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Preparation of $[\{Yb(C_5Me_5)_2\}_2\{Co_3(C_5H_4R)_2(\mu_3\text{-}CO)_4\}]$, R = H, Me, $SiMe_3$; an Example of a 47-Electron Transition Metal Fragment containing a Cobalt Atom with Hexagonal Planar Co-ordination

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The electron-transfer reaction of $Yb(C_5Me_5)_2(OEt_2)$ and $Co(C_5H_4R)(CO)_2$, R = H, Me, $SiMe_3$, yields the odd-electron-numbered complex, $[\{Yb(C_5Me_5)_2\}_2\{Co_3(C_5H_4R)_2(\mu_3\text{-}CO)_4\}]$ with a $Co_3C_4O_4$ unit that contains a cobalt atom with hexagonal planar co-ordination.

The metallocene, $Yb(C_5Me_5)_2(OEt_2)$ is an electron-transfer reagent towards a variety of transition metal carbonyls that contain formal metal–metal single bonds [$Co_2(CO)_8$,[1a] $Fe_3(CO)_{12}$,[1b] $Mn_2(CO)_{10}$,[1c] $Fe_2Cp_2(CO)_4$,[1d] and $Mo_2Cp_2(CO)_6$[1d] (Cp = η^5-C_5H_5)]. The electron-transfer results in oxidation of ytterbium from Yb^{II} to Yb^{III} and formation of metal carbonyl anions with one or more M–C(O)–Yb interactions. In all of the reactions studied the resulting metal carbonyl anion is an even-electron fragment. It was of interest to extend the electron-transfer chemistry of $Yb(C_5Me_5)_2(OEt_2)$ to mononuclear, eighteen-electron complexes to see if we could isolate odd-electron transition metal carbonyl fragments. The complex, $Co(C_5H_4R)(CO)_2$, is an ideal candidate since it undergoes reduction with alkali metals to give the radical anion $[Co_2(C_5H_4R)_2(\mu_2\text{-}CO)_2]^{\cdot -}$.[2]

The metallocene, $Yb(C_5Me_5)_2(OEt_2)$, reacts with $Co(Cp)(CO)_2$ in a 1:1 or 2:3 molar ratio in toluene (20 °C, 48 h) to give blue crystals from toluene [−10 °C, 59% yield, m.p. 130 °C (decomp.)] of $Yb_2Co_3(C_5Me_5)_4(Cp)_2(CO)_4$,† ^1H n.m.r. (C_6D_6, 25 °C), δ 32.5 (s, 10 H, $w_{\frac{1}{2}}$ 34 Hz) and 5.39 (s, 60 H, $w_{\frac{1}{2}}$ 47 Hz); ν_{CO} (Nujol) 1590 cm^{-1}. Reaction of the metallocene with $Co(C_5H_4Me)(CO)_2$ in toluene (90 °C, 12 h, 2:3 molar ratio) gives $Yb_2Co_3(C_5Me_5)_4(C_5H_4Me)_2(CO)_4 \cdot PhMe$† as purple prismatic crystals from toluene [−10 °C, 65% yield, m.p. 195 °C (decomp.)], ^1H n.m.r. (C_6D_6, 30 °C) δ 84.1 (s, 6 H, $w_{\frac{1}{2}}$ 49 Hz), 30.1 (s, 4 H, $w_{\frac{1}{2}}$ 32 Hz), 28.9 (s, 4 H, $w_{\frac{1}{2}}$ 39 Hz), 4.84 (s, 60 H, $w_{\frac{1}{2}}$ 48 Hz), and 2.09 (s, 3H, the methyl group of the toluene of solvation, the aryl protons are obscured by the solvent), ν_{CO} (Nujol) 1575 cm^{-1}. The $Co(C_5H_4SiMe_3)(CO)_2$ complex behaves similarly, giving purple $Yb_2Co_3(C_5Me_5)_4(C_5H_4SiMe_3)_2(CO)_4$† in 65% yield, ^1H n.m.r. (C_6D_6, 25 °C) δ 75.5 (s, 4 H, $w_{\frac{1}{2}}$ 39 Hz), 17.3 (s, 4 H, $w_{\frac{1}{2}}$ 40 Hz), 5.34 (s, 60 H, $w_{\frac{1}{2}}$ 49 Hz), and 4.09 (s, 18 H, $w_{\frac{1}{2}}$ 12 Hz), ν_{CO} (Nujol) 1575 cm^{-1}. The $\mu_{eff.}$ (per Yb^{III}) from 5—30 K is 4.61 ± 0.02 μ_B and from 100—300 K is 4.97 ± 0.01 μ_B and the e.s.r. spectrum (25 °C, cyclohexane) shows a broad featureless absorption at *g* 2.0827 × 10^4 T.

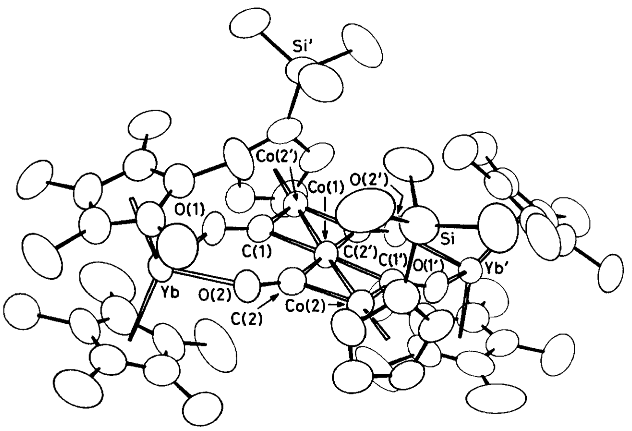

Figure 1. An ORTEP view of the molecular structure of the complex $Yb_2Co_3(C_5Me_5)_4(C_5H_4SiMe_3)_2(CO)_4$. Some important bond lengths (Å) and bond angles (°) are: Yb–centroid (av.) 2.29, Yb–O (av.) 2.230(4), Co–centroid (av.) 1.72; Co–C ($C_5H_4SiMe_3$) (av.) 2.115(8); Co–Co (av.) 2.363(1), Co(1)–C(1) 1.853(6), Co(1)–C(2) 1.874(6), Co(2′)–C(1) 1.778(6), Co(2)–C(2) 1.792(6), C(1)–O(1) 1.244(6), C(2)–O(2) 1.277(6); centroid–Yb–centroid (av.) 140, centroid–Co–C (CO) (av.) 130, O–Yb–O (av.) 74.0(1), Co(2′)–C(1)–O(1) 136.7(4), Co(2)–C(2)–O(2) 136.6(5), Co(1)–C(1)–O(1) 142.1(4), Co(1)–C(2)–O(2) 143.1(5), C(1)–Co(1)–C(2) 83.7(3), Co(1)–C(1)–Co(2′) 81.2(2), Co(1)–C(2)–Co(2) 80.2(2), Co(2)–Co(1)–Co(2′) 176.5(1).

The crystal structure of the R = $SiMe_3$ complex is shown in Figure 1. *Crystal data:* $C_{60}H_{86}Co_3O_4Si_2Yb_2$, *M* = 1450.5, tetragonal, space group $P4_12_12$, *a* = 12.883(2), *c* = 37.069(6) Å, *U* = 6152.7(28) $Å^3$, *Z* = 4, D_c = 1.566 g cm^{-3}, Mo-K_α radiation, λ = 0.71073 Å, μ(Mo-K_α) = 38.73 cm^{-1}. The structure was solved by a combination of Patterson and Fourier methods and refined using 3676 unique reflections [F^2

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† All new compounds gave satisfactory elemental analysis.

$> 3\sigma(F^2)$] measured on a Nonius CAD4 diffractometer ($2\theta_{max.}$ 45°). The current R value is 0.031. All non-hydrogen atoms were refined anisotropically; the hydrogen atoms were not located but were placed in idealized positions with fixed thermal parameters and were not refined.‡

The averaged Yb–C (C_5Me_5) distance is 2.59(2) Å, in the range found for the trivalent $Yb(C_5Me_5)_2$ group.[1] The transition metal fragment may therefore be formally described as the unique 47-electron, cluster anion '$[Co_3(C_5H_4SiMe_3)_2(\mu_3\text{-}CO)_4]^{2-}$.' The odd-electron formulation is supported by the e.s.r. and magnetic susceptibility measurements. The expected value of the susceptibility (5—30 K) of 4.5 μ_B per Yb^{III} is calculated by summing the susceptibility of Yb^{III} of 3.9 μ_B[1] with the spin-only value per Co(0) of 1.78 $\mu_B/3$. The atoms Co(1)C(1)C(2)C(1′)C(2′) are planar to within 0.015 Å. The Co(2,2′) atoms are 0.03 Å above this plane and the O(1,1′), O(2,2′), and Yb and Yb′ atoms are 0.14, 0.08, and 0.40 Å, respectively, below this reference plane. Thus, the central cobalt atom of the $Co_3C_4O_4$ unit has hexagonal planar co-ordination. The $C_5H_4SiMe_3$ ring centroids, related by a two-fold rotation axis, are orientated away from the C_2 axis by 7.5°. The averaged bond lengths and angles in '$[Co_3(C_5H_4SiMe_3)_2(\mu_3\text{-}CO)_4]^{2-}$' are virtually identical to those found in $[Co_2(C_5Me_5)_2(\mu_2\text{-}CO_2]^{\bullet -}$, and the bonding in the 'dianion' is doubtless similar to that in the radical anion.[2]

The complex $Yb_2Co_3(C_5Me_5)_4(C_5H_4SiMe_3)_2(\mu_3\text{-}CO)_4$ has idealized C_{2v} symmetry. This requires that the C_5Me_5 rings be non-equivalent in the solid state. The ^1H n.m.r. spectrum in $[^2H_8]$toluene at 25 °C shows a single resonance for the C_5Me_5 protons. This resonance splits into two resonances of equal area below −56 °C, the coalescence temperature (T_c). The chemical shifts of the two resonances are linear in $(T)^{-1}$ below T_c. Plotting δ for the two resonances with respect to $(T)^{-1}$ and extrapolating to T_c gives the peak separation at coalescence,[3] and $\Delta G(T_c)^{\ddagger}$ for this two site exchange process is 41.0 kJ mol^{-1}. This barrier is most reasonably ascribed to hindered rotation of the $C_5H_4SiMe_3$ groups about their pseudo-C_5 axes. Consistent with this, the C_5Me_5 rings are equivalent (−90 °C) in the sterically less hindered analogue, $Yb_2Co_3(C_5Me_5)_4(C_5H_4Me)_2(\mu_3\text{-}CO)_4$.

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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.