η^1- and η^3-Benzylcobalt Carbonyls

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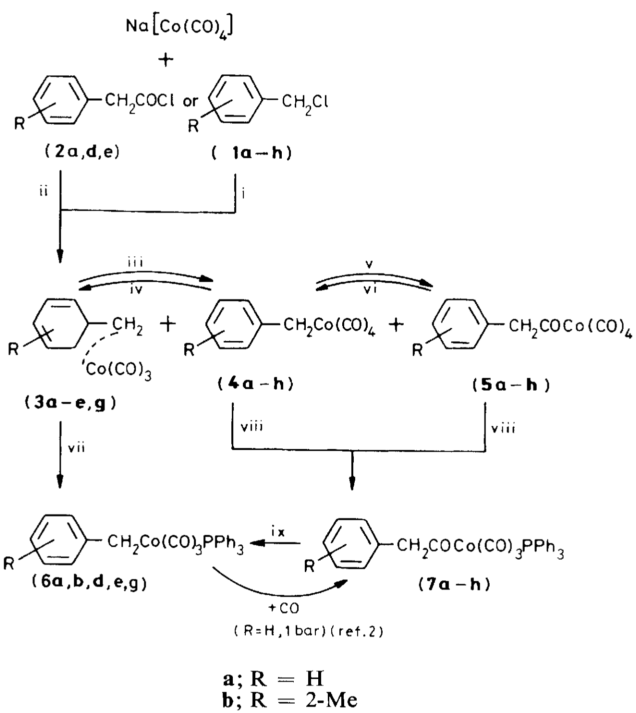
η^1- and η^3-Benzylcobalt tetra- and tri-carbonyls were prepared and characterized; their reversible interconversions and transformation to η^1-phenylacetylcobalt tetracarbonyls are discussed.

Alkylcobalt tetracarbonyls and $\eta^3(\pi)$-benzyl derivatives of transition metals are believed to be intermediates of various organometallic catalytic and stoicheiometric reactions but the number of examples isolated is limited in both cases. In the course of an attempt to prepare non-fluorinated stable alkylcobalt carbonyls[1] we noted an observation of Nagy-Magos *et al.*[2] that solutions obtained from the reaction of (**1a**) and Na[Co(CO)$_4$] reversibly took up and released CO.

Allowing variously substituted benzyl- (**1**) and phenylacetyl halides (**2**) to react with Na[Co(CO)$_4$], we observed a series of reactions and equilibria which are depicted in Scheme 1. Compounds (**3**)—(**7**) were characterized† by i.r., ^{1}H n.m.r., and mass spectra; types (**3**), (**6**), and (**7**) could be isolated and gave correct elemental analyses.

The transformations (**3**) → (**4**), (**4**) → (**3**), and (**5**) → (**4**) were realized by bubbling the corresponding gases through a diethyl ether or n-hexane solution of the starting compound, while (**4**) → (**5**) was observed in a pressurized i.r. cell (where



a; R = H
b; R = 2-Me
c; R = 3-Me
d; R = 4-Me
e; R = 4-OMe
f; R = 2-Cl
g; R = 3,4-(OMe)$_2$
h; R = 2,6-Cl$_2$

Scheme 1. i, Et$_2$O, 25 °C; ii, Et$_2$O, 0 °C; iii, 25 °C, 1 bar CO; iv, 0 °C, Ar; v, 25 °C, 1—10 bar CO; vi, 25 °C, Ar; vii, PPh$_3$, Et$_2$O or n-hexane, 0 °C; viii, PPh$_3$, Et$_2$O, 25 °C; ix, 78 °C, C$_6$H$_6$.

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† Examples of the spectroscopic characterization of each type are as follows: (**3d**) i.r. ν(C–O) (n-hexane) 2053.9 s, 1990.3 s, and 1973.2 vs cm^{-1} [analogous to η^3-C$_3$H$_5$Co(CO)$_3$ (ref. 3), with split *e*-band], ^{1}H n.m.r. (C$_6$D$_6$, Me$_4$Si) δ 2.04 (1H, d, *J* 2 Hz, α-C*H*$_2$), 3.01 (1H, d, *J* 3 Hz, α-C*H*$_2$), 3.16 and 3.21 (both 3H, s, 3- and 4-OC*H*$_3$), 5.41 and 5.90 (both 1H, d, *J* 6 Hz, 5- and 6-*H*), and 6.08 (1H, s, 2-*H*) [analogous to other η^3-benzyl-type complexes below the coalescence temp. (refs. 4,5)]; (**4d**) i.r. ν(C-O) (n-hexane) 2097.0 m, 2031.2 m, and 2013.2 vs cm^{-1} [analogous to other RCo(CO)$_4$ complexes (refs. 1,6)]; (**5d**) i.r. ν(C–O) (n-hexane) 2104.0 m, 2048.1 s, 2027.4 vs, 2004.0 vs, and 1750 m, br. cm^{-1} [analogous to MeCOCo(CO)$_4$ (ref. 7)]; (**6d**) i.r. ν(C–O) (CCl$_4$) 2033 vw and 1962 vs cm^{-1} [analogous to (**6a**) (ref. 2)], ^{1}H n.m.r. (C$_6$D$_6$, Me$_4$Si) δ 1.85 (3H, s, 4-C*H*$_3$), 3.5 (2H, d, *J* 2 Hz, α-C*H*$_2$), and 6.8—7.3 (19 H, m, ring-*H*); (**7d**) i.r. ν(C–O) (CCl$_4$) 2047 w, 1981 s, 1958 s, and 1720 w, br. cm^{-1} [analogous to (**7a**) (ref. 2)]; ^{1}H-n.m.r. (C$_6$D$_6$, Me$_4$Si) δ 1.90 (3H, s, 4-C*H*$_3$), 4.25 (2H, s, α-C*H*$_2$), and 6.5—7.5 (19H, m, ring-*H*).

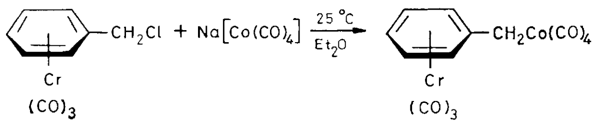
the pressure to be applied depended on the nature of R). Reactions **(4)** → **(7)** and **(5)** → **(7)** were quantitative at room temperature while transformation **(7)** → **(6)** needed some heating and reaction **(3)** → **(6)** proceeds well even at 0 °C.

Electron donor substituent(s) in the aromatic ring favour(s) the formation of complexes **(3)** which could not be observed when R had electron acceptor character. Complexes **(3)** are not fluxional even at 60 °C. Non-fluxionality has been observed in only one case[4] among the few known η^3-benzyl complexes. Compounds **(3)** which have 2- and/or 3-substituents on the ring could therefore form two geometrical isomers; the ^1H n.m.r. spectra show that the isomer in which the substituent(s) is/are oriented away from the cobalt is formed exclusively.

Compounds **(3)** seem to undergo reversible polymerization in the solid state upon standing, even at −80 °C for a few days, as indicated by decreasing solubility and the formation of ions corresponding to double-molecular weight in the mass spectra of such samples. This phenomenon was observed with other η^3-benzyl complexes too[8] but its nature could not be clarified.

Only one group has previously reported η^3-benzylcobalt complexes;[9] these are phosphite derivatives.

Compounds **(4)** and **(5)** generally could not be isolated in analytically pure form because of their easy interconversion, oily appearance, and decomposition during attempted chromatographic separation. In one case, however, we were able to isolate a benzylcobalt tetracarbonyl in pure form according to reaction (1).



(1)

(4i)

Compound **(4i)** is an orange crystalline substance (unfortunately the needle-shaped crystals are too thin to permit an *X*-ray study), it shows correct analyses, and the spectra were in accordance with our structural assignment: i.r. ν(C–O) (n-hexane) 2103.0 m, 2040.2 m, 2023.1 s, and 2015.4 s [the $Co(CO)_4$ group],[1] and 1977.0 vs and 1913.5 s cm^{-1} [the $Cr(CO)_3$ group]; ^1H n.m.r. (C_6D_6, Me_4Si) δ 2.25 (2H, s, α-C*H*$_2$) and 4.50 (5H, s, ring *H*).

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