Title

PREPARATION OF [Yb (C5Me5)2]2 [Co3(C5H4R)2 (u3-CO)4 , R = H, Me, SiMe3; AN EXAMPLE OF A HEXAGONAL-PLANAR, 47-ELECTRON TRANSITION METAL FRAGMENT

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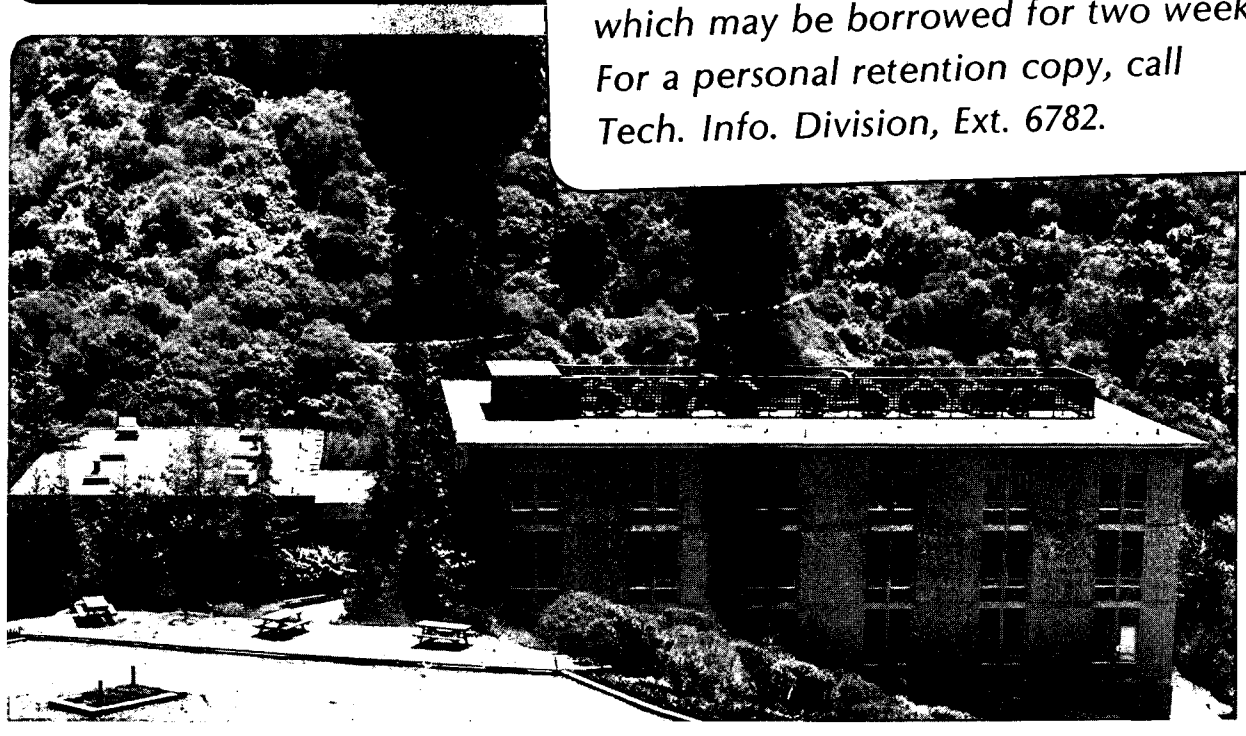

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DISCLAIMER

LBL-17336

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 Hexagonal-Planar, 47-Electron Transition Metal Fragment

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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 complex, $[Yb(C_5Me_5)_2]_2[Co_3(C_5H_4R)_2(\mu_3\text{-}CO)_4]$ with a hexagonal-planar $Co_3C_4O_4$ unit.

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]]. The electron-transfer results in oxidation of ytterbium from Yb(II) to Yb(III) and formation of metal carbonyl anions with one or more Yb-OC-M 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 $[Co_2(C_5H_4R)_2(\mu_2\text{-}CO)_2]^-$.[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, 48h) 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, $\nu\frac{1}{2}$ = 34 Hz) and 5.39 (s, 60 H, $\nu\frac{1}{2}$ = 47 Hz), i.r. (Nujol) νCO = 1590 cm^{-1}. Reaction of the metallocene with $Co(C_5H_4Me)(CO)_2$ in toluene (90°C, 12h, 2:3 molar ratio) gives $Yb_2Co_3(C_5Me_5)_4(C_5H_4Me)_2(CO)_4 \cdot PhMe$† as purple prisms 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, $\nu\frac{1}{2}$ = 49 Hz), 30.1 (s, 4 H, $\nu\frac{1}{2}$ = 32 Hz), 28.9 (s, 4 H, $\nu\frac{1}{2}$ = 39 Hz), 4.84 (s, 60 H, $\nu\frac{1}{2}$ = 48 Hz), δ 2.09 (s, 3 H, the methyl group of the toluene of solvation, the aryl protons are obscured by the solvent), i.r. (Nujol) νCO = 1575 cm^{-1}. The $Co(C_5H_4SiMe_3)(CO)_2$ 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

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† All new compounds gave satisfactory elemental analysis.

(s, 4 H, $\nu\frac{1}{2}$ = 39 Hz), 17.3 (s, 4 H, $\nu\frac{1}{2}$ = 40 Hz), 5.34 (s, 60 H, $\nu\frac{1}{2}$ = 49 Hz), 4.09 (s, 18 H, $\nu\frac{1}{2}$ = 12 Hz), i.r. (Nujol) νCO = 1575 cm^{-1}. The μ_{eff} [per Yb(III)] from 5-30 K is 4.61 ± 0.02 B.M. and from 100 - 300 K is 4.97 ± 0.01 B.M. and the e.s.r. spectrum (25°C, cyclohexane) shows a broad featureless absorption at g = 2.0827 gauss.

The crystal structure of the $SiMe_3$-complex is shown in the Figure. Crystal Data: $C_{60}H_{86}Co_3O_4Si_2Yb_2$, M = 1450.4, tetragonal, space group $P4_12_12$, a = 12.883(2), c = 37.069(6) Å, V = 6152.7(28) $Å^3$, Z = 4, D_c = 1.566 gcm^{-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 [$F^2 > 3\sigma(F^2)$] 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 $Yb(C_5M_5)_2$ group.[1] The transition metal fragment is therefore the unique 47 electron, cluster anion $[Co_3(C_5H_4SiMe_3)_2(\mu_3\text{-}CO)_4]^=$. The odd-electron formulation is supported by the e.s.r. and magnetic susceptibility measurements [the predicted μ_{eff} (5-30 K) is 3.9 B.M. (the value for Yb(III)[1]) plus (1.78 B.M.) ÷ 3 (spin-only value per Co(0)) = 4.5 B.M.]. The atoms defined by Co(1)C(1)C(2)C(1')C(2') are planar within 0.015 Å. The Co(2) atoms are 0.03 Å above this plane and the O(1), O(2), and Yb atoms are 0.14, 0.08, and 0.40 Å, respectively, below this reference plane. Thus, the $Co_3C_4O_4$ unit

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‡ The atom co-ordinators 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.

is hexagonal planar. The $C_5H_4SiMe_3$-ring centriods, 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 $[Co_3(C_5H_4SiMe_3)_2(\mu_3\text{-}CO)_4]^=$ are virtually identical to those found in $[Co_2(C_5Me_5)_2(\mu_2\text{-}CO)_2]^-$, 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 toluene-d_8 at 25°C shows a single resonance for the C_5Me_5 protons. This resonance splits into two equal area resonances below -56°C, the coalescence temperature (T_c). The chemical shift 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 $\Delta G^{\ddagger}_{T_c}$ for this two site exchange process is 9.8 kcal mol^{-1}. This barrier is most resonably 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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REFERENCES

(1) (a) T. D. Tilley and R. A. Andersen, J. Chem. Soc. Chem. Comm., **1981**, 985. (b) J. Am. Chem. Soc. **1982**, 104, 1772. (c) J. M. Boncella and R. A. Andersen, Inogr. Chem. in the press. (d) J. M. Boncella, unpublished results.

(2) (a) N. E. Schore, C. S. Ilenda, and R. G. Bergman, J. Am. Chem. Soc. **1977**, 99, 1781. (b) L. M. Cirjak, R. E. Ginsburg, and L. F. Dahl, Inorg. Chem. **1979**, 173, 301.

(3) L. H. Pignolet, R. A. Lewis, and R. H. Holm, Inorg. Chem. **1972**, 11, 99.

Figure Caption

Yb-centroid (ave.) = 2.29 Å

Yb-O (ave.) = 2.230(4) Å

Co-centroid (ave.) = 1.72 Å

Co-C($C_5H_4SiMe_3$) (ave.) = 2.115(8) Å

Co-Co (ave.) = 2.363(1) Å

Centroid-Yb-Centroid (ave.) = 140°

Centroid-Co-C(CO) (ave.) = 130°

O-Yb-O (ave.) = 74.0(1)°

Co(1)-C(1) = 1.853(6) Å

Co(1)-C(2) = 1.874(6) Å

Co(2)-C(1) = 1.778(6) Å

Co(2)-C(2) = 1.792(6) Å

C(1)-O(1) = 1.244(6) Å

C(2)-O(2) = 1.277(6) Å

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)°

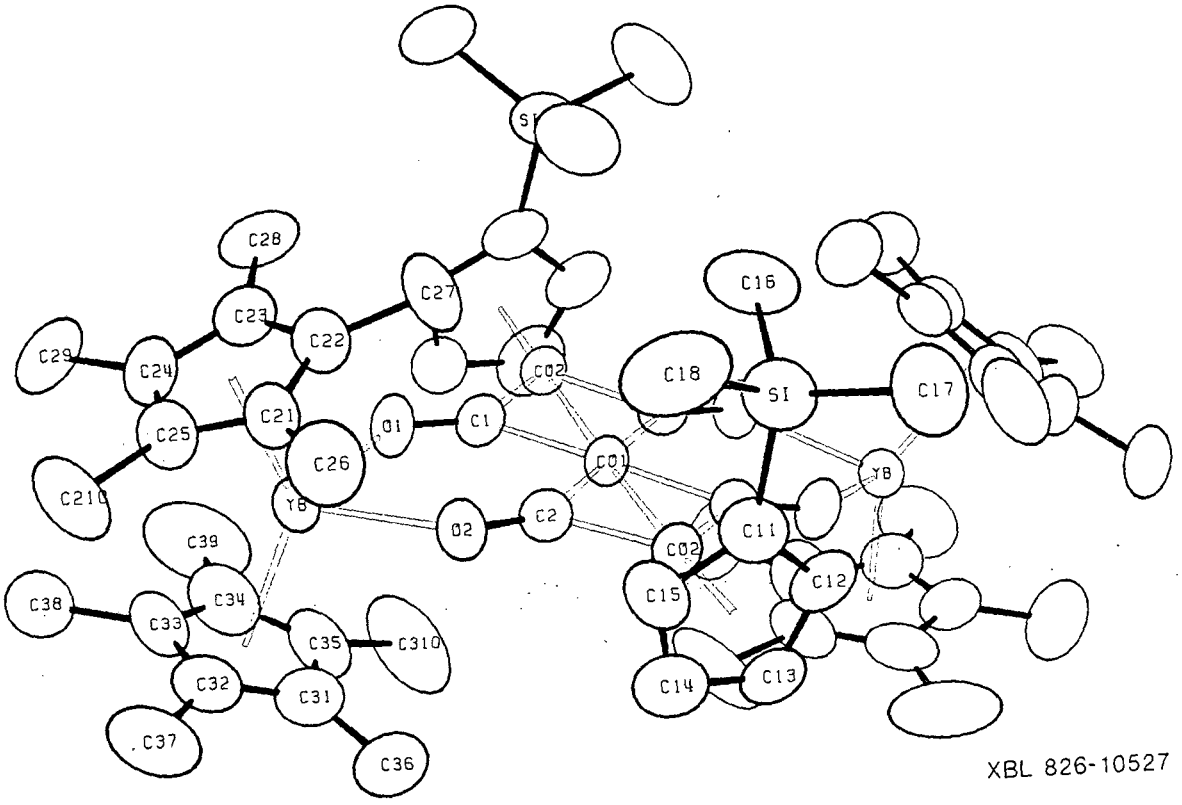
Co(1)-C(2)-O(2) = 143.1(5)°

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)°



XBL 826-10527

Positional and Thermal Parameters for:

$Yb_2Co_3(C_5Me_5)_4(C_5H_4SiMe_3)_2(\mu_3\text{-}CO)_4$

Atom	x	y	z
YB	-Ø.ØØ343(3)	Ø.Ø4512(3)	Ø.11715(1)
CO1	Ø.Ø45Ø8(8)	Ø.Ø45Ø8(Ø)	Ø.ØØØØØ(Ø)
CO2	Ø.178Ø2(8)	-Ø.Ø7988(8)	Ø.ØØ647(3)
SI	Ø.4356(2)	Ø.Ø138(2)	Ø.Ø1Ø14(8)
O1	-Ø.Ø48Ø(4)	Ø.1266(4)	Ø.Ø665(1)
O2	Ø.Ø991(4)	-Ø.Ø192(4)	Ø.Ø74Ø(1)
C1	-Ø.Ø314(6)	Ø.1194(6)	Ø.Ø336(2)
C2	Ø.1Ø48(6)	-Ø.Ø157(6)	Ø.Ø41Ø(2)
C11	Ø.3397(6)	-Ø.Ø973(7)	Ø.ØØ98(2)
C12	Ø.3Ø19(6)	-Ø.15Ø8(7)	-Ø.Ø214(2)
C13	Ø.23ØØ(7)	-Ø.2293(6)	-Ø.ØØ95(2)
C14	Ø.2238(7)	-Ø.2226(7)	Ø.Ø299(3)
C15	Ø.2924(7)	-Ø.14Ø5(7)	Ø.Ø42Ø(2)
C16	Ø.37Ø1(9)	Ø.1421(8)	-Ø.ØØ4Ø(3)
C17	Ø.5484(8)	-Ø.Ø2Ø6(11)	-Ø.Ø2Ø5(3)
C18	Ø.4858(1Ø)	Ø.Ø325(9)	Ø.Ø584(3)
C21	Ø.1685(7)	Ø.1Ø14(7)	Ø.1474(2)
C22	Ø.1451(7)	Ø.1775(7)	Ø.12Ø6(2)
C23	Ø.Ø548(8)	Ø.2323(7)	Ø.132Ø(2)
C24	Ø.Ø225(7)	Ø.1919(7)	Ø.1656(2)
C25	Ø.Ø931(7)	Ø.1Ø99(7)	Ø.1743(2)
C26	Ø.2615(8)	Ø.Ø3ØØ(8)	Ø.1471(2)
C27	Ø.2Ø9Ø(7)	Ø.2ØØ3(8)	Ø.Ø872(2)
C28	Ø.ØØ44(1Ø)	Ø.325Ø(7)	Ø.113Ø(2)
C29	-Ø.Ø6Ø3(9)	Ø.2372(8)	Ø.1899(3)
C21Ø	Ø.Ø99Ø(9)	Ø.Ø561(9)	Ø.2127(2)
C31	-Ø.Ø763(9)	-Ø.1433(8)	Ø.1144(3)
C32	-Ø.Ø791(7)	-Ø.1146(7)	Ø.1514(2)
C33	-Ø.1498(7)	-Ø.Ø359(7)	Ø.1549(2)
C34	-Ø.1917(7)	-Ø.Ø121(9)	Ø.1223(3)
C35	-Ø.1472(8)	-Ø.Ø791(8)	Ø.Ø955(2)
C36	-Ø.ØØ72(1Ø)	-Ø.2323(8)	Ø.Ø999(3)
C37	-Ø.Ø284(1Ø)	-Ø.1715(8)	Ø.1819(3)
C38	-Ø.19Ø3(9)	Ø.ØØ71(9)	Ø.1927(3)
C39	-Ø.2758(9)	Ø.Ø689(12)	Ø.116Ø(4)
C31Ø	-Ø.1753(11)	-Ø.Ø886(11)	Ø.Ø556(3)

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