Title

PREPARATION AND CRYSTAL STRUCTURE OF BIS[BIS(PENTAMETHYLCYCLOPENTADIENYL) YTTERBIUM (III)] TETRACARBONYLCOBALTATE) (-I) (TETRAHYDROFURAN); A YTTERBIUM ISOCARBONYL (Yb-OC-Co) BOND

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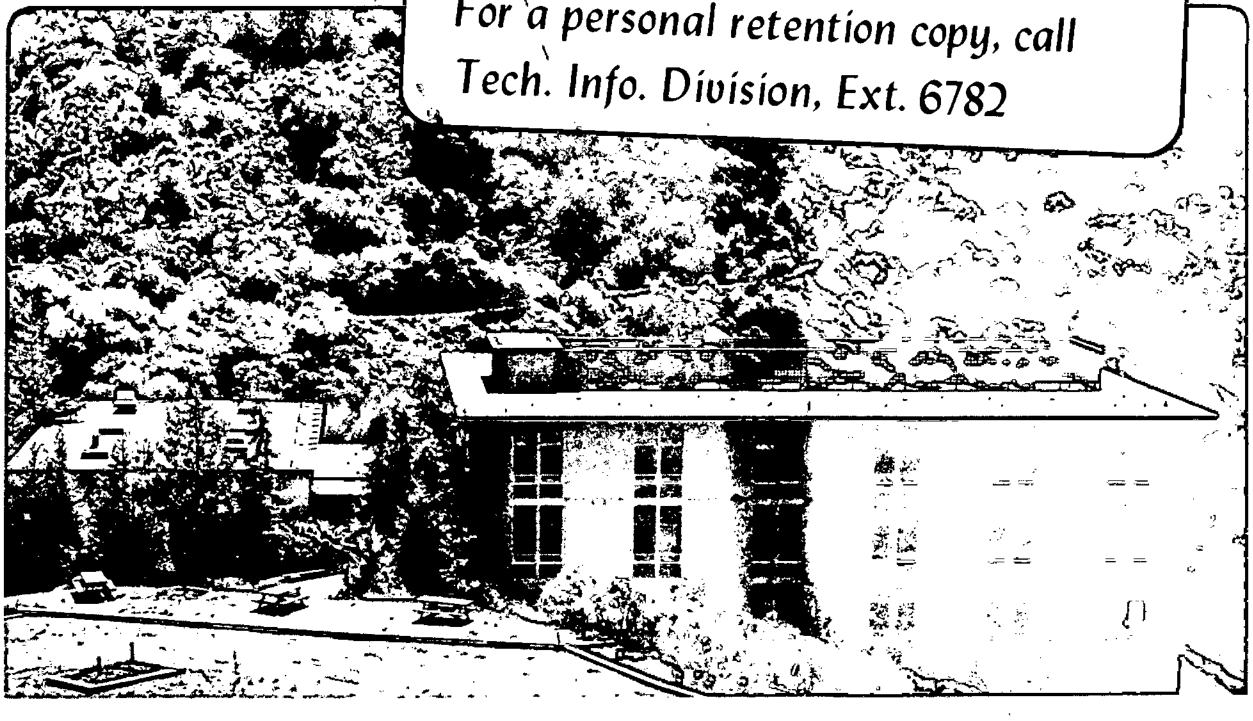
T. Don Tilley and Richard A. Andersen

June 1981



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Preparation and Crystal Structure of Bis(Pentamethylcyclopentadienyl) Ytterbium (III) (Tetracarbonylcobaltate)(-I) (Tetrahydrofuran); A Ytterbium Isocarbonyl (Yb-OC-Co) Bond

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Summary: Reaction of $(Me_5C_5)_2Yb(thf)$ with $Co_2(CO)_8$ in toluene gives $(Me_5C_5)_2YbCo(CO)_4(thf)$, in which the $Co(CO)_4$ fragment is bonded to the $(Me_5C_5)_2Yb(thf)$ unit by a single isocarbonyl bond.

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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 have 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-pentane (3:1:1) at -10°C. The i.r. spectrum νCO (Nujol mull) = 2023s, 1973w, 1939s, 1917s, 1823w, 1798msh and 1761s cm^{-1}) is consistent with Yb–OCCo$(CO)_3$ bonding. The complex is paramagnetic since the ^1H n.m.r. spectrum (26°C, PhMe-d_8) shows broad singlet ($\nu 1/2$ = 43 Hz) at δ8.36 due to the Me_5C_5 - protons. The resonances due to the tetrahydrofuran were not observed.

In order to elucidate the structure of this novel compound, a single crystal X-ray study was undertaken.[4] Crystal data: $C_{28}H_{38}CoO_5Yb$, triclinic, a=10.1626(11), b=10.9795(8), c=13.7124(12) Å, α=89.041(7), β=85.478(8), γ=71.774(7)°, U=1448.7(3) $Å^3$, space group $P\bar{1}$ (No. 2), M=686.6, Z=2, D_c=1.574g cm^{-3}, $\mu(Mo\text{-}K_\alpha)$=40.05 cm^{-1}, Mo-K_α radiation λ=0.71073 Å. The structure was solved by Patterson and Fourier methods and refined using 3769 unique reflections $[Fo>3\sigma(Fo)]$ measured on a Nonius CAD 4 diffractometer (2θ max 45°). The R value for all 3769 data is 0.0185.

The structure of the complex is shown in the Figure. The average ytterbium - carbon 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 coordination number but significantly shorter than that found in the divalent species, $(Me_5C_5)_2Yb(py)_2$,[6] (2.742(7) Å) of the same coordination 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 <u>ca.</u> 0.16 Å smaller than that of Yb(II). The ytterbium-oxygen (tetrahydrofuran) 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 ytterbium - oxygen (thf) bond length is longer than that of the Yb–O(CO) bond length of 2.258(2) Å. This may be ascribed to the different coordination 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 an isocarbonyl bond [<YbO(01)C(1)=163.0(2) and <CoC(21)O(01)= 177.8(2)]. This accounts for the low νCO absorptions at 1798 and 1761 cm^{-1}. The CO stretching frequency in the ion-pair $[(Ph_3P)_2N][Co(CO)_4]$ is 1890 cm^{-1}.[8] The difference between the average Co–C (terminal) bond length of 1.77±0.03 Å and that of the average C–O (terminal) bond length of 1.14±0.02 Å are longer (0.07Å) and shorter (0.05Å) than those of the singular Co–C (iso) bond length of 1.699(3) Å and the C–O (iso) bond length of 1.188(3) Å respectively. This is consistent with the current view of metal-carbonyl bonding, viz., increased backbonding strengthens the M–C bond and weakens the C–O bond. These bond length differences, however, are on the edge of significance and these conclusions must be treated as supportive rather than definative.

Acknowledgement

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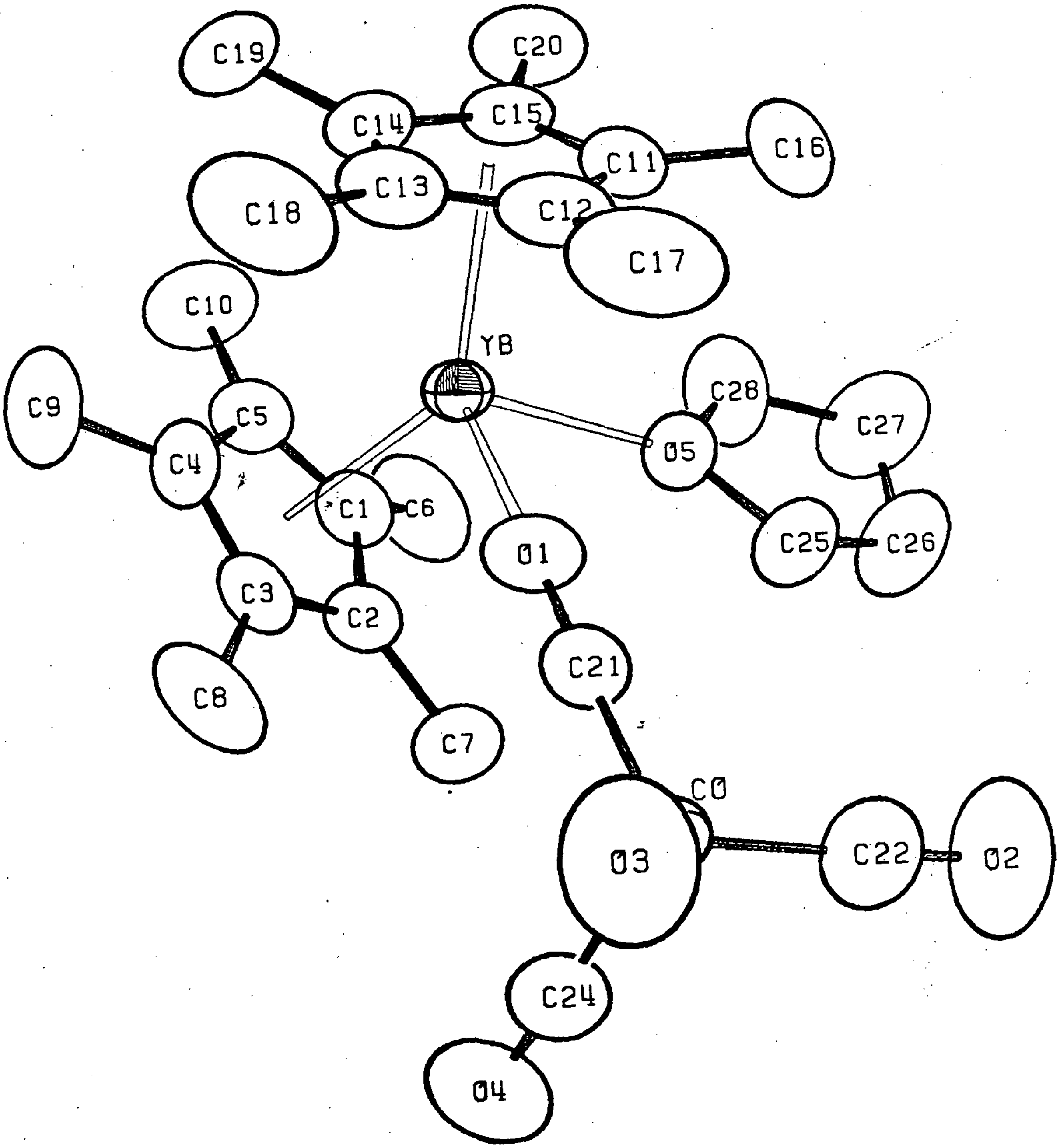
Figure Caption

An ORTEP drawing of $(Me_5C_5)_2YbCo(CO)_4(thf)$. Some bond lengths and bond angles are: Yb–C(centroid) = 2.302 Å, C(centroid) - Yb-(centroid) = 139.4°, 0(05)YbO(01) = 83.3(7)°, CO(terminal) - CoCO(terminal) = 108.9 ± 0.4°(ave.), and CO(terminal)CoCO(iso) = 110.0 ± 0.6°.


C19
C20
C14
C15
C16
C11
C13
C18
C12
C17
C10
YB
C28
C9
C5
C27
C4
O5
C1
C6
O1
C25
C26
C3
C2
C21
C8
C7
C0
O3
C22
O2
C24
O4

XBL 815-9586

Supplementary Table I. Fractional Atomic Coordinates

X,Y,Z (CRYSTAL)

YB	0.0926	0.2282	0.2526
CO	0.4345	-0.2206	0.2706
C1	-0.0230	0.2372	0.0887
C2	0.0396	0.1059	0.1091
C3	-0.0347	0.0756	0.1914
C4	-0.1420	0.1882	0.2225
C5	-0.1324	0.2879	0.1582
C6	0.0041	0.3054	-0.0028
C7	0.1576	0.0145	0.0485
C8	-0.0154	-0.0555	0.2330
C9	-0.2580	0.1916	0.2991
C10	-0.2379	0.4207	0.1514
C11	0.1949	0.3632	0.3619
C12	0.1760	0.2619	0.4211
C13	0.0318	0.2802	0.4359
C14	-010372	0.3930	0.3875
C15	0.0626	0.4424	0.3407
C16	0.3302	0.3915	0.3393
C17	0.2882	0.1625	0.4695
C18	-0.0357	0.2007	0.4998
C19	-0.1899	0.4671	0.4004
C20	0.0319	0.5691	0.2894
C21	0.3164	-0.0720	0.2838
C22	0.5981	-0.2107	0.2259
C23	0.4512	-0.3034	0.3850
C24	0.3767	-0.3090	0.1871
O1	0.2345	0.0325	0.2897
O2	0.7017	-0.1999	0.1962
O3	0.4566	-0.3509	0.4579
O4	0.3342	-0.3604	0.1304
O5	0.2851	0.2366	0.1511
C25	0.4219	0.1426	0.1435
C26	0.5058	0.1927	0.0695
C27	0.4360	0.3273	0.0626
C28	0.2900	0.3477	0.0924
HCP1	-0.0585	0.1790	0.1540
HCP2	0.0856	0.3481	0.3894
H6C	0.0992	0.2720	-0.0254
H7A	0.1216	-0.0227	-0.0010
H7B	0.2162	0.0595	0.0191
H7C	0.2093	-0.0511	0.0892
H8A	-0.0707	-0.0957	0.2010
H8B	0.0795	-0.1055	0.2234
H8C	-0.0432	-0.0482	0.3010
H9A	-0.3315	0.1740	0.2692
H9B	-0.2243	0.1289	0.3473
H9C	-0.2916	0.2742	0.3289
H10A	-0.3097	0.4162	0.1127
H10B	-0.2763	0.4510	0.2151
H10C	-0.1930	0.4778	0.1219
H16A	0.3440	0.4424	0.3904
H16B	0.4045	0.3133	0.3338
H16C	0.3267	0.4366	0.2793
H17A	0.3022	0.1946	0.5303
H17B	0.2616	0.0873	0.4802
H17C	0.3722	0.1419	0.4284
H18A	-0.0504	0.2328	0.5649
H18B	-0.1218	0.2039	0.4760
H18C	0.0237	0.1141	0.4988
H19A	-0.2075	0.5208	0.4567
H19B	-0.2161	0.5185	0.3443
H19C	-0.2422	0.4091	0.4081
H20A	0.0252	0.6348	0.3356
H20B	0.1047	0.5658	0.2406
H20C	-0.0533	0.5867	0.2598
H25A	0.4616	0.1332	0.2046
H25B	0.4169	0.0622	0.1227
H26A	0.5968	0.1779	0.0895
H26B	0.5111	0.1521	0.0080
H27A	0.4738	0.3730	0.1053
H27B	0.4465	0.3548	-0.0024
H28A	0.2527	0.4242	0.1302
H28B	0.2389	0.3533	0.0365
H6A	-0.0521	0.2933	-0.0516
H6B	-0.0183	0.3945	0.0109

Supplementary Table II

Interatomic Distances (Å) in $(C_5Me_5)_2(thf)Yb\text{-}O\text{-}C\text{-}Co(CO)_3$

Yb - C1	2.604(2)
- C2	2.583(2)
- C3	2.600(2)
- C4	2.620(2)
- C5	2.614(2)
- C11	2.610(2)
- C12	2.594(3)
- C13	2.570(2)
- C14	2.582(2)
- C15	2.583(2)
- 01	2.258(2)
- 05	2.335(2)
- Cp(1)[a]	2.312
- Cp(2)[a]	2.293
Co - C21	1.699(3)
C22	1.761(4)
C23	1.793(3)
C24	1.760(4)
Co... 01	2.887(2)
... 02	2.899(3)
... 03	2.909(2)
... 04	2.912(3)

[a] centroid

C1 - C2	1.416(4)
C2 - C3	1.402(4)
C3 - C4	1.415(4)
C4 - C5	1.416(4)
C5 - C1	1.385(4)
C1 - C6	1.501(4)
C2 - C7	1.501(4)
C3 - C8	1.500(4)
C4 - C9	1.507(4)
C5 - C10	1.522(4)
C11- C12	1.418(4)
C12- C13	1.414(4)
C13- C14	1.402(4)
C14- C15	1.402(4)
C15- C11	1.404(4)
C11- C16	1.509(4)
C12- C17	1.500(4)
C13- C18	1.502(4)
C14- C19	1.508(4)
C15- C20	1.502(4)
05 - C25	1.447(3)
C25- C26	1.482(5)
C26- C27	1.430(6)
C27- C28	1.455(5)
C28- 05	1.462(3)
C21- 01	1.188(3)
C22- 02	1.138(4)
C23- 03	1.117(4)
C24- 04	1.154(4)

Supplementary Table III

Selected Bond angles in $(C_5Me_5)_2(thf)Yb\text{-}0{\equiv}C\text{-}Co(CO)_4$

01	Yb	05	83.3(7)
01	Yb	Cp(1)	102.5
01	Yb	Cp(2)	103.2
05	Yb	Cp(1)	107.0
05	Yb	Cp(2)	106.9
Cp(1)	Yb	Cp(2)	139.4
C21	Co	C22	110.7(1)
C21	Co	C23	110.8(1)
C21	Co	C24	108.6(1)
C22	Co	C23	109.2(2)
C22	Co	C24	109.2(2)
C23	Co	C24	108.3(1)

Yb-01-C21	163.0(2)
Co-C21-01	177.8(2)
Co-C22-02	177.6(4)
Co-C23-03	177.0(3)
Co-C24-04	176.1(3)
Yb-05-C25	127.1(2)
Yb-05-C28	124.2(2)
C25-05-C28	108.4(2)
05-C25-C26	105.9(3)
C25-C26-C27	106.4(3)
C26-C27-C28	107.0(3)
C27-C28-05	106.1(3)

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