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NOTE

PHOSPHORUS-CONTAINING COBALT CARBONYLS III*. MONOSUBSTITUTED DERIVATIVES OF DICOBALT OCTACARBONYL WITH PHOSPHINES AND PHOSPHITES

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Since our paper[2] on the preparation of the first example of a complex of the type $Co_2(CO)_7L$ (I), *viz.* that with $L=(C_6H_5)_3P$ (Ia), no other compounds of this type have been reported. We now describe several such compounds containing various phosphine and phosphite ligands.

Compound (Ia) was prepared in pure form by direct reaction of $Co_2(CO)_8$ and $(C_6H_5)_3P$ in nujol solution[2]. The compounds $[Co(CO)_3L_2][Co(CO)_4]$[3,4] (IIa, $L=(C_6H_5)_3P$) and $Co_2(CO)_6L_2$[4,5] (IIIa, $L=(C_6H_5)_3P$) separated as insoluble precipitates, and the rather stable (Ia) could be purified by chromatography followed by crystallization. However, with $(n\text{-}C_4H_9)_3P$ (b) or $(C_6H_{11})_3P$ (c) as ligands, the compounds of type (I) could not be obtained in appreciable yields by direct reaction, since at room temperature compounds of type (II) were the main products even with small $PY_3/Co_2(CO)_8$ ratios. Compounds of type (I) could be detected in both cases in the reaction product through their characteristic IR spectra, but the separation of the small amounts involved by chromatography proved not to be a useful method because of the instability of the compounds, especially their tendency for disproportionation into $Co_2(CO)_8$ and compounds of type (III).

This disproportionation was found to be reversible according to eqn. (1), and this opened the way to a general preparatively useful method to obtain the complexes of type (I). Compounds of type (III) were prepared from the mixture of type (II) and

$$\underset{(I)}{2\,Co_2(CO)_7L} \rightleftharpoons Co_2(CO)_8+\underset{(III)}{Co_2(CO)_6L_2} \tag{1}$$

(III) complexes obtained from $Co_2(CO)_8$ and phosphines by refluxing these mixtures in benzene to effect the transformation of compounds of type (II) to compounds of type (III) (eqn. 2)

$$\underset{(II)}{[Co(CO)_3(PY_3)_2][Co(CO)_4]} \xrightarrow{\text{heat}} \underset{(III)}{Co_2(CO)_6(PY_3)_2}+CO \tag{2}$$

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* For Part II see Ref. 1.

This reaction has been described by Wilkinson and co-workers[6] for the triphenylphosphine complex and has now been found to be of general applicability.

We have found that the compounds of type (III) react reversibly in hexane solution with carbon monoxide at atmospheric pressure, according to eqn. (3).

$$\underset{\text{(III)}}{Co_2(CO)_6(PY_3)_2} + CO \rightleftharpoons \underset{\text{(I)}}{Co_2(CO)_7PY_3} + PY_3 \tag{3}$$

The formation of (I) is more complete if an equivalent amount of $Co_2(CO)_8$ is present to bind the phosphine liberated by carbon monoxide:

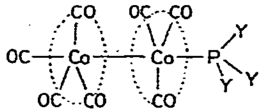
$$\underset{\text{(III)}}{Co_2(CO)_6(PY_3)_2} + Co_2(CO)_8 \xrightarrow[\text{1 atm}]{\text{CO}} \underset{\text{(I)}}{2\,Co_2(CO)_7PY_3} \tag{4}$$

The hexane solution of the tributylphosphine derivative (Ib) was prepared via this route and purified by chromatography on silica gel. The product, $Co_2(CO)_7$-$P(C_4H_9)_3$, was obtained in pure crystalline form by chilling the selected chromatographic fractions to −78°. (Found: Co, 22.9; P, 6.2. $C_{19}H_{27}Co_2O_7P$ calcd.: Co, 22.84; P, 6.00 %.) This compound was found to possess only limited stability. When it was stored in crystalline form under an inert atmosphere at room temperature, after two weaks considerable amounts of (IIIb) had been formed, as well as hexane-insoluble decomposition products.

In further experiments the reactions with the phosphites $(C_6H_5O)_3P$ (d), $(CH_3O)_3P$ (e), $(C_2H_5O)_3P$ (f), (iso-$C_3H_7O)_3P$ (g) or (n-$C_6H_{13}O)_3P$ (h) have been studied. In these cases compounds of type (II) were found only in minor amounts. Using appropriate ratios of $PY_3/Co_2(CO)_8$ the hexane-soluble compounds of type (I) were formed predominantly, along with smaller amounts of compounds of type (III). The formation of the monosubstituted derivatives (Id) to (Ih) was demonstrated by IR spectroscopy, and no efforts were made to obtain the complexes in a crystalline state.

Somewhat different behaviour was observed with dibutyl phosphite, $(C_4H_9O)_2$-POH (i), with which only the monosubstituted complex (Ii) was formed. Even increasing the phosphite/$Co_2(CO)_8$ ratio did not effect the formation of the disubstituted types. A hexane solution of this reaction product stored under carbon monoxide for a month showed only the C–O stretching bands of (Ii).

The IR spectra of compounds of type (I) show a remarkable similarity in the CO stretching region. The absence of bands in the C–O bridging region and the appearance of 4 to 5 bands in the terminal region proves that all these compounds have the structure proposed earlier[2] for (Ia):



Ia	$Y = C_6H_5$	Ie	$Y = CH_3O$
Ib	nC_4H_9	If	C_2H_5O
Ic	C_6H_{11}	Ig	iC_3H_7O
Id	C_6H_5O	Ih	$nC_6H_{13}O$

Ii $PY_3 = (nC_4H_9O)_2POH$

The spectrum of one representative of this series of compounds is shown in Fig. 1 and the corresponding wavenumbers for all compounds are given in Table 1.

It is striking how little the corresponding frequencies vary with the substituents having considerably different basicity, or donor–acceptor capacities, respectively. Apparently the "buffering" ability of seven CO groups *versus* a single phosphine or phosphite ligand ensures the optimal charge distribution[7] among metal atoms and ligands without dramatic differences in the metal–CO bond order.

Qualitatively similar results were obtained with $(C_6H_5)_3As$, with which the equilibrium reaction (1) was found to be rather rapid, thus preventing the preparation

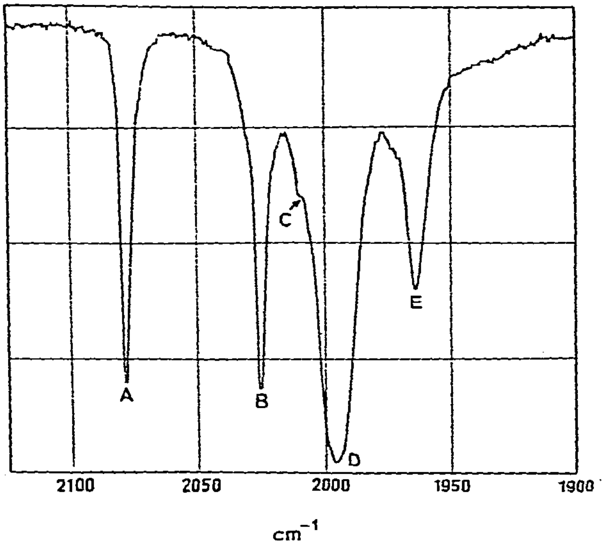


Fig. 1. Spectrum of a representative of $Co_2(CO)_7L$ compounds.

TABLE 1

C–O STRETCHING FREQUENCIES OF THE $Co_2(CO)_7L$ COMPOUNDS

The letters refer to the labelling of Fig. 1. Hexane solution, ±1 cm^{-1}.

L	Band positions (cm^{-1})				
	A	B	C	D	E
Phosphines					
$(C_6H_5)_3P$	2079	2026	2010(sh)	1996	1964
$(n\text{-}C_4H_9)_3P$	2078.5	2022	2005(sh)	1992	1955
$(C_6H_{11})_3P$	2078	2020.5		1993	1953
Phosphites					
$(C_6H_5O)_3P$	2087.5	2036		2003	1976
$(CH_3O)_3P$	2085.5	2033	2018(sh)	1999.5	1977
$(C_2H_5O)_3P$	2084	2031		1998	1974
$(n\text{-}C_6H_{13}O)_3P$	2083	2030		1997.5	1971
$(i\text{-}C_3H_7O)_3P$	2082	2029		1996	1971
$(n\text{-}C_4H_9O)_2P(OH)$	2072	2018		1982	1952
$(C_6H_5)_3As$	2080	2028		1997	1963

of pure $Co_2(CO)_7AsPh_3$ (IV) even in solution. The wave numbers of the principal bands could nevertheless be estimated in this case too, and are shown also in the Table. Several other strong bands are, however, present in the terminal C–O stretching region, *e.g.* at 2013 and 2034 cm^{-1}, indicating the formation of one or more other compounds of unknown nature.

It is worth to mention that in the solution spectra of the derivatives (Ia, b, c) and even more strikingly in that of (IV), there are two weak bands in the region characteristic for bridging CO ligands [*e.g.* with (Ib) at 1847 and 1829 cm^{-1}], observable only in concentrated solutions. These bands are absent in solid phase spectra (KBr pellet). Probably these compounds are, when dissolved, in equilibrium with a low concentration of their CO-bridged isomers, which is a type of structural isomerism, encountered frequently with dinuclear metal carbonyls[8].

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