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Preliminary communication

SYNTHESIS AND STRUCTURE OF A CARBONYL-BRIDGED DIMERIC COMPOUND CONTAINING GROUP IV AND GROUP VIII TRANSITION METALS: $(\eta^5\text{-}C_5H_5)Co(\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^2\text{-}CO)Zr(\eta^5\text{-}C_5Me_5)_2$

PAUL T. BARGER and JOHN E. BERCAW*

Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91125 (U.S.A.)*

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Summary

$(\eta^5\text{-}C_5H_5)Co(CO)_2Zr(\eta^5\text{-}C_5Me_5)_2$ is prepared by treatment of $(\eta^5\text{-}C_5H_5)Co(CO)_2$ with $(\eta^5\text{-}C_5Me_5)_2ZrH_2$ or $\{(\eta^5\text{-}C_5Me_5)_2ZrN_2\}N_2$. The mixed-metal dimer crystallizes in the monoclinic space group $P2_1/c$ with unit cell dimensions a 15.624(6), b 13.885(13) and c 11.221(4) Å, β 94.01(3)°, V 2424.91(1.0)Å^3, $Z = 4$. The structure of $(\eta^5\text{-}C_5H_5)Co(CO)_2Zr(\eta^5\text{-}C_5Me_5)_2$ contains a cobalt—zirconium single bond of length 2.926 Å. The two carbonyls exhibit different bonding modes. One bridges the metal centers in a standard μ_2 manner, while the other bridges via a σ-bond to the cobalt and an interaction between the zirconium and a CO π-bond in a μ_2-η^1,η^2 fashion.

The number of dimeric compounds containing two transition metal centers is now fairly substantial. The most common class involves metal—metal (single or multiple) bonding between the same element [1]. A growing class contains two different transition metals; however, most examples in this group involve transition metals of Groups VI—VII [2]. Notable exceptions containing at least one "early" transition metal include $(\eta^5\text{-}C_5H_5)_2(CO)Nb(\mu\text{-}H)Fe(CO)_4$ [3], $(\eta^5\text{-}C_5H_5)_2(CO)Nb(\mu\text{-}CO)Co(CO)_3$ [4], and $(\eta^5\text{-}C_5H_5)_2(CH_3)Zr\text{-}Mo(CO)_3(\eta^5\text{-}C_5H_5)$ [5].

In the course of investigating the reactivity of $(\eta^5\text{-}C_5Me_5)_2ZrH_2$ with transition metal carbonyls, we discovered an unusual carbonyl-bridged dimer of Co and Zr, $(\eta^5\text{-}C_5H_5)Co(CO)_2Zr(\eta^5\text{-}C_5Me_5)_2$. This compound appeared to be of some interest in view of the disparate electronegativities of the two transition metals involved and the possibility of an unusual bonding mode for the bridging carbonyls comparable to the η^2-acyl geometries previously observed for zirconium [6]. Accordingly, we have undertaken a structure determination of the title compound.

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Unlike its reactivity with several transition metal carbonyls [7], with $(\eta^5\text{-}C_5H_5)Co(CO)_2$ $(\eta^5\text{-}C_5Me_5)_2ZrH_2$ does not undergo hydride transfer to afford the expected zirconoxy carbene $(\eta^5\text{-}C_5H_5)(CO)Co{=}CHOZr(H)(\eta^5\text{-}C_5Me_5)_2$; one equivalent of H_2 is evolved at ca. −20°C with formation of the intense blue-green compound (eq. 1) which analyzes for $(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Me_5)_2CoZr(CO)_2$ (I)

$$(\eta^5\text{-}C_5H_5)Co(CO)_2 + (\eta^5\text{-}C_5Me_5)_2ZrH_2 \rightarrow (\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Me_5)_2CoZr(CO)_2 + H_2 \quad (1)$$

in 95% yield (^{1}H NMR). Compound I may be isolated as nearly black crystals from toluene. The color arises from the broad adsorption (λ_{max} 590 nm, ϵ ca. 10^4, petroleum ether solution) in the visible spectrum. It may also be prepared in quantitative yield substituting $\{(\eta^5\text{-}C_5Me_5)_2ZrN_2\}_2N_2$ for $(\eta^5C_5Me_5)_2ZrH_2$ (eq. 2).

$$2(\eta^5\text{-}C_5H_5)Co(CO)_2 + \{(\eta^2\text{-}C_5Me_5)_2ZrN_2\}_2N_2 \rightarrow 2(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Me_5)_2CoZr(CO)_2 + 3\ N_2 \quad (2)$$

$(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Me_5)_2CoZr(CO)_2$ exhibits two strong infrared absorptions at 1683 and 1737 cm^{-1} and two singlets in its ^{1}H NMR spectrum (benzene-d_6) at δ 4.91 and 1.71 ppm (relative intensity 1/6). These data led to the formulation of this product as a carbonyl-bridged dimer $(\eta^5\text{-}C_5H_5)Co(\mu\ CO)_2Zr(\eta^5\text{-}C_5Me_5)_2$. Interestingly, there appear to be no reasonable symmetric structures which

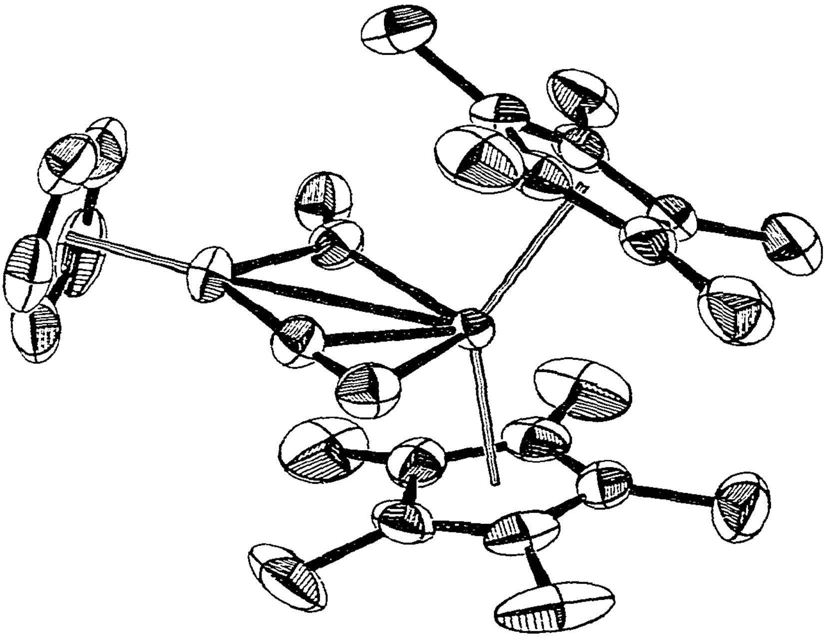

Fig. 1. ORTEP drawing of $(\eta^5\text{-}C_5H_5)Co(CO)_2Zr(\eta^5\text{-}C_5Me_5)_2$ showing 50% probability on thermal ellipsoids.

TABLE 1

BOND DISTANCES (Å) FOR $(\eta^5\text{-}C_5H_5)Co(CO)_2Zr(\eta^5\text{-}C_5Me_5)_2$

Zr—Co	2.926(1)	C(10)—C(11)	1.422(8)
Zr—C(1)	2.272(8)	C(11)—C(12)	1.390(8)
Zr—O(1)	2.431(5)	C(12)—C(8)	1.405(8)
Co—C(1)	1.689(8)	C(8)—C(13)	1.496(10)
Co—O(1)	2.888(5)	C(9)—C(14)	1.509(10)
C(1)—O(1)	1.200(9)	C(10)—C(15)	1.506(10)
Zr—C(2)	2.233(8)	C(11)—C(16)	1.501(9)
Zr—O(2)	3.266(6)	C(12)—C(17)	1.508(11)
Co—C(2)	2.034(8)	Zr—Cp*(1)[a]	2.238(6)
Co—O(2)	2.922(6)	Zr—C(18)	2.589(6)
C2—O(2)	1.179(10)	Zr—C(19)	2.542(6)
Co—C(3)	2.081(7)	Zr—C(20)	2.529(5)
Co—C(4)	2.106(7)	Zr—C(21)	2.501(6)
Co—C(5)	2.087(7)	Zr—C(22)	2.546(6)
Co—C(6)	2.082(7)	C(18)—C(19)	1.404(8)
Co—C(7)	2.091(7)	C(19)—C(20)	1.408(8)
C(3)—C(4)	1.409(10)	C(20)—C(21)	1.407(8)
C(4)—C(5)	1.390(10)	C(21)—C(22)	1.420(8)
C(5)—C(6)	1.393(10)	C(22)—C(18)	1.432(8)
C(6)—C(7)	1.363(10)	C(18)—C(23)	1.502(9)
C(7)—C(3)	1.382(10)	C(19)—C(24)	1.513(9)
Co—Cp[a]	1.725(7)	C(20)—C(25)	1.514(9)
Zr—C(8)	2.553(6)	C(21)—C(26)	1.518(9)
Zr—C(9)	2.548(6)	C(22)—C(27)	1.500(9)
Zr—C(10)	2.528(6)	Zr—Cp*(2)[a]	2.239(6)
Zr—C(11)	2.545(6)		
Zr—C(12)	2.518(6)		
C(8)—C(9)	1.421(8)		
C(9)—C(10)	1.396(8)		

[a] Cp = C(3)—C(7) ring centroid, Cp*(1) = C(8)—C(12) ring centroid, Cp*(2) = C(18)—C(22) ring centroid.

allow formal 18-electron, closed-shell electronic configurations for both metals. The structure was therefore investigated using X-ray diffraction techniques. A suitable crystal of I measuring 0.5 × 0.4 × 0.2 mm was grown by slow cooling of a saturated toluene solution. I crystallizes in the monoclinic space group $P2_1/c$ with unit cell dimensions a 15.624(6), b 13.885(13) and c 11.221(4) Å, β 94.01(3)°, V 2424.9(1.0) Å^3, $Z = 4$ as shown by preliminary rotation and Weissenberg photographs. 8824 independent reflections with $2.5 \leqslant 2\theta \leqslant 65°$ were collected on a Syntex P2$_1$ diffractometer using graphite-monochromated Mo-K_α radiation. Intensities were corrected for Lorentz and polarization factor; no absorption correction was applied (μ 1.95 cm^{-1}). Observational variances $\sigma^2(F_o^2)$ were based on counting statistics plus the lack-of-confidence term $(0.02 \times \text{scan counts})^2$. The structure was solved by generation of a series of Patterson and Fourier maps. Refinement was by least-squares techniques, using full and blocked matrices with anisotropic temperature parameters for all non-hydrogen atoms and inclusion of a secondary extinction factor [8], to a final R index $(\Sigma||F_o|-|F_c||/|F_o|)$ of 0.056 with a goodness of fit $([\Sigma w(F_o^2 - s^2F_c^2)/(N-P)]^{\frac{1}{2}}$, $w = 1/\sigma^2(F_o^2)$, $1/s$ = scale factor for F_o) of 1.81 for $N = 3842$ reflections with $F_o^2 \geqslant 3\sigma(F_o^2)$ and $P = 281$ parameters. The majority of the low intensity reflections ignored in the structure refinement were of $50° \leqslant 2\theta \leqslant 65°$.

The structure of $(\eta^5\text{-}C_5H_5)Co(CO)_2Zr(\eta^5\text{-}C_5Me_5)_2$ is shown in Fig. 1, and a view of the planar metal—carbonyl substructure with pertinent bond lengths

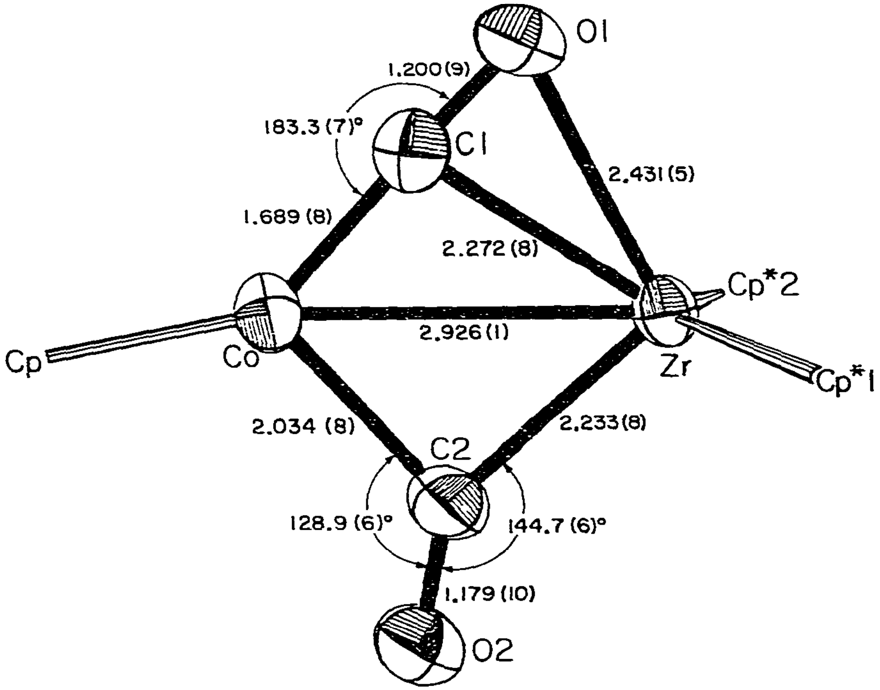

Fig. 2. The planar metal-carbonyl substructure of I showing pertinent bond lengths (Å) and angles. For clarity the η^5-C_5H_5 and η^5-C_5Me_5 rings have been omitted; their positions are indicated by the metal to ring centroid bonds.

TABLE 2

BOND ANGLES (deg) FOR $(\eta^5\text{-}C_5H_5)Co(CO)_2Zr(\eta^5\text{-}C_5Me_5)_2$

Zr—C(1)—O(1)	82.7(5)	C(9)—C(8)—C(13)	124.8(6)
Co—C(1)—O(1)	176.7(7)	C(12)—C(8)—C(13)	127.4(6)
Zr—C(1)—Co	94.1(3)	C(8)—C(9)—C(14)	124.7(6)
Zr—Co—C(1)	50.8(3)	C(10)—C(9)—C(14)	126.0(6)
Co—Zr—C(1)	35.2(2)	C(9)—C(10)—C(15)	124.0(6)
Co—Zr—O(1)	64.5(1)	C(11)—C(10)—C(15)	127.9(6)
Zr—C(2)—O(2)	144.7(6)	C(10)—C(11)—C(16)	128.1(6)
Co—C(2)—O(2)	128.9(6)	C(12)—C(11)—C(16)	122.3(6)
Zr—C(2)—Co	86.4(3)	C(11)—C(12)—C(17)	126.2(6)
Zr—Co—C(2)	49.6(2)	C(8)—C(12)—C(17)	124.5(6)
Co—Zr—C(2)	44.0(2)	C(18)—C(19)—C(20)	108.0(5)
Zr—Co—Cp	168.2(5)	C(19)—C(20)—C(21)	108.9(5)
Co—Zr—Cp*(1)	109.5(5)	C(20)—C(21)—C(22)	107.7(5)
Co—Zr—Cp*(2)	110.2(5)	C(21)—C(22)—C(18)	107.4(5)
Cp*(1)—Zr—Cp*(2)	139.2(5)	C(22)—C(18)—C(19)	108.0(5)
C(3)—C(4)—C(5)	106.7(6)	C(19)—C(18)—C(23)	127.2(5)
C(4)—C(5)—C(6)	108.0(6)	C(22)—C(18)—C(23)	124.6(5)
C(5)—C(6)—C(7)	108.8(7)	C(18)—C(19)—C(24)	125.6(5)
C(6)—C(7)—C(3)	108.2(6)	C(20)—C(19)—C(24)	125.3(5)
C(7)—C(3)—C(4)	108.3(6)	C(19)—C(20)—C(25)	123.3(5)
C(8)—C(9)—C(10)	108.2(5)	C(21)—C(20)—C(25)	126.3(5)
C(9)—C(10)—C(11)	107.7(5)	C(20)—C(21)—C(26)	126.7(5)
C(10)—C(11)—C(12)	107.9(5)	C(22)—C(21)—C(26)	125.1(5)
C(11)—C(12)—C(8)	108.8(5)	C(21)—C(22)—C(27)	125.9(5)
C(12)—C(8)—C(9)	107.3(5)	C(18)—C(22)—C(27)	126.4(5)

and angles is shown in Fig. 2. Bond distances are tabulated in Table 1 and bond angles are listed in Table 2*. The C_5H_5 and C_5Me_5 rings are bonded to the two metals in the standard *pentahapto* manner with Co—C(ring) distances of 2.081—2.106(7) Å and Zr—C (ring) distances of 2.501—2.589(6) Å. The Cp★ centroid—Zr—Cp★ centroid angle of 139.2(5)° is typical for bent zirconocene structures [9]. The metal—metal distance (2.926 Å) can be compared to that observed for $(\eta^5\text{-}C_5H_5)_2(CO)Nb(\mu\text{-}CO)Co(CO)_3$ of 2.992 Å [4], another example of an "early" to "late" transition metal bond. This bond length indicates the presence of a Co—Zr single bond as expected in light of the lone valence orbital of the zirconocene fragment available for metal—metal bonding [10].

Perhaps the most interesting feature of the structure of I is the bonding of the bridging carbonyls, which are distinctly different. One bridging carbonyl (C(2)O(2)) bridges the metal centers in a conventional μ_2 fashion, although there is some inherent asymmetry due to the large difference in size of the two metals. The second carbonyl bridges the two metals in a $\mu_2\text{-}\eta^1,\eta^2$ manner. This mode of carbonyl bridging was first observed by Colton et al., in the structure of $Mn_2(CO)_5(PPh_2CH_2PPh_2)_2$ [11]. Three other examples [12] have been reported in which carbon monoxide acts as a bridging ligand through donation from its π system to one or more transition metals. The Co—C(1)—O(1) angle indicates that the cobalt—carbonyl bonding is essentially terminal. The Co—C(1) bond length is also consistent with this assignment [13]. Both C(1) and O(1) are well within bonding distance to the Zr, indicative of interaction of a C(1)O(1) π bond with zirconium similar to that observed for ethylene in $(\eta^5\text{-}C_5H_5)_2Nb(C_2H_4)(C_2H_5)$ [14]. Thus in this $\mu_2\text{-}\eta^1, \eta^2$ bridging mode the carbonyl acts as a two electron donor to both the cobalt and zirconium, bringing both metal centers to closed-shell, 18-electron configurations.

There exists an intriguing possibility that the carbonyls could interchange bonding modes through a fluxional process. A variable temperature ^{13}C NMR study of I has been thwarted, however, due to ^{59}Co quadrupolar broadening of the ^{13}C resonances for the carbonyls. We are presently investigating the reactivity of $(\eta^5\text{-}C_5H_5)Rh(CO)_2$ with $(\eta^5\text{-}C_5Me_5)_2ZrH_2$ and $\{(\eta^5\text{-}C_5Me_5)_2ZrN_2\}_2N_2$, in an attempt to find a system suitable for study by NMR.

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*65 pages of supplementary material containing atomic positions and thermal parameters, least squares planes and structure factors will be filed as NAPS document (NAPS, c/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, NY 10017, U.S.A.).

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