Infrared Spectra of Some Derivatives of Octacarbonyldicobalt

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A number of cobalt carbonyl derivatives of the type $[L\ Co(CO)_3]_2$ [L = Et_3P, Bu_3P, $PhMe_2P$, $PhEt_2P$, Ph_3P, $(MeO)_3P$, $(PhO)_3P$, Et_3As, or Ph_3As] have been prepared, and their infrared spectra investigated in the range 225—4000 cm.$^{-1}$. Absorption bands due to the vibrations of the $Co_2(CO)_6$ moiety have been identified and assigned where possible.

The reactions between octacarbonyldicobalt and Group VA ligands, L, give $LCo_2(CO)_7$,[1,2] $L_2Co_2(CO)_6$,[3-6] and $[L_2Co(CO)_3][Co(CO)_4]$[3-8] depending upon the reaction conditions. The i.r. spectra of $Ph_3PCo(CO)_3Co(CO)_4$[1] and $[Ph_3PCo(CO)_3]_2$[9] indicate that both have structures similar to that proposed for the non-bridged isomer of octacarbonyldicobalt[10] with one or both axial carbonyl groups replaced by a triphenylphosphine ligand. More recently, it has been found that further substitution may be effected, and that mono-, bi-, and poly-substituted compounds are able to exist as bridged and non-bridged isomers related to the two forms of cobalt carbonyl found in solution.[2]

This paper describes an investigation of the preparation and i.r. spectra of the non-bridged derivatives $[L\ Co(CO)_3]_2$. The spectra have been assigned, partly by rationalization of the trends in frequencies of observed absorption bands, and partly by comparison with the related $[L\ Co(CO)_3]_2Hg$ compounds.[11]

EXPERIMENTAL

Octacarbonyldicobalt was purchased from Strem Chemicals, Inc.

The substituted compounds were prepared by addition of the ligand, L, as a pure liquid or a solution in dry benzene (10 ml.) to a solution of octacarbonyldicobalt (*ca.* 1 g.) in dry benzene (40 ml.) under purified nitrogen. Ligand : carbonylcobalt molar ratios of 2 : 1 were used. The reaction mixtures were heated on a steam-bath until only the dimeric compounds $[L\ Co(CO)_3]_2$ were present. The derivatives of Ph_3P and Ph_3As precipitated at this stage and, because of their low solubilities in organic solvent, could not be purified further. The other compounds were isolated by removal of the solvent from the reaction mixtures at reduced pressures, and purified by recrystallization of the residues from benzene, hexane, or methanol. The products were red or red-brown air-stable crystalline solids that decomposed slowly in solution. Their m.p.s and analytical data are given in Table 1.

I.r. spectra were recorded on a Perkin-Elmer 337 spectrometer equipped with a Hitachi-Perkin-Elmer readout

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TABLE 1

M.p.s and analytical data for the [L $Co(CO)_3]_2$ derivatives

L	M.p.	Found (%) C	Found (%) H	Found (%) P	Required (%) C	Required (%) H	Required (%) P
Et_3P	182—184°	40·8	5·7	12·6	41·3	5·7	11·9
$Bu^n{}_3P$......	109—111	52·2	7·6	9·2	52·2	7·8	9·0
$PhMe_2P$ ...	155 dec.	47·2	4·5	10·3	46·9	3·9	11·0
$PhEt_2P$ ...	129—131	50·2	5·2	10·2	50·4	4·8	10·0
Ph_3P	130 dec.	61·7	4·4	7·2	62·2	3·7	7·7
$(MeO)_3P$...	130 dec.	26·7	3·4	11·2	27·0	3·4	11·6
Et_3As......	135 dec.	35·5	5·2		35·5	4·9	
Ph_3As ...	195 dec.	56·2	4·0		56·1	3·3	

TABLE 2

I.r. spectra of [L $Co(CO)_3]_2$ derivatives

L	Absorption band A	B *	C	D	E *	F	G *
CO [10] ...						2022(10), 2031(5·8), 2069(9·3)	
$(PhO)_3P$ [b]	352	382	*a*	*a*	528	1979(10)	1998sh
$(MeO)_3P$	350	389	467	487	529	1975(10)	1992(1·3)
Ph_3P [c] ...			*a*	*a*	543	1957(10)	1977sh
$PhMe_2P$	378	423	486	501	545	1957(10)	1978(1·3)
$PhEt_2P$	378	425	488	503	544	1958(10)	1976(1·3)
Et_3P......	384	425	487	503	546	1953(10)	1971(1·3)
Et_3As ...	385	420	*a*	500	540	1953(10)	*a*
Bu_3P ...	385	427	490	505	546	1951(10)	1970(1·2)

Unless otherwise stated, benzene was used as solvent for the 300—600 cm.$^{-1}$ region and heptane for the 1900—2100 cm.$^{-1}$ region. Peak positions are in cm.$^{-1}$ Relative peak heights are enclosed in parentheses except for the 300—600 cm.$^{-1}$ region as the spectrum shown in Figure 1 is entirely typical in this respect.

* These bands are due to vibrations of a_{2u} symmetry (see text).

[a] Obscured by bands of other origins. [b] Chloroform solution in the 1900—2100 cm.$^{-1}$ region. [c] Chloroform solution for the whole spectrum.

recorder above 400 cm.$^{-1}$, and on a Grubb-Parsons D.M. 2 spectrometer below 400 cm.$^{-1}$. They are summarized in Table 2. The spectra were calibrated with deuterium chloride,[12] indene,[12] and water vapour so that peak positions are accurate to within ±1, ±2, and ±4 cm.$^{-1}$ in the 1900—2100, 400—700, and 225—400 cm.$^{-1}$ regions respectively.

RESULTS AND DISCUSSION

The products of the reactions between octacarbonyldicobalt and a Group VA ligand, L, have been found to depend on L. For example, using the reaction conditions described above, $PhEt_2P$ gave $[PhEt_2PCo(CO)_3]_2$ as the sole product in 75% yield when the reaction mixture was heated for 30 min. After the same time, Bu_3P gave $[Bu_3PCo(CO)_3]_2$ (10%) and $[(Bu_3P)_2Co(CO)_3][Co(CO)_4]$ (73%), but only $[Bu_3PCo(CO)_3]_2$ (90%) could be isolated if the heating was continued for 8 hr. Thus both the ionic and covalent derivatives may be formed initially in benzene solution, and the former decomposes to [L $Co(CO)_3]_2$ on heating.

Both $Co_2(CO)_8$ [10] and $[Et_3PCo(CO)_3]_2$ [2] have been shown to exist as bridged and non-bridged forms in solution. During the course of this work, it has been found that similar equilibria exist for all [L $Co(CO)_3]_2$ derivatives, but appreciable quantities of the bridged forms are only found for those of Et_3As and $PhMe_2P$. However, absorption bands due to the non-bridged isomers may readily be identified.

Vohler has shown that the i.r. spectrum of $[Ph_3PCo(CO)_3]_2$ in the 2000 cm.$^{-1}$ region is compatible with D_{3h} or D_{3d} local symmetry of the $Co_2(CO)_6$ moiety.[9] The latter is the more probable as steric interactions between the two sets of radial carbonyl groups would be reduced to a minimum if they were to adopt a staggered conformation (Figure 1).

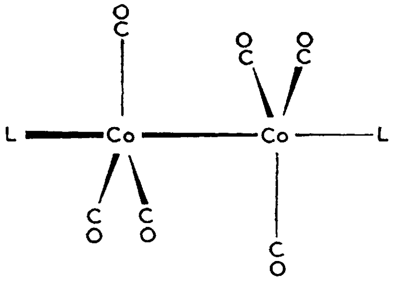

FIGURE 1 The geometry of [L $Co(CO)_3)_2$ molecules of D_{3d} symmetry

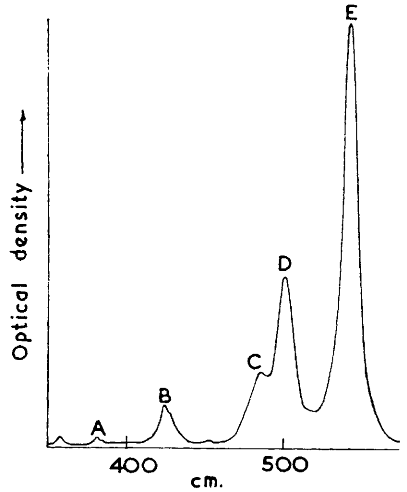

FIGURE 2 I.r. spectrum of $[Et_3P\,Co(CO)_3]_2$ in the 350—600 cm.$^{-1}$ region (benzene solution)

The two strong absorption bands in the 2000 cm.$^{-1}$ region of the i.r. spectra of the non-bridged derivatives (Table 2) are assigned to the two i.r.-allowed ν(CO) vibrations.* Using the intensity arguments described elsewhere for related molecules,[11,13] the weaker of the two absorption bands, G, is attributed to the vibration of a_{2u} symmetry, and the other, F, to the mode of e_u symmetry.

Five δ(MCO) and ν(MC) vibrations of the [L $Co(CO)_3]_2$ derivatives are i.r.-active. Absorption bands B, C, D, and E may readily be identified as due to four of them, but the fifth is more difficult to find. Consequently the assignment of A (sh) as such must be regarded as tentative

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* The i.r. allowed vibrations of the $CO_2(CO)_6$ moiety of D_{3d} symmetry are ν(MC) and ν(CO), a_{2u} and e_u; and δ(MCO), a_{2u} and $2e_u$. For a more complete description of the vibrations of this entity, see ref. 11.

[12] 'Tables of Wave-numbers for the Calibration of Infrared Spectrometers,' Butterworths, London, 1961.

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(Figure 2 and Table 2). The three more intense absorption bands C, D, and E, which lie at higher frequencies, are assigned to the three δ(MCO) modes whilst the two weaker bands, A and B, are attributed to ν(MC) vibrations.† Confirmatory evidence for this division may be obtained by comparing the spectra of $[(MeO)_3PCo(CO)_3]_2$ and $[Et_3PCo(CO)_3]_2$. As $(MeO)_3P$ is a better π-acceptor than Et_3P, both the Co–C bond order and the frequencies of the ν(MC) vibrations will be lower for the methoxy-compound than for the ethyl compound. As mixing probably occurs among vibrations of the same symmetry, all those whose frequencies lie in the 300—600 cm.$^{-1}$ region probably have some ν(MC) character, but the increase in frequency of the observed absorption bands on going from the methoxy-compound to the ethyl compound should be greatest for those modes having the most ν(MC) character. The observed differences follow the expected pattern. They are: A, 36; B, 36; C, 20; D, 16; and E, 17 cm.$^{-1}$.

The relative intensities of A, B, C, D, and E are very similar to those of the corresponding five absorption bands in the spectra of $[L\,Co(CO)_3]_2Hg$ derivatives. By comparison, B and E may be assigned to vibrations of a_{2u} symmetry and the others to modes of e_u symmetry.

The i.r.-allowed Co–L stretching vibrations of a_{2u} symmetry probably lie at lower frequencies than the δ(MCO) and ν(MC) modes in these molecules, but will mix with those of a_{2u} symmetry. The frequencies of the ν(ML) modes and their degree of mixing with δ(MCO) and ν(MC) vibrations will be greater in the phosphine than the arsine complexes. Consequently the δ(MCO) and ν(MC) vibrations of a_{2u} symmetry would be expected to lie at higher frequencies in the phosphine than in the arsine complexes, whereas very little difference would be expected for the e_u vibrations. Comparison of the spectra of $[Et_3PCo(CO)_3]_2$ and $[Et_3As\,Co(CO)_3]_2$ shows that absorption bands B and E are due to modes of a_{2u} symmetry. The final assignment is given in Table 2.

The vibrations of largely ν(MC) character lie at lower frequencies (*ca.* 50—60 cm.$^{-1}$) for the $[L\,Co(CO)_3]_2$ derivatives than for their $[L\,Co(CO)_3]_2Hg$ counterparts. Differences of only 10—25 cm.$^{-1}$ are observed for δ(MCO) modes, and ν(CO) vibrations have similar frequencies for both series.)‡ These observations indicate that although the C–O bond order is about the same for both series of compounds, the Co–C bond order is greater for the mercury cobalt carbonyl derivatives. An explanation is that in these complexes there is a drift of electrons from the cobalt atoms to the mercury atom. This allows an increase in C–Co σ-bonding with very little change in the Co–C and C–O π-bonding. Such an effect is not possible in the $[L\,Co(CO)_3]_2$ complexes.

[7/1589 *Received, December 4th,* 1967]

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† A similar division of the observed absorption bands into those of largely δ(MCO) character and those of largely ν(MC) character has been made for $[L\,Co(CO)_3]_2Hg$ derivatives,[11] and for many mononuclear complexes.[14-19]

‡ The frequencies of the relevant absorption bands in the spectrum of $[Et_3PCo(CO)_3]_2Hg$ are A, 443; B, 477; C, 511; D, 527; E, 557; F, 1947; and G, 1988 cm.$^{-1}$.[11]

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