A Monosubstituted Derivative of Dicobalt Octacarbonyl Containing Bridging Carbonyl Groups: $[Co_2(CO)_7]_2Ph_2PC{\equiv}CPPh_2$

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Summary The first synthesis of a carbonyl-bridged monosubstitution product of $Co_2(CO)_8$ with a phosphorus ligand is reported.

In the solid state $Co_2(CO)_8$ has a carbonyl-bridged C_s structure.[1] I.r. studies[2] have established that solutions of $Co_2(CO)_8$ contain two tautomeric forms, one corresponding to the solid-state structure, the other having no bridging CO groups *viz.* $(CO)_4CoCo(CO)_4$. Moreover $Co_2(CO)_8$ reacts with phosphines and phosphites to give substitution products of the types $[Co(CO)_3(PR_3)_2][Co(CO)_4]$, $Co_2(CO)_7PR_3$, and $Co_2(CO)_6(PR_3)_2$,[3] none of which has bridging CO groups.† An *X*-ray structure determination of $Co_2(CO)_6(PBu^n_3)_2$ has confirmed the presence of an unsupported Co–Co bond in this complex.[4] Reasons for the failure to prepare carbonyl bridged $Co_2(CO)_8$ derivatives remain obscure.

In view of our success in characterising a stable carbonyl-bridged monosubstitution product of $(\pi\text{-}C_5H_5)_2Fe_2(CO)_4$ with $Ph_2PC{\equiv}CPPh_2$[5] we have carried out a reaction of $Co_2(CO)_8$ with $Ph_2PC{\equiv}CPPh_2$ in an attempt to stabilise a carbonyl-bridged complex.

Reaction of $Ph_2PC{\equiv}CPPh_2$ (DPPA) (0·01 mole) with

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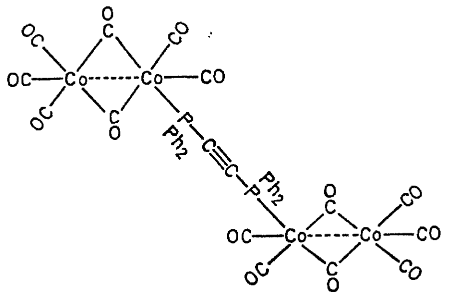
† *Note added in proof.* Recent reports describe carbonyl-bridged tri- and tetra-substitution products of $Co_2(CO)_8$: B. L. Booth, M. Gardner, and R. N. Haszeldine, *Chem. Comm.*, 1969, **1388**; C. Pegot and R. Poilblanc, *Compt. rend.*, 1969, *C*, **268**, 955.

$Co_2(CO)_8$ (0·02 mole) in benzene at room temperature for $2\frac{1}{2}$ hr. produced red-brown crystals (m.p. 221—222° from CH_2Cl_2–EtOH) analysing as $[Co_2(CO)_7]_2$ DPPA. In acetone, the molecular weight was 1009 (osmometry): calc. for $[Co_2(CO)_7]_2$ DPPA 1021. The solid-state i.r. spectrum (Nujol mull) shows both terminal and bridging carbonyl groups (2098 m, 2064 s, 2050 s, 2031 vs, 2008 s, 1976 vs, 1931 sh, 1819 s, and 1786 s) and demonstrates the absence of Co(CO)$_4^-$ ions. In solution ($CHCl_3$) both terminal and bridging ν(CO) frequencies appear but the latter are less intense than in the solid state and new peaks appear above 2000 cm^{-1} (2112 vw, 2108 w, 2098 s, 2089 m, 2063 s, 2048 vs, 2018 s, 1987 s, 1817 m, and 1796 m). This behaviour is reminiscent of $Co_2(CO)_8$ itself and suggests partial conversion into a non-carbonyl-bridged isomer in solution. The solid-state spectrum has features in common with the spectra of $Co_2(CO)_7Ph_3P$ [3] and $Co_2(CO)_8$[3] although it is noticeable that bridging ν(CO) frequencies are moved to lower frequency compared to $Co_2(CO)_8$, suggesting transmission of d_π electron density to the bridging CO groups from the substituted cobalt atom. In view of the now well established bridging properties of $Ph_2PC{\equiv}CPPh_2$[5,6] we suggest a structure (Figure) for the complex having two $Co_2(CO)_7$ units symmetrically bridged by the diphosphine. This is the first carbonyl-bridged monosubstitution product of $Co_2(CO)_8$. The stabilising effect of acetylenic diphosphines on bridging carbonyls is under further investigation.



FIGURE

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[5] A. J. Carty, T. W. Ng, W. Carter, G. Palenik, and T. Birchall, *Chem. Comm.*, 1969, 1101.
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