Preparation and Crystal Structure of μ-Carbonyl-*OC*-bis(pentamethylcyclopentadienyl)(tetrahydrofuran)ytterbium(III)tricarbonylcobalt(I); A Yb–OC–Co Linkage

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Summary Reaction of $(Me_5C_5)_2Yb(OEt_2)$ with $Co_2(CO)_8$ in toluene, followed by recrystallization from Et_2O–tetrahydrofuran(thf)–pentane, gives $(Me_5C_5)_2YbCo(CO)_4(thf)$, in which the $Co(CO)_4$ fragment is bonded to the $(Me_5C_5)_2$-Yb(thf) unit *via* a carbonyl group.

IT has been shown that $(Me_5C_5)_2Yb(thf)$[1] is readily oxidized to the trivalent species, $(Me_5C_5)_2YbCl(thf)$, by ytterbium trichloride or dichloromethane.[2] This suggested to us that the divalent metallocene could act as a gentle, hydrocarbon-soluble, one-electron reducing agent towards transition metal carbonyls, giving compounds that contain lanthanide metals and transition metals within the same molecule. Though lanthanide–transition metal derivatives have been described, none has been structurally characterized.[3]

Reaction of $(Me_5C_5)_2Yb(OEt_2)$ and $Co_2(CO)_8$ (1 : 1 or 2 : 1 molar ratio) in toluene gives a blue precipitate that yields blue prisms of $(Me_5C_5)_2YbCo(CO)_4(thf)$ from diethyl ether–tetrahydrofuran(thf)–pentane (3 : 1 : 1) at -10 °C. The i.r. spectrum ν_{CO} (Nujol mull) 2023s, 1973w, 1939s, 1917s, 1823w, 1798msh, and 1761s cm^{-1}) shows significantly lowered ν_{CO}'s relative to, *e.g.* $(Et_3NH)\{Co(CO)_4\}$,[4] which might indicate a bridging carbonyl group. The complex is paramagnetic (μ 4·1 B.M. at 30 °C in benzene solution, by Evans' method) and the ^1H n.m.r. spectrum (26 °C, $C_6D_5CD_3$) shows δ 8·36 (br.s, $w_{1/2}$ = 43 Hz, C_5Me_5). The resonances due to the tetrahydrofuran were not observed.

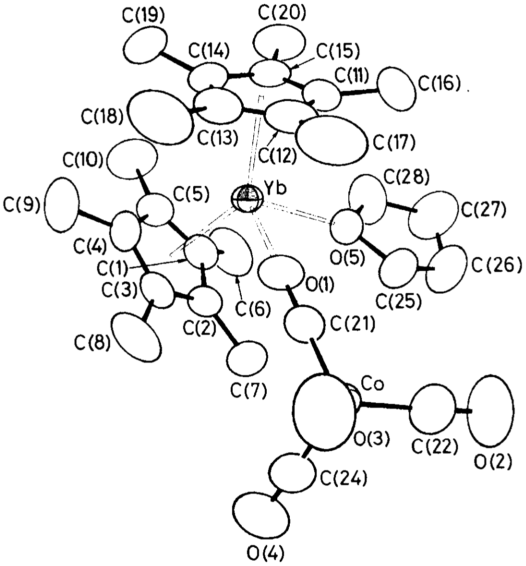

FIGURE. An ORTEP drawing of $(Me_5C_5)_2YbCo(CO)_4(thf)$. Some bond lengths and bond angles are: Yb–Cp (centroid) = 2·302 ± 0·01 Å (ave.) Cp(centroid)–Yb–Cp(centroid) = 139·4(7)°, O(05)–Yb–O(01) = 83·3(7)°, CO(terminal)–Co–CO(terminal) = 108·9 ± 0·4° (ave.), and CO(terminal)–Co–CO(bridging) = 110·0 ± 0·6° (ave.)

In order to elucidate the structure of this novel compound, a single crystal *X*-ray study was undertaken.†

Crystal data: $C_{28}H_{38}CoO_5Yb$, $M = 686{\cdot}6$, triclinic, space group $P\bar{1}$ (No. 2), $a = 10{\cdot}1626(11)$, $b = 10{\cdot}9795(8)$, $c = 13{\cdot}7124(12)$ Å, $\alpha = 89{\cdot}041(7)$, $\beta = 85{\cdot}478(8)$, $\gamma = 71{\cdot}774(7)°$, $U = 1448{\cdot}7(3)$ Å^3, $Z = 2$, $D_c = 1{\cdot}574$ g cm^{-3}, Mo-K_α radiation, $\lambda = 0{\cdot}71073$ Å, μ(Mo-K_α) $= 40{\cdot}05$ cm^{-1}. The structure was solved by Patterson and Fourier methods and refined using 3769 unique reflections [$F_o > 3\sigma(F_o)$] measured on a Nonius CAD 4 diffractometer ($2\theta_{max}$ 45°). The current R value is 0·0185.

The structure of the complex is shown in the Figure. The average Yb–C bond length of 2·596(2) Å is similar to that found in the trivalent species $(Me_5C_5)_2YbS_2CNEt_2$[5] [2·63(3) Å] of identical co-ordination number, but significantly shorter than that found in the divalent species, $(Me_5C_5)_2Yb(pyridine)_2$,[6] [2·742(7) Å] of the same co-ordination number. These bond length changes are consistent with the view that the ytterbium atom in $(Me_5C_5)_2YbCo(CO)_4(thf)$ is trivalent since Shannon[7] suggests that the ionic radius of Yb^{III} is *ca.* 0·16 Å smaller than that of Yb^{II}. This is in agreement with the magnetic data. The Yb–O(thf) bond length of 2·335(2) Å which is shorter than that found in $(Me_5C_5)_2Yb(thf)$ [2·412(5) Å] can be accounted for similarly. The Yb–O(thf) bond length is longer than the Yb–O(CO) bond length of 2·258(2) Å. This may be ascribed to the different co-ordination number (hybridization) of the two different types of oxygen atoms. The $Co(CO)_4$ group is bonded to the $(Me_5C_5)_2Yb(thf)$ centre by way of a bridging carbonyl bond [$\angle$YbO(01)C(1) = 163·0(2) and $\angle$CoC(21)O(01) = 177·8(2)]. This accounts for the low ν_{CO} absorptions at 1798 and 1761 cm^{-1}.

The difference between the average C–O(terminal) bond length (1·14 ± 0·02 Å) and the C–O(bridging) bond length of 1·188(3) Å (0·05 Å) also suggests a weakening of the C–O bond upon co-ordination to the $(Me_5C_5)_2Yb(thf)$ unit. In concert with this, the Co–C(bridging) bond length appears to be strengthened by this interaction; the difference between the average Co–C(terminal) bond length (1·77 ± 0·03 Å) and the Co–C(bridging) bond length [1·699(3) Å] is 0·07 Å.

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‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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