A Carbonyl-bridged, Phosphite-substituted Cobalt Carbonyl Derivative

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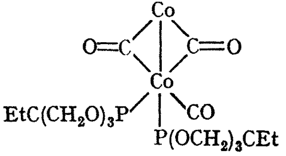
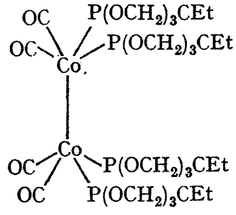
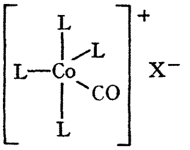
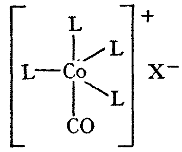
Summary The carbonyl-bridged isomer of the compound $\{Co(CO)_2[P(OCH_2)_3CEt]_2\}_2$ has been isolated from the reaction between $HCo(CO)_2[P(OCH_2)_3CEt]_2$ and butadiene.

OCTACARBONYLDICOBALT[1] and its mono- and di-substituted derivatives[2,3] have been shown by i.r. spectroscopy to exist as equilibrium mixtures of bridged and non-bridged forms in solution. Carbonyl-bridged isomers of the compounds $Co_2(CO)_5(PMe_3)_3$ and $Co_2(CO)_4(PMe_3)_4$ have recently been briefly reported,[4] and a novel route to related bridged isomers of cobalt carbonyl is now described.


(I)(bridged)


(II)(non-bridged)


(VIIa) L=$P(OCH_2)_3CEt$
X=$Co(CO)_4$
(VIIIa) L=$P(OCH_2)_3CEt$
X=BPh_4


(VIIb) L=$P(OCH_2)_3CEt$
X=$Co(CO)_4$
(VIIIb) L=$P(OCH_2)_3CEt$
X=BPh_4

When $HCo(CO)_2[P(OCH_2)_3CEt]_2$,[5] prepared (81%) from the reaction between $HCo(CO)_4$ and $P(OCH_2)_3CEt$ at 0° in diethyl ether,[6] reacts with an excess of butadiene at room temp. for 7 days, the major product, isolated (60%) after chromatography, was a yellow-brown solid of molecular formula $\{Co(CO)_2[P(OCH_2)_3CEt]_2\}_2$. Its i.r. spectrum, which showed two strong bands in both the terminal and bridging metal carbonyl regions, was similar to the spectra reported for the compounds $(Ph_3P)_2(CO)Rh(CO)_2Rh(CO)(PPh_3)_2$,[7] and $(Me_3P)_2(CO)Co(CO)_2Co(CO)(PMe_3)_2$,[4] and is thus assigned the bridged structure $[EtC(CH_2O)_3P]_2(CO)Co(CO)_2Co(CO)[P(OCH_2)_3CEt]_2$ (I).

Other minor products isolated from the reaction with butadiene included another carbonyl-bridged complex $[EtC(CH_2O)_3P]_2(CO)Co(CO)_2Co(CO)_2[P(OCH_2)_3CEt]$ (II; 6%); the π-allyl complex, $(\pi\text{-}C_4H_7)Co(CO)[P(OCH_2)_3CEt]_2$ [(III); 3%]; the hydride $HCo(CO)[P(OCH_2)_3CEt]_3$ [(IV); 4%], which has also been prepared (70%) by heating $HCo(CO)_2[P(OCH_2)_3CEt]_2$ with an excess of the phosphite ligand at 80° for 1 hr. in the solid state;[6] and an ionic complex $\{Co(CO)_2[P(OCH_2)_3CEt]_3\}^+ [Co(CO)_4]^-$ [(V); 9%]. This last compound had good conductivity in nitromethane solution, and showed a strong band in its i.r. spectrum at 1896 cm.$^{-1}$ for the $[Co(CO)_4]^-$ group;[8] this band was absent from the spectrum fo its tetraphenylborate derivative $\{Co(CO)_2[P(OCH_2)_3CEt]_3\}^+ BPh_4^-$ (VI).

Compound (I) does not rearrange to the corresponding non-bridged isomer after several hours in solution under a nitrogen atmosphere. On heating at 80° for 2 days in solution compound (I) decomposes to give an unidentified ionic cobalt–carbonyl complex.

Attempts to obtain (I) or its non-bridged isomer from octacarbonyldicobalt by heating it with an excess of $P(OCH_2)_3CEt$ at 65—70° for 30 hr. in the absence of solvent were unsuccessful. The major product from this reaction was the ionic complex $\{Co(CO)[P(OCH_2)_3CEt]_4\}^+[Co(CO)_4]^-$ [(VII); 93%], identified by preparation of its tetraphenylborate derivative (VIII), and by synthesis (80%) from compound (V) by heating with an excess of phosphite ligand in the solid state for 50 hr. at 65—70°. A comparison of the i.r. spectra of (VII) or (VIII) taken on a mull in Nujol and on a solution in CH_2Cl_2 (Table) indicates that in solution these compounds exist as a mixture of the two possible isomers (VIIa or VIIIa) and (VIIb or VIIIb).

TABLE

Compound	Colour	M.p. (°)	ν_{CO} bands (cm.$^{-1}$)[a]
(I)	Yellow-brown	100 (decomp.)	2001s, 1979s, 1798s, 1777s
(II)	Dark-brown	95 (decomp.)	2038m, 2000s, 1980s, 1812s, 1795s
(III)	Yellow	155 (decomp.)	1955m—s
(IV)	White	180 (decomp.)	2000s [ν_{C_o-H} 1972m]
(V)	Pale yellow	135 (decomp.)	2079m, 2028s, 1896vs
(VI)	Pale yellow	160 (decomp.)	2079, 2028s
(VII)	Pale yellow	200 (decomp.)	2057m, 2024s, 1897vs (2000s, 1890vs)[b]
(VIII)	Pale yellow	200 (decomp.)	2057m, 2024s (2000s)[b]
(IX)	Yellow-brown	—	*ca.* 2000br.s, *ca.* 1780br.s
(X)	Orange	87—88	1969m—s

[a] Unless stated spectra recorded on solutions in CH_2Cl_2; [b] spectrum recorded as a mull in Nujol.

The reaction of butadiene with $HCo(CO)_2[P(OPh)_3]_2$,[9] prepared (65%) from the reaction between $HCo(CO)_4$ and $P(OPh)_3$ in diethyl ether at 0°,[5] gave a 47% yield of an unstable, yellow-brown oil of molecular formula $\{Co(CO)_2[P(OPh)_3]_2\}_2$. This compound showed a strong, broad band in both the terminal and bridging metal carbonyl regions of its i.r. spectrum suggesting a structure $[(PhO)_3P]_2(CO)Co(CO_2)Co(CO)[P(OPh)_3]_2$ (IX). Other products isolated from this reaction were the π-allyl complex $(\pi\text{-}C_4H_7)Co(CO)[P(OPh)_3]_2$ [(X); 19%], and the previously reported[10] compound $[Co(CO)_3P(OPh)_3]_2$ (16%).

Satisfactory elemental analyses have been obtained for all the compounds mentioned.

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