Inorg. Chem. **1980**, *19*, 3812-3817

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Crystal and Molecular Structure of Two Early Transition-Metal Dicarbonyldicyclopentadienyl Complexes: $(\eta^5\text{-}C_5H_5)_2Zr(CO)_2$ and $[(\eta^5\text{-}C_5H_5)_2V(CO)_2][B(C_6H_5)_4]$

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Received May 12, 1980

The crystal structures of $(\eta^5\text{-}C_5H_5)_2Zr(CO)_2$ and $[(\eta^5\text{-}C_5H_5)_2V(CO)_2][B(C_6H_5)_4]$ have been determined from X-ray data measured by counter methods. Dicarbonyldicyclopentadienylzirconium(II) crystallizes in the monoclinic space group $P2_1/m$ with unit cell parameters a = 6.528 (4) Å, b = 11.444 (6) Å, c = 8.130 (4) Å, β = 113.58 (4)°, and Z = 2 for ρ_{calcd} = 1.65 g cm^{-3}. Least-squares refinement led to a final R factor of 0.029 based on 998 independent observed reflections. The molecule resides on a crystallographic mirror plane which passes through the cyclopentadienyl groups and bisects the C(σ)–Zr–C(σ) angle. The Zr–C(carbonyl) bond length, 2.187 (4) Å, is slightly longer than expected on the basis of the $(\eta^5\text{-}C_5H_5)_2Ti(CO)_2$ structure. The C(σ)–Zr–C(σ) bond angle is 89.2 (2)°, while that for the centroid–Zr–centroid is 143.4°. Dicarbonyldicyclopentadienylvanadium(III) tetraphenylborate belongs to the orthorhombic space group $Pna2_1$ with cell constants a = 20.532 (2) Å, b = 10.084 (1) Å, c = 13.914 (1) Å, and Z = 4 for ρ_{calcd} = 1.28 g cm^{-3}. Refinement based on 1565 observed reflections produced an R factor of 0.108. The cation is crystallographically disordered, and a definitive comparison with $(\eta^5\text{-}C_5H_5)_2Ti(CO)_2$ is not possible. However, the structural parameters V–C(σ) = 1.98 (2) Å, C(σ)–V–C(σ) = 92 (1)°, and centroid–V–centroid = 138° are in substantial agreement with those found for the isoelectronic titanium compound.

Introduction

Much interest has focused on dicyclopentadienylzirconium(II), $(C_5H_5)_2Zr$, and precursor compounds such as $[(Me_5C_5)_2ZrN_2]_2$[1] and $(\eta^5\text{-}C_5H_5)_2Zr(CO)_2$,[2-4] for the expected high reactivity of this carbene-like species in molecular activation processes. The chemistry of $(\eta^5\text{-}C_5H_5)_2Ti(CO)_2$ suggests that this is the only authentic source of the carbene-like titanocene, $(C_5H_5)_2Ti$, which adds to many unsaturated substrates or splits different covalent bonds.[5] An attractive result is the utlization of $(\eta^5\text{-}C_5H_5)_2Ti(CO)_2$[6] and $(Me_5C_5)_2Zr(CO)_2$[1,7] as model compounds in the reduction of coordinated carbon monoxide by molecular hydrogen. The recent synthesis and low yield[2-4] have not allowed the wide exploration of $(\eta^5\text{-}C_5H_5)_2Zr(CO)_2$ reactivity.[8] This notwithstanding, two features appear to control its chemistry: the high tendency to form Zr–O bonds[9] and the stability of the oxidation state 4+ vs. 3+.[8] The comparison between $(\eta^5\text{-}C_5H_5)_2Ti(CO)_2$ and $(\eta^5\text{-}C_5H_5)_2Zr(CO)_2$ chemistries does not definitely confirm the expected higher kinetic lability and catalytic activity for zirconium compared to titanium. Metal basicity,[5] one of the properties upon which the reactivity of the dicarbonyl could depend, may be roughly evaluated from the Zr–C and C–O bond distances. in addition, the structures of the title compounds were sought for the purpose of comparison with the other known dicarbonyldicyclopentadienyl complexes of the early transition metals $(\eta^5\text{-}C_5H_5)_2Ti(CO)_2$[10] and $(\eta^5\text{-}C_5H_5)_2Hf(CO)_2$.[11]

Experimental Section

X-ray Data Collection and Structure Solution for $(\eta^5\text{-}C_5H_5)_2Zr(CO)_2$. Dicarbonyldicyclopentadienylzirconium(II) was prepared by a literature method[2] and recrystallized from a heptane solution. An appropriate single crystal was sealed in a thin-walled glass capillary. Final lattice parameters as determined from 15 high-angle reflections (2θ > 40°) carefully centered on an Enraf-Nonius CAD-4 diffractometer are given in Table I. Intensity data were recorded on the diffractometer in the usual manner.[12] All reflections in one independent quadrant out to 2θ = 54° were measured; 998 reflections were considered observed [$I \geq 3\sigma(I)$]. The intensities were corrected for Lorentz and polarization effects but not for absorption.

Table I. Crystal Data and Summary of Intensity Data Collection and Structure Refinement

	$(\eta^5\text{-}C_5H_5)_2Zr(CO)_2$	$[(\eta^5\text{-}C_5H_5)_2V(CO)_2]$-$[B(C_6H_5)_4]$
mol wt	277.4	556.4
space group	$P2_1/m$	$Pna2_1$
cell const		
a, Å	6.528 (4)	20.532 (2)
b, Å	11.444 (6)	10.084 (1)
c, Å	8.130 (4)	13.914 (1)
β, deg	113.58 (4)	
cell vol, Å^3	556.6	2880.8
molecules/unit cell	2	4
ρ_{calcd}, g cm^{-3}	1.65	1.28
μ_{calcd}, cm^{-1}	9.44	30.2
radiatn	Mo Kα	Cu Kα
max cryst dimens, mm	0.32 × 0.40 × 0.34	0.24 × 0.21 × 0.35
scan width, deg	0.3	
std reflctns	(300), (003)	
decay of stds, %	±2	
reflctns measd	1335	2238
2θ range, deg	54	120
reflctns considered obsd	998	1565
no. of parameters varied	73	
GOF	0.75	
R	0.029	0.108
R_w	0.034	

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Table II. Final Fractional Coordinates and Thermal Parameters[a] for $(\eta^5\text{-}C_5H_5)_2Zr(CO)_2$

atom	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Zr	0.20734 (9)	0.2500	0.17441 (7)	0.0195 (1)	0.00563 (4)	0.00935 (8)	0.0000	0.00466 (8)	0.0000
O	0.5769 (6)	0.0446 (3)	0.1947 (5)	0.042 (1)	0.0096 (3)	0.033 (1)	0.0072 (6)	0.0165 (9)	0.0006 (5)
C(1)	0.031 (1)	0.2500	0.388 (1)	0.034 (3)	0.023 (1)	0.017 (1)	0.0000	0.015 (2)	0.0000
C(2)	0.160 (1)	0.1538 (6)	0.4279 (7)	0.088 (4)	0.0117 (6)	0.016 (1)	−0.011 (1)	0.020 (2)	−0.0004 (6)
C(3)	0.380 (1)	0.1896 (6)	0.4981 (6)	0.057 (2)	0.022 (1)	0.0123 (8)	0.019 (1)	0.009 (1)	0.0054 (7)
C(4)	0.130 (1)	0.2500	−0.1507 (9)	0.041 (3)	0.022 (1)	0.011 (1)	0.0000	0.011 (1)	0.0000
C(5)	0.024 (1)	0.1533 (5)	−0.1217 (7)	0.056 (2)	0.0098 (5)	0.0164 (9)	0.005 (1)	−0.004 (1)	−0.0046 (6)
C(6)	−0.1437 (8)	0.1913 (5)	−0.0734 (6)	0.033 (2)	0.0173 (7)	0.0137 (8)	−0.0108 (9)	−0.0012 (9)	0.0033 (6)
C(7)	0.4513 (7)	0.1158 (4)	0.1862 (6)	0.028 (1)	0.0071 (4)	0.0183 (8)	0.0005 (6)	0.0093 (8)	0.0006 (4)

atom[b]	x	y	z	atom[b]	x	y	z
H(1)[C(1)]	−0.143	0.250	0.331	H(4)[C(4)]	0.237	0.250	−0.221
H(2)[C(2)]	0.085	0.072	0.377	H(5)[C(5)]	0.076	0.078	−0.111
H(3)[C(3)]	0.515	0.136	0.566	H(6)[C(6)]	−0.241	0.142	−0.032

[a] Anisotropic thermal parameters defined by $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [b] Hydrogen atoms placed in calculated positions with $B = 5.5$ Å^2.

The existence of two molecules per unit cell in space group $P2_1/m$ was interpreted to mean that that the zirconium atom was located on a crystallographic mirror plane. Deduction of the metal atom coordinates from a Patterson map and the subsequent calculation of a difference Fourier map allowed the location of all nonhydrogen atoms. Refinement with isotropic temperature factors led to a reliability index of $R = \sum(||F_o| - |F_c||)/\sum|F_o| = 0.091$. Conversion to anisotropic thermal parameters and further refinement gave $R = 0.038$. The hydrogen atoms of the cyclopentadienyl rings were placed at calculated positions 1.00 Å from the bonded carbon atoms, and their parameters were not varied. Additional cycles of refinement led to final values of $R = 0.029$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2} = 0.034$. The largest parameter shifts in the final cycle of refinement were less than 0.01 of their estimated standard deviations.

A final difference Fourier showed no feature greater than 0.2 e/Å^3. The standard deviation of an observation of unit weight was 0.75. Unit weights were used at all stages; no systematic variation of $w(|F_o| - |F_c|)$ vs. $|F_o|$ or $(\sin\theta)/\lambda$ was noted. The function $w(|F_o| - |F_c|)^2$ was minimized.[13] Neutral atom scattering factors were taken from the compilations of Cromer and Waber[14] for Zr, O, and C, and that of Zr was corrected for the real and imaginary components of anomalous dispersion.[15] Scattering factors for H were from ref 16. The final values of the positional and thermal parameters are given in Table II.[17]

X-ray Data Collection and Structure Solution for $[(\eta^5\text{-}C_5H_5)_2V(CO)_2][B(C_6H_5)_4]$. Dicarbonyldicyclopentadienylvanadium(III) tetraphenylborate was prepared by a literature method[18] and recrystallized from a toluene solution. A single crystal was sealed in a thin-walled glass capillary. Cell dimensions were initially determined from rotation and Weissenberg photographs; the values quoted in Table I were obtained by least-squares refinement of the angular settings for 32 reflections with $2\theta > 60°$.

The crystal was mounted with the [001] axis along the ϕ axis of the diffractometer. Intensity data were collected on the "on-line" single-crystal automated Siemens AED diffractometer using nickel-filtered Cu Kα radiation ($\lambda = 1.5418$ Å) at a takeoff angle of 6°. The pulse height discriminator was set to accept 90% of the Cu Kα peak. The moving-counter–moving-crystal scan technique was employed with a drive speed related to the number of counts on the peak (lowest speed 2.5°/min). One reflection was remeasured after every 20 reflections. No significant change in the measured intensity of this reflection was observed during data collection. For intensity and background the "five-point technique"[19] was used. A total of 2238 reflections was collected in the interval $6° < 2\theta < 120°$; of these, 1565 having $I > 2\sigma(I)$ were considered observed and used in the analysis $[\sigma^2(I) = (\text{total counts}) + (0.01 \times \text{intensity})^2]$.

The structure factor amplitudes were obtained after the usual Lorentz and polarization reduction, and the absoute scale was established by Wilson's method.[20] Absorption corrections were applied.

The examination of the vector distribution of a Patterson map did not afford a distinction between the two possible space groups. The distribution of the higher peaks could be accounted for in either the noncentrosymmetric $Pna2_1$ or the centrosymmetric one, $Pnam$. In the latter case, the vanadium atom was assumed to lie on a mirror plane, as indicated by the number of molecules in the unit cell. The Fourier map, computed in the space group $Pna2_1$, showed an approximate centrosymmetric distribution of the atoms: a mirror plane passed through the vanadium atom and related the two cyclopentadienyl rings, and another passed through the $B(C_6H_5)_4^-$ anion. Only one carbonyl group, lying on the mirror plane, was found in this map. The refinement, carried out in the space group $Pnam$, was not satisfactory, however, due to the high R value ($R = 0.19$) and to the unreasonable distortions in the cyclopentadienyl and phenyl rings (one C–C distance in the cyclopentadienyl ring was 1.96 Å). In addition, a difference map, computed at this stage, gave the approximate positions of another cyclopentadienyl ring, C(1)···C(5), not related to the first one by any symmetry operation and of the other carbonyl group C(30)–O(2) in a general position. The structure was then considered as a noncentrosymmetric one. Full-matrix least-squares refinement for this model, applying a rigid-body constraint to the phenyl and cyclopentadienyl rings, coverged to the R value of 0.134. The isotropic thermal parameters of the atoms C(1)···C(5) and C(30)···O(2) were very high (e.g., $B = 17$ Å^2 for O(2)), and no further improvement could be achieved. The subsequent difference Fourier map confirmed the presence of disorder by revealing residual peaks with electron density of about 2 e/Å^3, not consistent with the C(1)···C(5) ring and the C(20)–O(30) carbonyl group but perfectly consistent with the rest of the structure. Disorder was interpreted in terms of partial occupancy considering the C(1)···C(5) cyclopentadienyl ring and the C(30)–O(2) carbonyl group statistically distributed over two positions. The site occupancy factors, deduced from difference maps, were 0.67 for the "atoms" C(1), C(2), C(3), C(4), C(5), C(20), and O(2) and 0.33 for the corresponding "atoms" denoted by asterisks. Full-matrix least-squares refinement for this

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Table III. Final Fractional Coordinates and Thermal Parameters for $[(\eta^5\text{-}C_5H_5)_2V(CO)_2][B(C_6H_5)_4]$

atom	*x/a*	*y/b*	*z/c*	*B*, Å^2
V	0.1034 (1)	0.2080 (2)	0.2500	*a*
O(1)	0.1978 (6)	0.4479 (12)	0.2604 (21)	*a*
C(20)	0.1652 (8)	0.3581 (15)	0.2613 (21)	*a*
O(2)	0.0144 (12)	0.3805 (22)	0.1223 (19)	9.63 (4)
C(30)	0.0419 (15)	0.3161 (25)	0.1771 (19)	6.47 (4)
O(2*)[b]	0.2314 (20)	0.0452 (33)	0.2594 (38)	13.20 (4)
C(30*)	0.1889 (19)	0.1185 (33)	0.2692 (34)	6.08 (4)
C(1)	0.1457 (9)	0.1782 (16)	0.1029 (12)	5.21 (4)
C(2)	0.0914 (9)	0.0916 (16)	0.1090 (12)	8.92 (4)
C(3)	0.1039 (9)	−0.0019 (16)	0.1830 (12)	7.74 (4)
C(4)	0.1660 (9)	0.0269 (16)	0.2227 (12)	7.42 (4)
C(5)	0.1919 (9)	0.1382 (16)	0.1732 (12)	8.37 (4)
C(1*)	0.1198 (11)	0.1882 (20)	0.0917 (17)	3.47 (4)
C(2*)	0.0869 (11)	0.0731 (20)	0.1247 (17)	3.79 (4)
C(3*)	0.0253 (11)	0.1129 (20)	0.1612 (17)	4.26 (4)
C(4*)	0.0202 (11)	0.2526 (20)	0.1507 (17)	2.53 (4)
C(5*)	0.0786 (11)	0.2991 (20)	0.1077 (17)	4.58 (4)
C(6)	0.1144 (7)	0.2394 (14)	0.4059 (9)	7.03 (4)
C(7)	0.0959 (7)	0.1047 (14)	0.3939 (9)	7.50 (4)
C(8)	0.0316 (7)	0.1023 (14)	0.3564 (9)	8.13 (4)
C(9)	0.0104 (7)	0.2355 (14)	0.3452 (9)	8.05 (4)
C(10)	0.0616 (7)	0.3202 (14)	0.3758 (9)	7.03 (4)
B	0.1181 (3)	0.2565 (6)	0.7563 (9)	3.63 (4)
C(11)	0.1589 (5)	0.3300 (11)	0.8465 (8)	4.90 (4)
C(12)	0.1367 (5)	0.4472 (11)	0.8884 (8)	5.13 (4)
C(13)	0.1740 (5)	0.5104 (11)	0.9585 (8)	5.37 (4)
C(14)	0.2335 (5)	0.4564 (11)	0.9869 (8)	5.45 (4)
C(15)	0.2557 (5)	0.3391 (11)	0.9450 (8)	5.21 (4)
C(16)	0.2184 (5)	0.2759 (11)	0.8748 (8)	4.74 (4)
C(21)	0.1265 (4)	0.0909 (7)	0.7510 (8)	3.55 (3)
C(22)	0.1393 (4)	0.0125 (7)	0.8314 (8)	4.11 (3)
C(23)	0.1453 (4)	−0.1246 (7)	0.8215 (8)	4.97 (3)
C(24)	0.1385 (4)	−0.1833 (7)	0.7313 (8)	5.37 (3)
C(25)	0.1257 (4)	−0.1049 (7)	0.6509 (8)	7.42 (4)
C(26)	0.1197 (4)	0.0322 (7)	0.6607 (8)	6.08 (4)
C(31)	0.0377 (4)	0.2790 (8)	0.7406 (7)	4.26 (3)
C(32)	−0.0018 (4)	0.2963 (8)	0.8212 (7)	6.55 (4)
C(33)	−0.0692 (4)	0.3074 (8)	0.8105 (7)	7.50 (4)
C(34)	−0.0970 (4)	0.3012 (8)	0.7191 (7)	7.11 (4)
C(35)	−0.0575 (4)	0.2838 (8)	0.6385 (7)	7.03 (4)
C(36)	0.0098 (4)	0.2727 (8)	0.6493 (7)	6.24 (4)
C(41)	0.1536 (5)	0.3301 (10)	0.6612 (8)	2.53 (3)
C(42)	0.1270 (5)	0.4466 (10)	0.6240 (8)	5.29 (4)
C(43)	0.1604 (5)	0.5175 (10)	0.5534 (8)	7.03 (4)
C(44)	0.2204 (5)	0.4719 (10)	0.5200 (8)	5.61 (4)
C(45)	0.2470 (5)	0.3555 (10)	0.5572 (8)	5.21 (4)
C(46)	0.2137 (5)	0.2846 (10)	0.6278 (8)	3.79 (3)
H(6)	0.161	0.274	0.433	4.0
H(7)	0.126	0.019	0.410	4.0
H(8)	0.004	0.015	0.339	4.2
H(9)	−0.037	0.267	0.318	4.2
H(10)	0.061	0.427	0.376	4.0
H(12)	0.091	0.489	0.866	4.0
H(13)	0.157	0.601	0.991	4.2
H(14)	0.262	0.505	1.041	4.1
H(15)	0.302	0.297	0.967	4.1
H(16)	0.236	0.185	0.842	4.1
H(22)	0.145	0.058	0.901	4.1
H(23)	0.155	−0.185	0.884	4.0
H(24)	0.143	−0.290	0.724	4.1
H(25)	0.120	−0.150	0.581	4.1
H(26)	0.110	0.093	0.599	4.1
H(32)	0.020	0.301	0.892	4.0
H(33)	−0.100	0.321	0.873	4.0
H(34)	−0.149	0.310	0.711	4.0
H(35)	−0.079	0.279	0.568	4.1
H(36)	0.040	0.259	0.587	4.2
H(42)	0.081	0.482	0.650	3.9
H(43)	0.140	0.608	0.525	4.1
H(44)	0.246	0.527	0.465	4.1
H(45)	0.294	0.320	0.531	4.0
H(46)	0.234	0.194	0.657	4.1

[a] Anisotropic thermal parameters as defined in Table II: for V, $\beta_{11} = 0.0024$ (1), $\beta_{22} = 0.0087$ (1), $\beta_{33} = 0.0061$ (1), $\beta_{12} = -0.0004$ (2), $\beta_{13} = -0.0001$ (2), $\beta_{23} = -0.0010$ (2); for O(1), $\beta_{11} = 0.0031$ (4), $\beta_{22} = 0.0186$ (4), $\beta_{33} = 0.0197$ (4), $\beta_{12} = -0.0030$ (4), $\beta_{13} = 0.0006$ (4), $\beta_{23} = -0.0045$ (4); for C(20), $\beta_{11} = 0.0030$ (4), $\beta_{22} = 0.0136$ (4), $\beta_{33} = 0.0047$ (4), $\beta_{12} = -0.0017$ (4), $\beta_{13} = 0.0034$ (4), $\beta_{23} = -0.0044$ (4). [b] The site occupancy factors for the disordered atoms are 0.67 for O(2), C(30), C(1), C(2), C(3), C(4), and C(5) and 0.33 fur the corresponding starred atoms.

disordered model was carried out with anisotropic thermal parameters only for V, C(20), and O(1). The final *R* value was 0.108. High correlations between pseudocentrosymmetric atomic parameters and the presence of disorder did not allow a better fit. During refinement a bond length constraint was applied to the pairs of atoms C(30)–O(2), C(30*)–O(2*), B–C(11), B–C(21), B–C(31), and B–C(41). A rigid-body constraint was applied to the cyclopentadienyl and phenyl rings, with hydrogen atoms placed in calculated positions.[21] In the last stage of the refinement no parameters shifted by more than 0.4 of its estimated standard deviation.

A final difference map showed no peak with electron density greater than 0.5 e/Å^3. The effects of the anomalous dispersion were included in all structure factor calculations. No evidence for secondary extinction was found. The function minimized in the least-squares calculations was $\sum w|\Delta F|^2$ with unit weights. The atomic scattering factors were those of ref 16 for V, those of Cromer and Mann[22] for O and C, and those of Stewart, Davidson, and Simpson[23] for H. The final atomic parameters are listed in Table III.[17]

Description of the Structures and Discussion

$(\eta^5\text{-}C_5H_5)_2Zr(CO)_2$. The molecule, shown in Figure 1, resides on a crystallographic mirror plane which passes through both cyclopentadienyl rings and bisects the C(σ)–Zr–C(σ) bond angle. $(\eta^5\text{-}C_5H_5)_2Zr(CO)_2$ is isostructural with the hafnium[11] analogue but not with that of titanium.[10] The major difference in the structures for the group 4B congeners is that the cyclopentadienyl rings are eclipsed for the titanium case

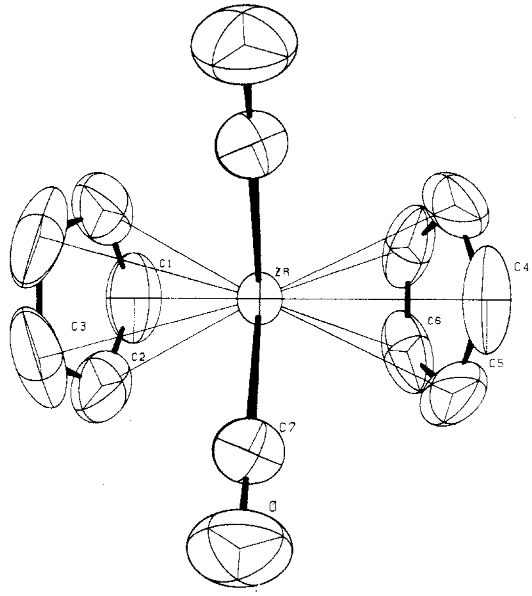

Figure 1. Molecular structure of $(\eta^5\text{-}C_5H_5)_2Zr(CO)_2$ with the atoms represented by their 50% probability ellipsoids for thermal motion.

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(21) Computer programs used on a CYBER 7600 computer of the Centro di Calcolo dell'Italia Nord-Orientale (Bologna) were those of the SHELX-76 (G. M. Sheldrick, University of Cambridge, England). Calculations were performed with the financial support of the University of Parma.

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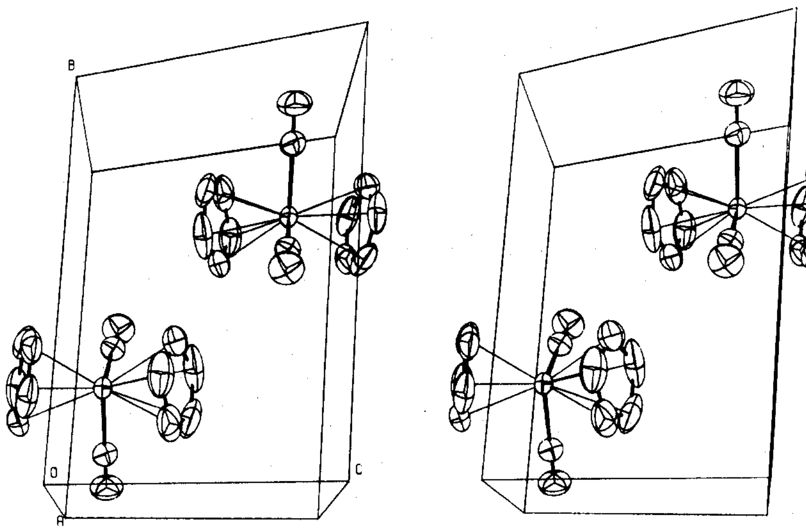

Figure 2. Stereoscopic view of the unit cell packing for $(\eta^5\text{-}C_5H_5)_2Zr(CO)_2$.

Table IV. Comparison of Bond Distances (Å) and Angles (Deg) for $(\eta^5\text{-}C_5H_5)_2M(CO)_2$ (M = Ti,[a] Zr,[b] Hf[c]) and $[(\eta^5\text{-}C_5H_5)_2V(CO)_2]^+$ [b]

	neutral complex			
atoms	M = Ti	M = Zr	M = Hf	V ion
M–C(σ)	2.030 (11)	2.187 (4)	2.16 (2)	1.98 (2)
$M\text{–}C(\eta^5)_{av}$	2.347	2.48 (2)	2.45 (5)	2.27
$M\text{–centroid}_{av}$	2.025	2.184	2.16	1.92
C(σ)–M–C(σ)	87.9 (6)	89.2 (2)	89.3 (9)	92 (1)
centroid–M–centroid	138.6	143.4	141	137.9 (7)
$\text{centroid–M–C}(\sigma)_{av}$	104.8	102.9	104	104
M–C–O	179.4 (9)	178.6 (4)	178 (1)	174 (3)

[a] Reference 10. [b] This study. [c] Reference 11.

and staggered for those of zirconium and hafnium.

A detailed comparison (Table IV) of the Zr–C(σ) bond, 2.187 (4) Å, with the Ti–C(σ) bond, 2.030 (11) Å, reveals that the former is slightly longer than expected. On the basis of metallic radii[24] ($\Delta = r_{Zr} - r_{Ti} = 0.13$ Å), one would predict a Zr–C distance of ca. 2.16 Å. The discrepancy is more significant if the M–C(σ) bonds in the series $(\eta^5\text{-}C_9H_7)_2M(CH_3)_2$[25] are taken into consideration. The Ti–C(σ) length is 2.21 (2) Å, and Zr–C(σ) is 2.251 (6) Å. This would lead one to expect ca. 2.07 Å for the Zr–C(σ) bond in $(\eta^5\text{-}C_5H_5)_2Zr(CO)_2$. It is surprising that the apparent lengthening of the metal–carbonyl bond does not manifest itself in the chemistry of these compounds.

In the crystal structure of $(\eta^5\text{-}C_5H_5)_2Ti(CO)_2$, the average Ti–C(π) length, 2.347 (13) Å, was shorter than that normally found for complexes of Ti^{4+}.[26,27] Although the range was wide and standard deviations high, the same result was obtained from the study of $(\eta^5\text{-}C_5H_5)_2Hf(CO)_2$.[11] In $(\eta^5\text{-}C_5H_5)_2Zr(CO)_2$, the C(π) distances range from 2.438 (4) to 2.510 (4) Å (Table V) and average 2.48 (2) Å. Dicyclopentadienyl compounds of Zr^{4+} show average Zr–C(π) lengths of 2.51 Å or greater.[28-30] There now exist three structures which support the idea that the d electrons in M^{2+} complexes of Ti, Zr, and Hf reside in an orbital which is slightly bonding with respect to the metal–cyclopentadienyl interaction.

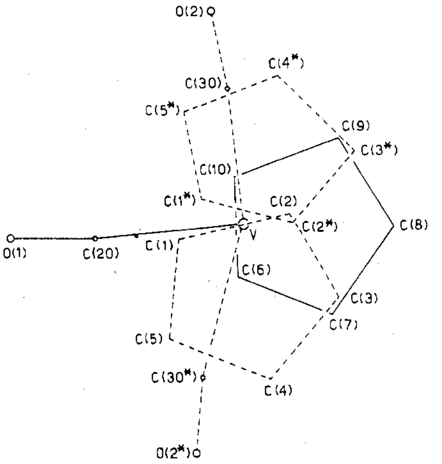

Figure 3. Projection of $[(\eta^5\text{-}C_5H_5)_2V(CO)_2][B(C_6H_5)_4]$ showing the disorder of the cation. The site occupancy factors of the atoms linked by dotted lines are given in Table III.

The centroid–Zr–centroid angle, 143.4°, agrees well with the 138.6 and 141° values for the titanium[10] and hafnium[11] compounds, respectively. A significant feature is that the above-mentioned angle for Zr^{2+} is much larger than that found in Zr^{4+} complexes: 134.8° in $(\eta^5\text{-}C_5H_5)_2Zr[C_4(C_6H_5)_4]$,[28] 134.1° in $(\eta^5\text{-}C_5H_5)_2Zr(CH_3)_2$,[29] and 128.4° in $(\eta^5\text{-}C_5H_5)_2Zr[CH(C_6H_5)_2]_2$.[30] It might also be noted that the 143.4° value is larger than the equivalent angle for any $(\eta^5\text{-}C_5H_5)_2MX_2$ system[31] with the exception of the 148.2° alluded to for $(\eta^5\text{-}C_5H_5)_2MoD_2$.[32]

Considering only organometallic structures, the C(σ)–Zr–C(σ) bond angle, 89.2 (2)°, is smaller than those reported for all but the metallocycles:[28,33] 96.2 (2)° in $(\eta^5\text{-}C_5H_5)_2Zr(CH_3)_2$[29] and 95.5 (4)° in $(\eta^5\text{-}C_5H_5)_2Zr[CH(C_6H_5)_2]_2$.[30] However, the angle falls well within the range of those tabu-

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Table V. Other Bond Lengths (Å) and Angles (Deg)

A. $(\eta^5\text{-}C_5H_5)_2Zr(CO)_2$

Distances

Zr-C(1)	2.438 (7)	Zr-C(4)	2.484 (6)
Zr-C(2)	2.464 (5)	Zr-C(5)	2.480 (5)
Zr-C(3)	2.510 (4)	Zr-C(6)	2.463 (4)
Zr-C(7)	2.187 (4)	$Zr\text{-}C(\pi)_{av}$	2.48 (2)
C(1)-C(2)	1.342 (8)	C(4)-C(5)	1.372 (8)
C(2)-C(3)	1.379 (8)	C(5)-C(6)	1.376 (8)
C(3)-C(3)′ [a]	1.38 (1)	C(6)-C(6)′	1.34 (1)

Angles

C(7)-Zr-C(7)′	89.2 (2)		
centroid(1)-Zr-C(7)	103.6	centroid(1)-Zr-centroid(2)	142.2
Zr-C(7)-O	178.6 (4)	centroid(2)-Zr-C(7)	103.1
C(1)-C(2)-C(3)	107.6 (6)	C(4)-C(5)-C(6)	107.8 (5)
C(2)-C(1)-C(2)′	110.3 (8)	C(5)-C(4)-C(5)′	107.6 (7)
C(2)-C(3)-C(3)′	107.3 (4)	C(5)-C(6)-C(6)′	108.4 (4)

B. $[(\eta^5\text{-}C_5H_5)_2V(CO)_2][B(C_6H_5)_4]$ [b]

Distances

V-C(1)	2.24 (2)	V-C(1*) [c]	2.24 (2)	V-C(6)	2.20 (2)
V-C(2)	2.30 (2)	V-C(2*)	2.24 (2)	V-C(7)	2.26 (1)
V-C(3)	2.31 (2)	V-C(3*)	2.24 (2)	V-C(8)	2.34 (2)
V-C(4)	2.27 (2)	V-C(4*)	2.24 (2)	V-C(9)	2.34 (2)
V-C(5)	2.22 (2)	V-C(5*)	2.24 (2)	V-C(10)	2.25 (1)
	av 2.27 (2)		av 2.24 (2)		av 2.28 (2)
V-C(20)	1.98 (2)	V-centroid(1)	1.92 (2)	C(20)-O(1)	1.13 (2)
V-C(30)	1.95 (3)	V-centroid(1*)	1.89 (2)	C(30)-O(2)	1.15 (4) [d]
V-C(30*)	1.99 (4)	V-centroid(2)	1.94 (1)	C(30*)-O(2*)	1.15 (5)

Angles

C(20)-V-C(30)	92 (1)	C(20)-V-centroid(1*)	115 (1)
C(30*)-V-C(20)	77 (2)	C(30*)-V-centroid(1*)	115 (2)
C(20)-V-centroid(1)	107 (1)	C(30*)-V-centroid(2)	104 (2)
C(20)-V-centroid(2)	104 (1)	centroid(2)-V-centroid(1*)	130 (2)
C(30)-V-centroid(1)	105 (1)	V-C(20)-O(1)	174 (3)
centroid(1)-V-centroid(2)	137.9 (7)	V-C(30)-O(2)	168 (3)
		V-C(30*)-O(2*)	161 (5)

[a] Primed atoms are related to those in Table II by a mirror plane. [b] Atoms of the cyclopentadienyl rings and the $[B(C_6H_5)_4]^-$ anion were constrained by the refinement as rigid groups. [c] Starred atoms refer to the disordered fragments. [d] Constrained.

lated by Prout et al. for $(\eta^5\text{-}C_5H_5)_2MX_2$ species: 87.5–90.0°.[31] In both $(\eta^5\text{-}C_5H_5)_2Zr(CO)_2$ and $[(\eta^5\text{-}C_5H_5)_2V(CO)_2]^+$ the angle produced by the two σ-bond vectors is much higher than the value calculated by Lauher and Hoffmann[34] for a d^2 configuration: ca. 78°.

The cyclopentadienyl rings are each planar to 0.004 Å,[17] and the Zr–C–O angle, 178.6 (4)°, shows that the carbonyl bonds in a linear fashion. The cell packing (Figure 2) is typical of a molecular compound of this sort and presents no unusually close intermolecular contacts.

$[(\eta^5\text{-}C_5H_5)_2V(CO)_2][B(C_6H_5)_4]$. The structure consists of discrete cations $[(\eta^5\text{-}C_5H_5)_2V(CO)_2]^+$ and anions $[B(C_6H_5)_4]^-$. In Figure 3 the disorder involving the cations is shown. Unfortunately bond distances and angles in the disordered groups must be discussed with care, since disorder prevents the accurate location of the atoms involved. The geometry of coordination is, however, similar to that observed in other related complexes, in particular if the two disordered orientations of the cation are considered separately, as shown in Figure 4. Cyclopentadienyl ligands are η^5 bonded to vanadium in a bent arrangement, and the groups of atoms V, C(20), C(30), O(1), and O(2) (Figure 4a) and V, C(20), C(30*), O(1), and O(2*) (Figure 4b) define orthogonal molecular planes to those containing the ring normals. The two disordered parts of the cation are nearly related by a noncrystallographic mirror plane. One of them (Figure 4b) corresponds to a pseudocentrosymmetric structure (*Pnam*) with a crystallographic mirror plane containing vanadium and carbonyl groups and correlating the two cyclopentadienyl rings. It can be concluded that disorder is due to a distribution of the cyclopentadienyl rings in part (67%) in a noncentrosymmetric fashion (Figure 4a) and in part (33%) in a centrosymmetric one (Figure 4b). With respect to the V–CO unit, we must refer to the V–C(20) which is the nondisordered carbonyl.

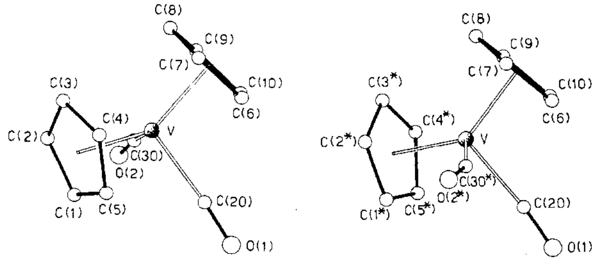

Figure 4. A separate view of the two possible orientations of the $[(\eta^5\text{-}C_5H_5)_2V(CO)_2]^+$ ion: (a) 67%; (b) 33%.

The V–C(σ) bond length, 1.98 (2) Å, is not significantly different from those formed for terminal carbonyls in $(\eta^5\text{-}C_5H_5)_2V_2(CO)_5$, 1.91 (1) and 1.98 (1) Å,[35] and $[\{(C_6H_5)_2P\}_2N][V(CO)_6]$, 1.931 (9) Å.[36] The C(σ)–V–C(σ) angle, 92 (1)°, is considerably larger than the related parameter for

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(η^5-C_5H_5)$_2$Ti(CO)$_2$,[10] 87.9 (6)°, but the centroid–metal–centroid angles are nearly equivalent, 138 (1)° in the former vs. 138.6° in the latter.

Acknowledgment. We are grateful to the National Science Foundation for partial support (to J.L.A.).

Registry No. (η^5-C_5H_5)$_2$Zr(CO)$_2$, 59487-85-3; [(η^5-C_5H_5)$_2$V(CO)$_2$][B(C_6H_5)$_4$], 57088-91-2.

Supplementary Material Available: A listing of structure factor amplitudes for both compounds and least-squares plane results for dicarbonyldicyclopentadienylzirconium(II) (26 pages). Ordering information is given on any current masthead page.

Contribution from the Departments of Chemistry, University of Massachusetts, Amherst, Massachusetts 01003,
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Formation and Molecular Structure of a Novel Organometallic Titanoxane Derived from the Reaction of Dicarbonyltitanocene and Hexafluoro-2-butyne

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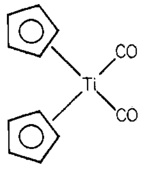
Received June 9, 1980

The reaction between dicarbonyltitanocene (1) and hexafluoro-2-butyne in benzene solution in a sealed system at 55 °C has produced an orange air-stable titanoxane, [(η^5-C_5H_5)$_2$Ti(CF_3C=C(H)CF_3)]$_2$O, in 30–35% yield. The product has been characterized by ^{1}H NMR, ^{19}F NMR, IR, and mass spectrometric techniques, and its crystal structure has been determined from three-dimensional X-ray data as measured by counter techniques. The compound crystallizes in the triclinic space group $P\bar{1}$ with a = 11.522 (5) Å, b = 15.015 (6) Å, c = 17.959 (6) Å, α = 77.52 (4)°, β = 77.93 (4)°, γ = 70.27 (4)°, and ρ_{calcd} = 1.64 g cm^{-3} for Z = 4. Full-matrix least-squares refinement led to a final R value of 0.041 based on 4888 reflections. The two independent molecules in the asymmetric unit display similar bond distances and angles but exist in different rotational conformations about the Ti–O–Ti bond: the C(σ)–Ti···Ti–C(σ) torsional angles are +54.1 and –53.7°. The Ti–O–Ti linkage is nearly linear (170°), and the Ti–O bond distance, 1.856 (6) Å, is larger than normal. This is attributed to steric effects, as are the elongated Ti–C(sp^2) distance, 2.239 (3) Å, and the Ti–C(η^5) distance, 2.421 (23) Å.

Although dicarbonyltitanocene [bis(η^5-cyclopentadienyl)dicarbonyltitanium] (1) was first obtained by Murray in 1958,[2] the chemistry of this unique metal carbonyl has been slow to develop, due primarily to the considerable experimental difficulties and low yields incurred in its preparation by the original literature method. Recently, however, several greatly improved methods for the synthesis of 1 have been reported,[3,4] and a variety of reactions involving displacements of the carbonyl ligands by diphenylketene, trimethylphosphine, TCNE, 2,2′-bipyridine, alkyl halides, acyl halides, 9,10-phenanthroquinone, etc. have been described.[3,5] An X-ray structural determination of 1 has also recently been completed in our laboratories.[6]

In contrast to the rich and varied chemistry resulting from reactions of the metal carbonyls and acetylenes,[7] however, at the present time there exist only two reports[8,9] on the interaction of 1 with acetylenes. As part of our continuing joint program on the formation and structure of organometallic products derived from metal carbonyls and acetylenes, we report herein on the reaction of 1 and hexafluoro-2-butyne, as well as on the results of a single-crystal X-ray crystallographic study which together with spectral measurements fully characterize the organometallic product produced as a novel titanoxane (4).

Results and Discussion



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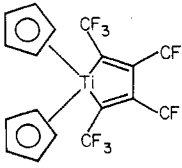

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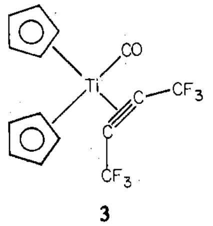

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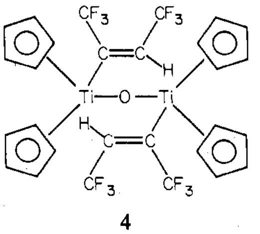

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Formation of 4. It was our original expectation that the interaction of dicarbonyltitanocene (1) with hexafluoro-2-butyne would lead either to a titanole (2) or to an η^2-acetylene complex (3),[10] in analogy with earlier reported reactions of 1 with diphenylacetylene.[8,9] Accordingly, 1 was allowed to react with an excess of hexafluoro-2-butyne in benzene solution at 55 °C in a sealed system for 16 h. Chromatography of the dark orange reaction mixture on silica gel under argon produced an orange solid, which upon crystallization from tolu-

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