120. *Some Diolefincobalt Carbonyl Complexes.*

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Binuclear olefin-substituted cobalt carbonyl complexes of the type $Co_2(CO)_6$(diolefin) and $Co_2(CO)_4$(diolefin)$_2$, in which the bridging carbonyl groups are retained, have been prepared by direct interaction of dicobalt octacarbonyl with norbornadiene, cyclohexa-1,3-diene, and 2,3-dimethylbuta-1,3-diene; the existence of complexes with isoprene and buta-1,3-diene has been shown spectroscopically. Infrared spectra are given and the proton magnetic resonance spectrum of the dimethylbutadiene complex is reported.

OLEFIN-SUBSTITUTED complexes of cobalt carbonyl have been postulated as intermediates in the hydroformylation and other reactions,[1] but relatively few complexes have been isolated. Stable carbonyl compounds have been prepared by direct interaction with tetracyclone [2] and cyclo-octatriene [3] and π-butenyl [4] and π-allyl [5] complexes have been obtained indirectly; π-cyclopentadienylcobalt complexes with cyclopentadienes are also well characterised.[6]

We have now isolated several new binuclear carbonyl complexes (see Table) from the direct interaction of dicobalt octacarbonyl with bicyclo[2,2,1]hepta-2,5-diene (norbornadiene), cyclohexa-1,3-diene, and 2,3-dimethylbuta-1,3-diene. The alkyne-bridged cobalt carbonyl, $Co_2(CO)_6(PhC{\equiv}CPh)$,[7] also reacts with norbornadiene to give the same compound as the octacarbonyl.

Preparations and Properties.—The reactions of the olefins and cobalt carbonyl were carried out in an inert solvent at 40—60° under nitrogen and were completed in 2—4 hr.; higher temperatures and prolonged heating lead to partial decomposition and formation of tetracobalt dodecacarbonyl and metallic cobalt. Both mono- and di-substituted complexes were obtained, and were separated from the reaction products by fractional

$$Co_2(CO)_8 + \text{Diolefin} = Co_2(CO)_6(\text{diolefin}) + 2CO$$
$$Co_2(CO)_8 + 2\text{Diolefin} = Co_2(CO)_4(\text{diolefin})_2 + 4CO$$

extraction and crystallisation and by chromatography on alumina.

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[1] See, *e.g.*, Sternberg and Wender, Internat. Conference on Co-ordination Chemistry, London, 1959, *Chem. Soc. Special Publ. No.* 13.

[2] Weiss and Hubel, *J. Inorg. Nuclear Chem.*, 1959, **11**, 42.

[3] Fischer and Palm, *Z. Naturforsch.*, 1959, **14**, b, 508.

[4] Jonassen, Stearns, Kenttämaa, Moore, and Whittaker, *J. Amer. Chem. Soc.*, 1958, **80**, 2586; Aldridge, Jonassen, and Pulkinnen, *Chem. and Ind.*, 1960, 374.

[5] Heck and Breslow, *J. Amer. Chem. Soc.*, 1960, **82**, 750.

[6] Green, Pratt, and Wilkinson, *J.*, 1959, 3753.

[7] Greenfield, Sternberg, Friedel, Wotiz, Markby, and Wender, *J. Amer. Chem. Soc.*, 1956, **78**, 120.

The disubstituted compounds from norbornadiene and dimethylbutadiene were isolated in good yield, from cyclohexadiene in low yield; in all cases the yield of the monosubstituted compound was very low and for cyclohexadiene the product could not be isolated in a pure state.

Under similar conditions we were unable to obtain evidence for complexes from bicyclo[2,2,2]octa-2,5-diene, cyclo-octatetraene, cyclo-octa-1,5-diene, or *p*-benzoquinone, but when isoprene and butadiene were used spectroscopic evidence for the existence of complexes was obtained though the products could not be obtained in a pure state. Chromatography of the isoprene reaction mixture also yielded a fraction which showed no bridging carbonyl stretching frequencies but has not been fully investigated at present.

The compounds form orange-red needles from ether or light petroleum, apart from the cyclohexadiene complex which crystallises in golden-yellow plates. The solids are stable in air at room temperature but decompose without melting when heated; the disubstituted products are the most stable thermally but even the monosubstituted products are more stable than cobalt carbonyl itself. The compounds cannot be sublimed in a vacuum without extensive decomposition. Whereas the monosubstituted compounds are readily soluble in common organic solvents, the disubstituted ones are fairly soluble only in chloroform, less in benzene and carbon disulphide, and sparingly soluble in ether and petroleum. All solutions are quite air-sensitive, decomposition being particularly rapid in chloroform which decomposes the norbornadiene and cyclohexadiene compounds even in absence of air.

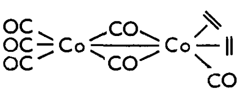
Spectra.—The infrared spectra of the compounds in solution show frequencies characteristic for both terminal and bridging carbon monoxide groups (see Table); these, together with the diamagnetism and analyses of the compounds, show that the carbon monoxide bridging groups in the octacarbonyl are preserved and that the diolefin has replaced two or four of the terminal carbon monoxide groups in the carbonyl.

Infrared spectra of the olefin complexes (in CCl_4 *and* CS_2 *with* CaF_2 *optics, 2200—1700 cm.*$^{-1}$ *region).*

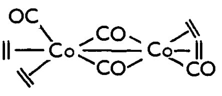
	C–O stretching modes [a]	
Compound	Terminal	Bridging
$Co_2(CO)_6$(norbornadiene)	2083s, 2054m, 2030vs	1840sh, 1820s
$Co_2(CO)_4$(norbornadiene)$_2$	2021vs, 1996ms	1798s
$Co_2(CO)_4$(cyclohexa-1,3-diene)$_2$	2045vs, 2015vs	1809s
$Co_2(CO)_6$(2,3-dimethylbutadiene)	2087s, 2046vs, 2021vs	1850sh, 1830s
$Co_2(CO)_4$(2,3-dimethylbutadiene)$_2$	2005vs, 2025sh	1805s
Isoprene complex [b]	2080m, 2063m, 2040vs	1834s
Butadiene complex [b]	~2050m	~1815m

[a] Dicobalt octacarbonyl shows bands at 2070, 2043, 2025, and 1858 cm.$^{-1}$ (Cable, Nyholm, and Sheline, *J. Amer. Chem. Soc.*, 1954, **76**, 3373) but under high resolution further splitting of both terminal and bridging frequencies is observed (Cotton and Monchamp, *J.*, 1960, 1882). [b] Not obtained pure.

The monosubstituted complexes (I) show three frequencies characteristic of terminal carbon monoxide groups only slightly shifted compared to the octacarbonyl.



(I)



(II)

In the spectra of the disubstituted compounds (II) (which can in principle have isomers, although no evidence was obtained for them in chromatographic separations), two terminal carbonyl frequencies of unequal intensity are observed; in the dimethylbutadiene complex only one band with a weak shoulder was observed. It is not possible to draw reliable structural conclusions from the spectra in the absence of *X*-ray data, particularly since the bridge system may be non-planar, as suggested for cobalt octacarbonyl,[8] and other complications such as those observed [9] for the similar molecule [π-$C_5H_5Fe(CO)_2]_2$ which also has two briding carbonyl groups and a carbon monoxide on each metal atom. The spectra in the bridging carbonyl region show one band, but since shoulders were observed in some cases, this band may be more complex under high resolution. The shift to lower wave numbers in the sequence $Co_2(CO)_8$, $Co_2(CO)_6$(diolefin), $Co_2(CO)_4$(diolefin)$_2$ (see Table), may be due to a lowering of strain in the bridge-ring system or to the lower capability of the olefins relative to carbon monoxide to accept π-electron density from the metal atom, which would also be in accordance with the lower terminal carbonyl frequencies in the disubstituted compounds as compared to the octacarbonyl.

The pattern of the remainder of infrared spectra is generally similar to that of the olefins themselves; the stretching frequencies for $>CH_2$ and $>CH$ groups are lowered by 25—60 cm.$^{-1}$ on co-ordination but the C=C stretching frequencies in the free hydrocarbons (1650—1550 cm.$^{-1}$) are not observed in the complexes, being replaced by absorptions in the region 1470—1425 cm.$^{-1}$.

Owing to the low solubility or instability in suitable solvents the proton magnetic resonance spectra could not be obtained except in the case of the disubstituted dimethylbutadiene complex, $Co_2(CO)_4(C_6H_{10})_2$. In chloroform solution the compound shows three lines. The methyl groups give a line at $\tau = 8{\cdot}19$ of width about 1·4 c./sec. The terminal protons give two lines of equal intensity and width (2·4 c./sec.) at $\tau = 7{\cdot}84_5$ and 8·37. In each $=CH_2$ group the protons are probably not equivalent,[6,10] each contributing to one of the observed lines. These lines must have fine structure, since they are broader than the methyl line, but it was not possible to resolve this structure and all the lines appear to be slightly broadened by the presence of small amounts of paramagnetic impurity or decomposition product. In the parent 2,3-dimethylbuta-1,3-diene, the terminal olefinic protons would occur at about $\tau = 5{\cdot}2$, and their shift to higher fields on bonding to the transition metal is similar to that found in other, similar complexes.[6,10]

EXPERIMENTAL

Microanalyses and molecular weights (ebullioscopic in benzene) by the Microanalytical Laboratory, Imperial College.

Infrared spectra were measured on a Perkin–Elmer model 21 spectrometer with both sodium chloride and calcium fluoride optics. High-resolution proton magnetic resonance spectra were taken at 56·5 Mc./sec. on a Varian Associates Model 4300B spectrometer at 22° ± 2° in concentrated solution in chloroform in spinning 5-mm. (outside diameter) tubes; shifts are referred to tetramethylsilane (τ values).

All preparations and most operations were performed in a nitrogen atmosphere.

Reaction of Cobalt Carbonyl with Norbornadiene.—A mixtre of cobalt octacarbonyl (0·86 g., 2·5 mmoles) and norbornadiene (4·6 g., 50 mmoles) in light petroleum (b. p. 40—60°) (30 ml.) was refluxed for 2 hr. Gas was evolved and an orange-red product precipitated. After removal of solvent and exces of olefin at 30°/1 mm., the product, *dinorbornadienedicobalt tetracarbonyl,* was crystallised repeatedly from ether, forming red needles [0·72 g., 70% based on $Co_2(CO)_8$], decomp. 147° (Found: C, 52·0; H, 3·8; O, 15·7; Co, 28·6%; *M*, 424. $C_{18}H_{16}O_4Co_2$ requires C, 52·2; H, 3·9; O, 15·5; Co, 28·5%; *M*, 414). Small quantities of the monosubstituted derivative were also found in the reaction mixture; this compound was obtained in higher yield by using equimolar quantities (2·5 mmoles) of the reagents under conditions similar to the above. After removal of solvent and excess of carbonyl the product was chromatographed on an alumina column using benzene–light petroleum as eluant. The first fraction gave *norbornadienedicobalt hexacarbonyl,* which was crystallised from petroleum at −40° as red needles, decomp. 97° (0·05 g., 5%) (Found: C, 41·2; H, 2·6; O, 25·1%; *M*, 379. $C_{13}H_8O_6Co_2$ requires C, 41·3; H, 2·1; O, 25·4%; *M*, 378). The second fraction gave the disubstituted product (0·3 g.).

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[8] Mills and Robinson, *Proc. Chem. Soc.*, 1959, 156.

[9] Cf. Cotton, Stammreich, and Wilkinson, *J. Inorg. Nuclear Chem.*, 1959, **9**, 3.

[10] Cf. Green, Pratt, and Wilkinson, *J.*, 1960, 989.

Reaction of Cobalt Carbonyl with Cyclohexa-1,3-*diene*.—A mixture of dicobalt carbonyl (0·86 g.) and cyclohexa-1,3-diene (1·6 g.) in light petroleum (b. p. 60—80°) (40 ml.) was refluxed for 4 hr. After removal of solvent and excess of olefin, the dark residue was extracted with chloroform and chromatographed on alumina with light petroleum–chloroform as eluant. Crystallisation of the eluted product from ether gave golden plates, decomp. $>100°$ (0·06 g., 6%), of *dicyclohexa*-1,3-*dienedicobalt tetracarbonyl* (Found: C, 49·2; H, 4·8; O, 16·4. $C_{16}H_{16}O_4Co_2$ requires C, 49·3; H, 4·1; O, 16·4%). In the infrared spectrum of the crude reaction mixture, a weak peak at *ca.* 1830 cm.$^{-1}$ was observed, indicating the presence of a small quantity of the monosubstituted compound.

Reaction of Cobalt Carbonyl with 2,3-*Dimethylbuta*-1,3-*diene*.—Cobalt carbonyl (0·86 g.) and the olefin (4·1 g.) in light petroleum (40 ml.) were refluxed for 2 hr. After removal of volatile matter, the orange residue was dissolved in ether and chromatographed on alumina with light petroleum–ether (85 : 15) as eluant. The first fraction, after recrystallisation from ether, gave red needles of *di*-(2,3-*dimethylbuta*-1,3-*diene*)*dicobalt tetracarbonyl* (0·6 g., 60%) (Found: C, 48·8; H, 5·3; O, 16·5; Co, 29·9%; *M*, 433. $C_{16}H_{20}O_4Co_2$ requires C, 48·8; H, 5·1; O, 16·2; Co, 29·9%; *M*, 394). The second fraction gave red needles, from light petroleum at $-20°$, of 2,3-*dimethylbuta*-1,3-*dienedicobalt hexacarbonyl* (0·04 g., 5%) (Found: C, 37·9; H, 3·8; O, 24·8. $C_{12}H_{10}O_6Co_2$ requires C, 39·2; H, 3·7; O, 26·1%).

Reaction of Diphenylacetylenedicobalt Hexacarbonyl with Norbornadiene.—The compound and excess of norbornadiene in light petroleum were refluxed for 2 hr. The red product, on crystallisation from ether, was found to be identical with the disubstituted product from the reaction of cobalt carbonyl and norbornadiene.

Infrared Spectra.—Details of the spectra excluding the carbonyl region (in CCl_4 and CS_2; cm.$^{-1}$) are as follows (the spectra of the disubstituted compounds are incomplete owing to low solubility):

$(C_7H_8)Co_2(CO)_6$: 3008m, 2963m, 2927m, 2850w, 1475w, 1430m, 1310m, 1185m, 1162m, 1087w, 907w, 870w, 720w, 673m, 655s.

$(C_7H_8)_2Co_2(CO)_4$: 3010m, 2960m, 2925m, 2840w, 1425m, 1308m, 1184m, 1156w, 657m.

$(C_6H_8)_2Co_2(CO)_4$: 2980m, 2929w, 2859m, 1460w, 1434m, 1385m, 1353m, 1180m, 806m.

C_6H_{10}: 3082s, 3005sh, 2960s, 2910sh, 2880sh, 1791m, 1707m, 1605s, 1447vs, 1376vs, 1180s, 809vs.

$C_6H_{10}Co_2(CO)_4$: 3060w, 2980s, 2925s, 2860m, 1485s, 1469m, 1462m, 1434m, 1403m, 1382m, 1260m (to 1200 cm.$^{-1}$ only).

$(C_6H_{10})_2Co_2(CO)_4$: 3055m, 2990s, 2920s, 2870sh, 1480s, 1464s, 1453s, 1430s, 1402m, 1382s, 1272w, 1187w, 1029vs, 1005m, 922m, 673m, 635m.

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