Structures and Some Reactions of π-Diene Derivatives of Octacarbonyldicobalt

By **Josephine Newman** and **A. R. Manning,*** Department of Chemistry, University College, Dublin 4, Ireland

Norbornadiene and conjugate dienes react with $Co_2(CO)_8$ to give $\{(\pi\text{-diene})Co_2(CO)_6\}$ (I) and then $\{(\pi\text{-diene})Co(CO)_2\}_2$ (II) (diene = norbornadiene, isoprene, and 2,3-dimethylbuta-1,3-diene). The hexacarbonyl derivatives (I) are not tautomeric, and have structures based on that of the bridged isomer of octacarbonyldicobalt. Both (I) and (II) react with iodine to give $\{(\pi\text{-diene})Co(CO)_2I\}$ derivatives which could be detected but not isolated, with SnX_4 to give mixtures of $\{(\pi\text{-diene})Co(CO)_2SnX_3\}$ and $\{Co(CO)_4SnX_3\}$ (X = Cl, Br, or I), and with Ph_3PAuCl, HgX_2, and Ph_3SnCl to give only $Ph_3PAuCo(CO)_4$, $Hg\{Co(CO)_4\}_2$, and $Ph_3SnCo(CO)_4$ respectively. Monodentate tertiary phosphines convert (I) to a mixture of (II) and $\{(R_3P)Co(CO)_3\}_2$ *via* the unstable intermediate ionic species $[(\pi\text{-diene})Co(CO)_2PR_3][Co(CO)_4]$. Similar salts are stable and have been isolated with $Ph_2PCH_2CH_2PPh_2$, *i.e.* $[\{(\pi\text{-diene})Co(CO)_2\}_2\{Ph_2PCH_2CH_2PPh_2\}][Co(CO)_4]_2$. They are reduced by $NaBH_4$ to $\{(\pi\text{-allyl})Co(CO)_2\}_2\{Ph_2PCH_2CH_2PPh_2\}$. The i.r. spectra of the products are reported and their structures discussed. The reactions are compared, and contrasted, with those of the related isoelectronic and isostructural π-cyclopentadienyl complexes of iron.

ALTHOUGH the $(\pi\text{-diene})Co(CO)_2$ and $(\pi\text{-}C_5H_5)Fe(CO)_2$ moieties are isoelectronic, little attention has been directed towards a study of complexes containing the former. Therefore, we have reinvestigated the reactions of various dienes with $Co_2(CO)_8$,[1] and have studied the chemistries of the two products, $\{(\pi\text{-diene})Co_2(CO)_6\}$ (I) and $\{(\pi\text{-diene})Co(CO)_2\}_2$ (II) {diene = C_7H_8(norbornadiene), C_5H_8(isoprene), and C_6H_{10}(2,3-dimethylbuta-1,3-diene)}.

EXPERIMENTAL

Most chemicals were purchased commercially, but 2,3-dimethylbuta-1,3-diene [2] and 1,2-bis(diphenylphosphino)ethane [3] were prepared by published methods.

All reactions were carried out under an atmosphere of nitrogen using purified solvents, and were monitored by i.r. spectroscopy.

Equimolar quantities of octacarbonyldicobalt (*ca.* 1 g) and a diene (norbornadiene, isoprene, or 2,3-dimethylbuta-1,3-diene) in pentane (25 ml) were heated to reflux. After *ca.* 30 min, the hot reaction mixtures were filtered, and cooled to give crystals of the $\{(\pi\text{-diene})Co_2(CO)_6\}$ derivatives. Although the yields were high (60—80%), good analyses could only be obtained for the norbornadiene complex.† The other compounds always underwent slight decomposition during any attempt to purify them by recrystallization from pentane.

When diene : $Co_2(CO)_8$ mole ratios of 20 : 1 were used, the hexacarbonyl derivatives first formed underwent further CO replacement. The $\{(\pi\text{-diene})Co(CO)_2\}_2$ complexes thus obtained were isolated by removal of the pentane and the excess of diene at reduced pressures, and the residues purified by recrystallization from benzene–hexane mixtures.

The only product which could be isolated from the reactions of $\{(\pi\text{-diene})Co_2(CO)_6\}$ or $\{(\pi\text{-diene})Co(CO)_2\}_2$ with iodine in chlorinated solvents was $Co_4(CO)_{12}$. However, with a two-fold molar excess of SnX_4 (X = Cl, Br, or I) in benzene at room temperature, both series gave mixtures of the $\{(\pi\text{-diene})Co(CO)_2SnX_3\}$ and $\{Co(CO)_4SnX_3\}$ derivatives. They may be separated by fractional crystallization and the former isolated in yields of between 40 and 80%. In refluxing benzene, tin(II) bromide and $\{(\pi\text{-}C_7H_8)Co(CO)_2\}_2$ gave $\{(\pi\text{-}C_7H_8)Co(CO)_2SnBr_3\}$ (yield = 30%).

Equimolar quantities of $\{(\pi\text{-}C_7H_8)Co_2(CO)_6\}$ and Ph_2MeP reacted to give an oil containing the $\{Co(CO)_4\}^-$ ion. This was unstable and decomposed rapidly. Both $\{(Ph_2MeP)Co(CO)_3\}_2$ and $\{(\pi\text{-}C_7H_8)Co(CO)_2\}_2$ were isolated in yields of *ca.* 10% each. If the amount of phosphine was doubled, and Ph_2MeP replaced by Ph_3P, Bu_3P, Ph_2MeP, $(MeO)_3P$, or $(PhO)_3P$, (L), the initial ionic products decomposed within 30 min to $\{LCo(CO)_3\}_2$ only. On the other hand, when a bidentate ligand $Ph_2PCH_2CH_2PPh_2$ was used in place of the monodentate ligands, the initial ionic product was stable and precipitated from solution as $[\{(\pi\text{-diene})Co(CO)_2\}_2\{Ph_2PCH_2CH_2PPh_2\}][Co(CO)_4]_2,2C_6H_6$. Reaction of these salts with $NaBPh_4$ or tetrafluoroboric acid in acetone–water brings about replacement of $\{Co(CO)_4\}^-$ by $\{BPh_4\}^-$ or $\{BF_4\}^-$ respectively.

The reaction of $\{(\pi\text{-}C_5H_5)FeCo(CO)_6\}$ with Ph_3P in tetrahydrofuran solution (mole ratio 1 : 1) gave $\{(\pi\text{-}C_5H_5)Fe(CO)_2PPh_3\}\{Co(CO)_4\}$ in high yield. It was purified by crystallisation from tetrahydrofuran.

The reduction of $[\{(\pi\text{-}C_6H_{10})Co(CO)_2\}_2\{Ph_2PCH_2CH_2PPh_2\}][Co(CO)_4]_2,2C_6H_6$ with sodium borohydride in aqueous acetone solution was carried out at room temperature. The product was isolated by removal of the solvent at reduced pressure and recrystallized from acetone.

The i.r. spectra of the complexes were obtained using a Perkin-Elmer 337 spectrometer fitted with a Hitachi readout recorder. They were calibrated with deuterium chloride and bromide.[4]

The m.p.s, analyses, and i.r. spectra of the various compounds are summarised in Tables 1 and 2.

RESULTS AND DISCUSSION

Winkhaus and Wilkinson[1] have shown that both $\{(\pi\text{-diene})Co_2(CO)_6\}$ compounds (I) and $\{(\pi\text{-diene})Co(CO)_2\}_2$ derivatives (II) are formed from the reactions of norbornadiene and some conjugated dienes with octacarbonyldicobalt. We have found that such reactions take place in two steps with the first, the formation of (I), being more rapid than the second, their

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† Found: C, 40·8; H, 2·5. $(C_7H_8)Co_2(CO)_6$ Requires C, 41·3; H, 2·2%.

[1] G. Winkhaus and G. Wilkinson, *Chem. and Ind.*, 1960, 1083, and *J. Chem. Soc.*, 1961, 602.

[2] *Org. Synth.*, Coll. vol. 3, p. 312.

[3] J. Chatt and F. A. Hart, *J. Chem. Soc.*, 1960, 1378.

[4] 'Tables of Wavenumbers for the Calibration of Infrared Spectrometers,' Butterworths, London, 1965.

conversion to (II). It may be brought about by mild conditions.

The hexacarbonyl complexes (I) are rather unstable orange crystalline solids. Although they are formed by many dienes, we have only isolated three {diene = C_7H_8 (norbornadiene), C_5H_8 (isoprene), or C_6H_{10} (2,3-dimethylbuta-1,3-diene)}, and could only obtain consistent analyses for the most stable, {(π-C_7H_8)$Co_2(CO)_6$}.

TABLE 1

Melting points, analyses (%), and i.r. spectra of some compounds [a]

		Analyses [c]							
		Found			Required				
	M.p. [b]	C	H	X	C	H	X	Absorption bands [d]	
(C_7H_8)$Co(CO)_2SnCl_3$	dec. 88	25·1	1·8	24·5	25·0	1·9	24·6	2013(10)	2050(8·1)
(C_7H_8)$Co(CO)_2SnBr_3$	dec. 90	18·7	1·3	42·1	19·1	1·4	42·3	2012(10)	2049(8·4)
(C_7H_8)$Co(CO)_2SnI_3$	dec. 97	14·8	0·9	53·9	15·3	1·1	53·9	2006(10)	2043(8·5)
(C_6H_{10})$Co(CO)_2SnCl_3$	dec. 115	22·3	2·4	25·0	22·7	2·4	25·2	2036(10)	2071(9·0)
(C_6H_{10})$Co(CO)_2SnBr_3$	dec. 105	16·9	1·7		17·3	1·8	43·2	2035(10)	2070(9·7)
(C_5H_8)$Co(CO)_2SnCl_3$	64—66	20·1	2·0	26·1	20·6	2·0	26·2	2040(10)	2075(9·0)
(C_5H_8)$Co(CO)_2SnBr_3$	77—78	15·7	1·7	44·3	15·5	1·5	44·3	2039(10)	2074(9·0)
(C_5H_5)$Fe(CO)_2SnCl_3$	153—154	20·9	1·5		20·9	1·2		1999(10)	2037(9·8)
[{(C_7H_8)$Co(CO)_2$}$_2${dp}][$Co(CO)_4$]$_2$,2C_6H_6	288—290	58·7	4·2		58·6	4·0		1958(10)	2009(5·2) [e]
[{(C_7H_8)$Co(CO)_2$}$_2${dp}][BPh_4]$_2$,4H_2O	124—126	72·4	5·3		72·5	5·8		1957(10)	2008(4·5)
[{C_7H_8)$Co(CO)_2$}$_2${dp}][BF_4]$_2$,4H_2O	98—100	50·1	4·4		49·9	4·5		1958(10)	2009(4·6)
[{(C_6H_{10})$Co(CO)_2$}$_2${dp}][$Co(CO)_4$]$_2$,-2C_6H_6	296—298	57·2	4·2		57·6	4·3		1957(10)	2011(4·7) [e]
[{(C_6H_{10})$Co(CO)_2$}$_2${dp}][BPh_4]$_2$,4H_2O	122—124	71·5	5·9		71·8	6·1		1957(10)	2010(4·4)
[{(C_5H_8)$Co(CO)_2$}$_2${dp}][$Co(CO)_4$]$_2$,-2C_6H_6	280—282	57·4	4·0		57·1	4·1		1958(10)	2009(4·1) [e]
[{(C_5H_8)$Co(CO)_2$}$_2${dp}][BPh_4]$_2$	139—141	74·8	5·7		75·3	5·7		1958(10)	2009(4·0)
[(C_5H_5)$Fe(CO)_2PPh_3$][$Co(CO)_4$]	dec. 140	56·6	3·2		57·0	3·3		2014(10·0)	2056(9·2) [e]
{(C_6H_{11})$Co(CO)_2$}$_2${dp}	288—290	63·4	5·5		63·5	5·8		1930(10)	1987(6·3)

[a] dp = $Ph_2PCH_2CH_2PPh_2$. [b] °C, determined in sealed tubes. dec. = decomposes without melting. [c] X = halogen. [d] Peak positions (cm^{-1} in chloroform solution) with relative peak heights in parentheses. [e] These spectra show an absorption band at 1890 cm^{-1} due to the $Co(CO)_4^-$ ion.

TABLE 2

The i.r. spectra of {(π-diene)$Co_2(CO)_6$} complexes between 1700 and 2100 cm^{-1} in heptane solution {peak positions (cm^{-1}) with relative peak heights in parentheses}

Diene	Absorption bands					
C_7H_8	1834(10)	1849(1·9)	2009(sh)	2012(13·1)	2024(16·8)	2076(11·0)
C_5H_8	1842(10)	1856(2·3)	2010(sh)	2015(15·0)	2036(24·7)	2079(13·7)
C_6H_{10}	1840(10)	1849(1·5)	2008(12·9)	2012(13·1)	2035(15·2)	2076(11·7)

The {(π-diene)$Co(CO)_2$}$_2$ compounds (II) are isostructural with {(π-C_5H_5)$Fe(CO)_2$}$_2$ and have an almost planar $M(CO_\mu)_2M$ bridging system.[5-7] Thus it would be expected that {(π-diene)$Co_2(CO)_6$} would adopt structures which are intermediate between those of (II) and $Co_2(CO)_8$,[8] and comparable to that of {(π-C_9H_7)$FeCo(CO)_6$} (C_9H_7 = indenyl) in the solid state.[9] However, this is not the case. An *X*-ray diffraction study has shown that {(π-C_7H_8)$Co_2(CO)_6$} has a structure which is virtually identical with that of $Co_2(CO)_8$ but with two carbonyl groups *trans* to the bridging ligands replaced by the chelating, bidentate diene.[10] The similarity of the i.r. spectrum of {(π-C_7H_8)$Co_2(CO)_6$} to those of other hexacarbonyl derivatives (Table 2) points to a similar structure in all instances. It is probable that the bonding between the conjugated dienes and the cobalt atoms is similar to that in (II) {diene = C_6H_{10} and C_6H_8 (cyclohexa-1,3-diene)}.[6,7] There are no indications that (I) are tautomeric as their spectra are independent of the solvent provided that they do not react with it. In view of the behaviour of $Co_2(CO)_8$ [11] and (II),[5] this was unexpected, and contrasts with the presence of carbonyl-bridged and non-bridged forms in solutions of the isoelectronic {(π-dienyl)$FeCo(CO)_6$} compounds (dienyl = C_5H_5, MeC_5H_4, or C_9H_7).[12] It is further evidence that polynuclear transition metal complexes containing the (π-diene)Co moiety are more likely than their isoelectronic (π-dienyl)Fe counterparts to adopt CO-bridged as opposed to non-bridged structures.

The structures of the tetracarbonyl derivatives (II) have been discussed elsewhere.[5-7]

An important class of reactions of {(π-dienyl)$Fe(CO)_2$}$_2$ are those which involve cleavage of the metal–metal bond. Halogens, X_2, give {(π-dienyl)$Fe(CO)_2X$} *via*

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[5] P. McArdle and A. R. Manning, *J. Chem. Soc.* (*A*), 1970, 2123.

[6] F. S. Stephens, *J. Chem. Soc.* (*A*), 1970, 2745.

[7] F. S. Stephens, *J.C.S. Dalton*, 1972, 1752.

[8] G. G. Sumner, H. P. Klug, and L. E. Alexander, *Acta Cryst.*, 1964, **17**, 732.

[9] F. S. Stephens, personal communication.

[10] F. S. Stephens, *J.C.S. Dalton*, 1972, 1754.

[11] K. Noack, *Spectrochim. Acta*, 1963, **19**, 1925; *Helv. Chim. Acta*, 1962, **45**, 1847; 1964, **47**, 1555; G. Bor, *Spectrochim. Acta*, 1963, **19**, 2065.

[12] A. R. Manning, *J. Chem. Soc.* (*A*), 1971, 2321.

ionic $[\{(\pi\text{-dienyl})Fe(CO)_2\}_2X]X$ intermediates.[13] Although $Co_4(CO)_{12}$ was the final product in all instances, iodine converts both (I) and (II) to transient intermediate species. These give rise to two absorption bands of comparable intensities in their i.r. spectra which, when the diene = C_6H_{10}, have frequencies of 2039 and 2076 cm^{-1}. They are probably due to the $\nu(CO)$ vibrations of the hoped-for, but unstable, $\{(\pi\text{-diene})Co(CO)_2I\}$ complexes.

With tin(IV) halides, SnX_4, $\{(\pi\text{-dienyl})Fe(CO)_2\}_2$ give mixtures of $(\pi\text{-dienyl})Fe(CO)_2X$ and $\{(\pi\text{-dienyl})Fe(CO)_2SnX_3\}$ (dienyl = C_5H_5, MeC_5H_4, and C_9H_7).[14,15] Similarly, both (I) and (II) yield the orange, air-stable $\{(\pi\text{-diene})Co(CO)_2SnX_3\}$ derivatives in good yields, but substantial quantities of the well known $\{Co(CO)_4SnX_3\}$ compounds[16] were also obtained. This is to be expected for (I), but it indicates that with (II) considerable internal ligand rearrangement must have occurred. In other reactions, *e.g.* with Ph_3PAuCl, Ph_3SnCl, and HgX_2 (X = Cl or Br), the rearrangement route predominates, and the only products isolated were $\{Ph_3PAuCo(CO)_4\}$,[17] $\{Ph_3SnCo(CO)_4\}$,[16] and $Hg[Co(CO)_4]_2$ respectively.[18] There appears to be no record of a similar type of reaction with $\{(\pi\text{-dienyl})Fe(CO)_2\}_2$. $\{(\pi\text{-}C_7H_8)Co(CO)_2SnBr_3\}$ may also be prepared from the reaction of $\{(\pi\text{-}C_7H_8)Co(CO)_2\}_2$ with tin(II) bromide, but no $\{(\pi\text{-}C_7H_8)Co(CO)_2\}_2SnBr_2$ was formed (*cf.* ref. 15). There are two absorption bands in the i.r. spectra of the $\{(\pi\text{-diene})Co(CO)_2SnX_3\}$ complexes (X = Cl, Br, or I) which are due to their $\nu(CO)$ vibrations (Table 1). Their relative intensities suggest that the OC–Co–CO angles are close to 90°.[19] Thus these compounds may have structures which are similar to that of $\{(\pi\text{-}C_5H_5)Fe(CO)_2SnBr_3\}$, or are based on trigonal bipyramidal co-ordination about the Co atom with the CO groups occupying an axial and an equatorial co-ordination position. In either event this contrasts with observed structures of $\{(\pi\text{-}C_7H_8)Co(CO)_2\}_2SnX_2$ (X = Cl or Ph) where the carbonyl ligands occupy equatorial co-ordination positions of trigonal bipyramids.[20]

The second group of reactions we have investigated are those of (I) and (II) with tertiary phosphines. Monodentate ligands replace one CO group of $\{(\pi\text{-}C_5H_5)Fe(CO)_2\}_2$,[21] but bidentate ligands replace two to give both ionic and covalent products.[21,22] Bidentate ligands L–L displace the dienes rather than CO groups from (II) to give products of the general type $\{(L\text{–}L)Co(CO)_2\}$.[23] Monodentate phosphines and phosphites, L, give a complex mixture of products which could not be separated. However, i.r. spectroscopic studies showed that both $\{LCo(CO)_3\}_2$ and $\{L_2Co(CO)_2\}_2$ derivatives are formed.

The corresponding reactions of phosphines with (I) are far more interesting. In all instances investigated, monodentate phosphines, L, give the ionic complexes $\{(\pi\text{-diene})Co(CO)_2L\}\{Co(CO)_4\}$ as the initial products. Although these precipitate from benzene as oils, they are unstable and decompose. With equimolar amounts of Ph_2MeP and $\{(\pi\text{-}C_7H_8)Co_2(CO)_6\}$, the final products are $\{(Ph_2MeP)Co(CO)_3\}_2$ and $\{(\pi\text{-}C_7H_8)Co(CO)_2\}_2$. When L : (I) mole ratios of 2 : 1 were used for L = Ph_3P, Ph_2MeP, $Bu^n{}_3P$, $(PhO)_3P$, and $(MeO)_3P$, and diene = C_7H_8 and C_6H_{10}, the only products are of the type $\{LCo(CO)_3\}_2$. The yield of $\{(Ph_3P)Co(CO)_3\}_2$ is quantitative. In the case of the bidentate ditertiary phosphine $Ph_2PCH_2CH_2PPh_2$, the ionic products are stable. The cations, $\{(\pi\text{-diene})Co(CO)_2(Ph_2PCH_2CH_2PPh_2)Co(CO)_2(\pi\text{-diene})\}^{2+}$, may be isolated as salts with $\{Co(CO)_4\}^-$, $\{BF_4\}^-$, or $\{BPh_4\}^-$ counteranions. The related, isoelectronic $\{(\pi\text{-dienyl})FeCo(CO)_6\}$ complexes also undergo $\{Co(CO)_4\}^-$ rather than CO displacement with tertiary phosphines. The ionic products, *e.g.* $\{(\pi\text{-}C_5H_5)Fe(CO)_2PPh_3\}\{Co(CO)_4\}$ are obtained in near quantitative yields, and on heating decompose to mixtures of, for example, $\{(\pi\text{-}C_5H_5)Fe(CO)_2\}_2$ and $\{(Ph_3P)Co(CO)_3\}_2$.

The i.r. spectra of the $[\{(\pi\text{-diene})Co(CO)_2\}_2\{Ph_2PCH_2CH_2PPh_2\}]^{2+}[X^-]_2$ salts {X = $Co(CO)_4$, BF_4, or BPh_4} (Table 1) show two absorption bands due to the $\nu(CO)$ vibrations of the cations. The relative intensities are consistent with a OC–Co–CO angle of *ca.* 120° rather than the *ca.* 90° found in $\{(\pi\text{-}C_5H_5)Fe(CO)_2PPh_3\}^+$ and *e.g.* $\{(\pi\text{-diene})Co(CO)_2SnBr_3\}$. This suggests that there is trigonal bipyramidal co-ordination about the cobalt atoms with the carbonyl ligands in equatorial positions (*cf.* $\{(C_7H_8)Co(CO)_2\}_2SnCl_2$[20]).

The similarity between the $\{(\pi\text{-}C_5H_5)Fe(CO)_2PPh_3\}^+$ and $[\{(\pi\text{-}C_6H_{10})Co(CO)_2\}_2\{Ph_2PCH_2CH_2PPh_2\}]^{2+}$ salts extends to their reactions with sodium borohydride. In both there is hydride ion attack upon the co-ordinated hydrocarbon ligands to give the neutral π-cyclopentadiene and π-allyl complexes, $\{(\pi\text{-}C_5H_6)Fe(CO)_2PPh_3\}$[24] and $\{(\pi\text{-}C_6H_{11})Co(CO)_2\}_2\{Ph_2PCH_2CH_2PPh_2\}$ respectively.

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