weak bands in the i.r. spectra of $Rh_2(CO)_6L_2$ at *ca.* 1800 cm^{-1} indicates some contribution from a structure containing bridging carbonyl groups. This may be due to a mixture of bridged and non-bridged isomers as has been recently postulated for the $Co_2(CO)_6(AsEt_3)_2$ system in solution.[10]

Carbonyl stretching frequencies of triphenylphosphine-substituted rhodium carbonyls

$Rh_4(CO)_{12}$	$Rh_4(CO)_{11}PPh_3$	$Rh_4(CO)_{10}(PPh_3)_2$	$Rh_2(CO)_6(PPh_3)_2$†
	2087s	2087m	
2074vs		2067vs	2063vw,sh
	2057vs	2058s,sh	2053vw,sh
2040s		2041vs	2037w
	2027s		
	2021sh		
		2012vs	2013w,sh
			1979s,sh
			1954vs
	1898w		1911m,sh
1873s	1859s		
	1843s	1840s	
		1818m	
			1790vw
			1766vw

Spectra measured in 1,2-dichloroethane.
† KBr disc.

The addition of three or four equivalents of phosphine or arsine to $Rh_4(CO)_{12}$ at atmospheric pressure appears to cause breakdown of the cluster yielding mixtures of products, of which $Rh_4(CO)_{10}L_2$ and $Rh_2(CO)_6L_2$ are both components.

Satisfactory elemental analyses have been obtained for all the new complexes discussed.

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