Synthesis and Crystal Structure of $[(\eta^6\text{-}C_6H_5CH_3)V(CO)_2]_2$, a Compound with a Vanadium–Vanadium Triple Bond

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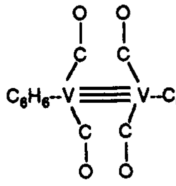
Received September 1, 1992

The synthesis and crystal structure of bis(toluene)tetracarbonyldivanadium, $[(\eta^6\text{-}C_6H_5CH_3)V(CO)_2]_2$, are reported. This complex crystallizes as black plates in the monoclinic space group $P2_1/c$. Unit cell parameters are $a = 8.302(6)$ Å, $b = 12.511(7)$ Å, $c = 8.387(4)$ Å, $\beta = 111.43(5)°$, $V = 810.8(8)$ Å^3, and $Z = 2$. The structure was refined by full-matrix least-squares methods to $R = 7.47\%$ and $R_w = 4.68\%$ for all 1426 independent data with $2\theta(\text{Mo K}\alpha) = 4.5\text{–}50.0°$ ($R = 3.57\%$ and $R_w = 3.36\%$ for those 850 data for which $F_0 > 6.0\sigma(F)$). The structure consists of two $(\eta^6\text{-}C_6H_5CH_3)V$ units which are linked by a direct metal–metal interaction and by four close-to-linear, asymmetrically bridging carbonyl ligands. The vanadium–vanadium distance of 2.388(2) Å is consistent with a bond order of 3 between the metal atoms. There are two molecules per unit cell, located at the inversion centers at 0, 0, 0 and 0, $^1/_2$, $^1/_2$. The (centroid of the arene)–V–V angle of 161° is similar to that of 159° observed in the isoelectronic species $Cp_2Cr_2(CO)_4$.

Introduction

The reactivity and nature of metal–metal bonds have been areas of intense interest.[1,2] An important subgroup of the multiply bonded bimetallic compounds utilizes the ubiquitous cyclopentadienyl[3] (Cp) ligand and related carbocyclic systems such as cyclohexadienyl and arene ligands. Representative compounds include $Cp_2Cr_2(CO)_4$,[4] $[(dmCh)(CO)_2Mo]_2$[5] (where dmCh = η^5-6,6-$Me_2C_6H_5$), and $(\eta^6\text{-}C_6H_6)_2Cr_2(CO)_3$.[6] Although a large number of unsaturated bimetallic compounds has been reported, few have been produced from group 5 metals. Thus we decided to pursue crystallographic studies of bis(arene)tetracarbonyldivanadium complexes, species which are isoelectronic with $Cp_2Cr_2(CO)_4$ and are expected to contain a V–V triple bond.

Calderazzo[7] has reported that vanadium hexacarbonyl reacts with aromatic solvents to produce brown solids from which he isolated complexes of the type $[(\text{arene})V(CO)_4]^+[V(CO)_6]^-$. We later found that treatment with diethyl ether of the solids formed in the reaction of $V(CO)_6$ with benzene produced a brown, crystalline material for which microanalysis was in agreement with that expected for the empirical formula $(C_6H_6)V(CO)_2$. On the basis of infrared spectra (semibridging CO at 1820 cm^{-1}), ^{1}H NMR data, and comparison with the isoelectronic chromium complex, $(C_5H_5)_2Cr_2(CO)_4$, we assigned the following dimeric structure (1)[8] to this compound.



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Preliminary X-ray data on poor quality, twinned crystals, indicated a very short vanadium–vanadium distance, but further information was not forthcoming.[8] All subsequent attempts to grow good quality single crystals of $(C_6H_6)_2V_2(CO)_4$ have failed. We decided, therefore, to synthesize the toluene analogue in the hope that the lowered molecular symmetry would reduce the propensity toward twinning.

Experimental Section

All manipulations were performed using a KSE glovebox or standard Schlenk techniques. Diethyl ether, toluene, and hexanes were distilled under nitrogen from Na/benzophenone. $[Na(diglyme)_2]^+[V(CO)_6]^-$ was purchased from Strem Chemical Co. Infrared spectra were recorded on a Mattson Polaris FT spectrophotometer using 0.5-mm path length NaCl solution cells. ^{1}H NMR spectra were recorded on a Varian VXR-400. $V(CO)_6$ was prepared from $[Na(diglyme)_2]^+[V(CO)_6]^-$, as described previously.[9]

Synthesis of $(C_6H_5CH_3)_2V_2(CO)_4$. In a glovebox, approximately 1 g (4.5 mmol) of $V(CO)_6$ was added to 50 mL of toluene. The resulting solution was stirred magnetically at room temperature. The reaction flask was wrapped in foil to exclude light and vented to allow escape of CO. After 3 days, a brown-green precipitate formed and only a trace of $V(CO)_6$ remained in

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solution. Infrared spectra indicate no other soluble, CO-containing species.

The solution was filtered using a fine glass frit. Treatment of the collected solids with diethyl ether resulted in visible gas evolution and the formation of an intensely colored, brown solution. Removal of the ether by rotary evaporation yielded a brown powder. Chromatography on a Florosil column using an 80/20 mixture of ether/toluene as the eluent caused the reaction mixture to separate into brown and yellow bands. The yellow material has not yet been characterized. The brown band was collected, and the eluent was removed by rotary evaporation, producing black microcrystals (0.09 g, 10%). The complex $(C_6H_5CH_3)_2V_2(CO)_4$ was recrystallized by slow vapor diffusion of hexanes into a toluene solution. The compound is extremely air-sensitive but otherwise appears stable. Well-formed black crystals appeared after approximately 3 weeks. IR (CH_2Cl_2, CO region): 1808 (vs) cm^{-1}. ^1H NMR (C_6D_6, δ): 5.03, m, 3H, (m,p-C_6H_5); 4.42, d, 2H (J_{AB} = 5.6 Hz) (o-C_6H_5); 1.56, s, 3H (CH_3–Ph).

Collection of X-ray Diffraction Data for $(C_6H_5CH_3)_2V_2(CO)_4$. A black crystal of approximate dimensions 0.1 × 0.3 × 0.3 mm was sealed in a thin-walled capillary and aligned on a Siemens R3m/V diffractometer. The observed diffraction symmetry ($2/m$; C_{2h}) and systematic absences($h0l$ for $l = 2n + 1$ and $0k0$ for $k = 2n + 1$) indicated the centrosymmetric space group $P2_1/c$ (C_{2h}^5; No. 14).[10] Two equivalent forms of data, 2999 reflections in all, were collected and corrected for Lorentz and polarization effects. An empirical absorption correction was applied. The data were merged to produce 1426 independent reflections (R_{int} = 2.86% for the averging of the two equivalent data forms).

Solution and Refinement of the Structure. All crystallographic calculations were carried out on a VAX 3100 workstation using the SHELXTL PLUS program package. The analytical scattering factors for neutral atoms were corrected for both the $\Delta f'$ and the $i\Delta f''$ components of anomalous dispersion. The vanadium atom was located by means of a Patterson synthesis; all other non-hydrogen atoms were located from difference-Fourier maps. Hydrogen atoms of the C_6H_5 moiety were placed in calculated positions with d(C–H) = 0.96 Å.[11] Hydrogen atoms of the methyl group were located on a difference-Fourier map and their positions were idealized. Positional and anisotropic thermal parameters of all non-hydrogen atoms were refined, leading to convergence ($(\Delta/\sigma)_{max}$ = 0.021) with R = 7.47%, R_w = 4.68%, and GOF = 1.09 for all 1426 reflections (R = 3.57% and R_w = 3.36% for those 850 data for which $F_0 > 6.0\sigma(F)$). A final difference-Fourier synthesis showed no unusual features, having residual electron density only in the range −0.55 to +0.73 e/Å^3. Details of the data collection and refinement appear in Table I. Final atom coordinates appear in Table II.

Results and Discussion

In contrast to its group 6 neighbors, vanadium has produced few examples of multiple bonds between metal atoms. Although there are several species which have multiple bond character (e.g. $Cp_2V_2(CO)_5$),[12] there are, to our knowledge, only two compounds in which a triple bond between vanadium atoms is suggested. In each case the compound contains ligands which bridge the vanadium–vanadium bond. Although the presence of bridging groups complicates the use of metal–metal distances as a measure of bond multiplicity,[1] a bond order of 3, based primarily on the very short metal–metal distance, has been assigned to $[V(2,6\text{-dimethoxyphenyl})_2]_2$·THF, (d(V–V) = 2.200(2) Å);[13] a bond order of 3 is also assigned to (μ-η^5:η^5-cyclooctatetraene)bis{η^5-cyclopentadienyl)vanadium}[14] (d(V–V) = 2.44 Å). There have been theoretical discussions

Table I. Experimental Data for the X-ray Diffraction Study on $[(\eta^6\text{-}C_6H_5CH_3)V(CO)_2]_2$

Crystal Data	
molecular formula	$C_{18}H_{16}O_4V_2$
color; habit	black plates
cryst size (mm)	0.1 × 0.2 × 0.4
cryst syst	monoclinic
space group	$P2_1/c$
unit cell dimens	
a (Å)	8.302(6)
b (Å)	12.511(7)
c (Å)	8.387(4)
β (deg)	111.43(5)
vol (Å^3)	810.8(8)
Z	2
fw	398.2
density (calc) (Mg/m^3)	1.631
abs coeff (mm^{-1})	1.133
F(000)	404
Data Collection	
diffractometer used	Siemens R3m/V
radiation	Mo Kα (λ = 0.710 73 Å)
temp (K)	298
monochromator	highly oriented graphite crystal
2θ range (deg)	4.5–50.0
scan type	2θ–θ
scan speed (deg/min)	constant; 2.76 in ω
scan range (ω) (deg)	0.60 plus Kα separation
backgd measmt	stationary crystal and stationary counter at beginning and end of scan, each for 25.0% of total scan time
index ranges	$-9 \le h \le 9, 0 \le k \le 14, -9 \le l \le 9$
no. of reflns collcd	2999
no. of ind reflns	1426 (R_{int} = 2.86%)
no. of reflns ($F > 6.0\sigma(F)$)	850
abs Corr	semiempirical
min/max transm	0.7674/0.8253
Solution and Refinement	
system used	Siemens SHELXTL PLUS (VMS)
solution	direct methods
refinement method	full-matrix least squares
quantity minimized	$\sum w(F_0 - F_c)^2$
extinction corr	χ = 0.0006(3), where $F^* = F[1 + 0.002\chi F^2/\sin(2\theta)]^{-1/4}$
hydrogen atoms	riding model, fixed isotropic U
weighting scheme	$w^{-1} = \sigma^2(F) + 0.0003F^2$
no. of params refined	110
final R indices (obs data) (%)	R = 7.47, R_w = 4.68
R indices (6σ data) (%)	R = 3.57, R_w = 3.36
goodness-of-fit	1.09
largest and mean Δ/σ	0.021, 0.004
data-to-parameter ratio	13.0:1
largest diff peak (Å^{-3})	0.73
largest diff hole (Å^{-3})	−0.55

Table II. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for $[(\eta^6\text{-}C_6H_5CH_3)V(CO)_2]_2$

	x	y	z	U(eq)[a]
V(1)	1182(1)	363(1)	1167(1)	31(1)
C(1)	−506(6)	1522(4)	409(6)	46(2)
O(1)	−1376(4)	2258(3)	66(5)	62(1)
C(2)	−1543(5)	−612(3)	908(5)	35(2)
O(2)	−1963(4)	−823(3)	2065(4)	53(1)
C(11)	1942(6)	−1(4)	4054(6)	48(2)
C(12)	2901(6)	−632(3)	3400(5)	38(2)
C(13)	3963(5)	−164(4)	2603(6)	37(2)
C(14)	4059(5)	940(3)	2469(5)	38(2)
C(15)	2993(7)	1554(4)	3041(6)	50(2)
C(16)	1928(7)	1090(5)	3817(6)	57(2)
C(17)	5300(8)	1434(6)	1731(8)	64(3)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

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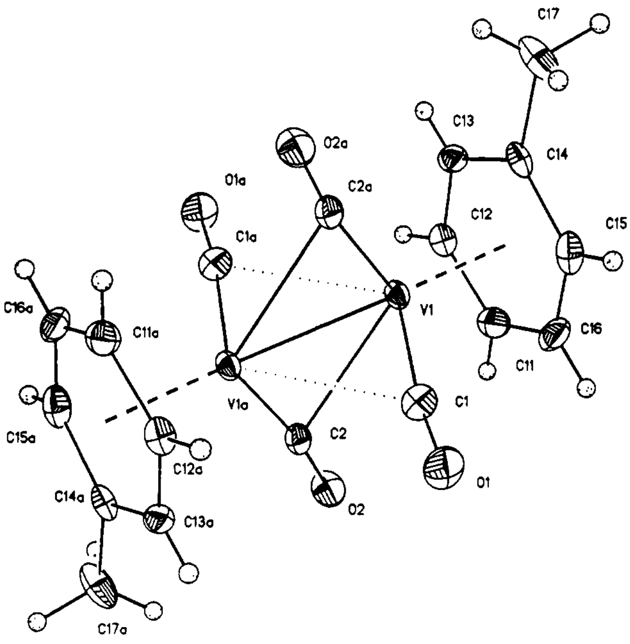

Figure 1. Atomic labeling for $[(\eta^6\text{-}C_6H_5CH_3)V(CO)_2]_2$ (ORTEP2 diagram, 20% probability ellipsoids, with hydrogen atoms artificially reduced).

Table III. Bond Lengths (Å) for $[(\eta^6\text{-}C_6H_5CH_3)V(CO)_2]_2$

V(1)–V(1A)	2.388(2)		
V(1)–C(1)	1.954(5)	V(1)···C(1A)	2.660(5)
V(1)···C(2)	2.509(5)	V(1)–C(2A)	1.896(5)
C(1)–O(1)	1.141(6)	C(2)–O(2)	1.174(7)
V(1)–C(11)	2.314(5)	C(11)–C(12)	1.370(8)
V(1)–C(12)	2.268(4)	C(12)–C(13)	1.413(7)
V(1)–C(13)	2.277(4)	C(13)–C(14)	1.390(7)
V(1)–C(14)	2.347(4)	C(14)–C(15)	1.384(8)
V(1)–C(15)	2.286(5)	C(15)–C(16)	1.401(9)
V(1)–C(16)	2.268(5)	C(16)–C(11)	1.379(8)
		C(14)–C(17)	1.514(9)

Table IV. Interatomic Angles (deg) for $[(\eta^6\text{-}C_6H_5CH_3)V(CO)_2]_2$

C(1)–V(1)–C(2)	79.4(2)	V(1)–C(2)–O(2)	124.6(3)
C(1)–V(1)–V(1A)	74.9(1)	O(2)–C(2)–V(1A)	171.5(3)
C(1)–V(1)–C(2A)	85.1(2)	C(2)–V(1)–V(1A)	45.5(1)
C(2)–V(1)–C(2A)	116.1(1)	V(1)–C(1)–O(1)	173.6(4)
V(1A)–V(1)–C(2A)	70.6(1)	V(1)–C(2)–V(1A)	63.9(1)

concerning the nature of the multiple bonds in these compounds and V–V multiple bonds in general.[15–17]

Molecular Structure of $[(\eta^6\text{-}C_6H_5CH_3)V(CO)_2]_2$. The crystal structure consists of an ordered arrangement of discrete molecular units, which are separated by normal van der Waals' distances. There are no abnormally short intermolecular contacts. The molecular geometry and labeling scheme are shown in Figure 1.

Interatomic distances and angles are listed in Tables III and IV, respectively. The crystallographic asymmetric unit consists of a $(C_6H_5CH_3)V(CO)_2$ unit which is bound to a neighboring unit by a metal–metal interaction whose midpoint is located at the inversion centers of 0, 0, 0 or 0, $^1/_2$, $^1/_2$. Thus, each molecule consists of two halves which are crystallographically interrelated by a center of symmetry.

Each vanadium atom is involved in a V≡V linkage, an $(\eta^6\text{-}C_6H_5CH_3)\rightarrow V$ sytem, two strong V—CO linkages, and two weaker V···CO interactions. Each $(C_6H_5CH_3)V(CO)_2$ unit contains a nearly planar η^6-toluene ligand for which the ring centroid (X1) to vanadium vector forms an angle of 160.6° with the vanadium—vanadium bond. There are two close-to-linear, semibridging carbonyl ligands which are not equivalent. The two carbonyl ligands define an acute angle at the metal center with C(1)—V(1)—C(2A) = 85.1(2)°). Each CO is bent away from the toluene ligand (X1—V(1)—C(1) = 119.5°; X1—V(1)—C(2A) = 121.0°) and over the metal—metal bond (V(1A)—V(1)—C(2A) = 70.6(1)°; V(1A)—V(1)—C(1) = 74.9(1)°). The geometry around each metal center may be considered as a five-legged piano stool or alternatively (considering a single connectivity to the toluene ligand) as a very distorted octahedron.

Toluene Ligand. The toluene ligand is very nearly planar (the average deviation of carbon atoms from the least-squares plane formed by C(11)-C(16) is 0.021 Å); noteworthy, however, is that the greatest deviations occur at the ipso and para positions of the aromatic ring. C(11) lies 0.038 Å from the least-squares plane and C(14) is displaced from the plane by 0.030 Å; both atoms are displaced away from the vanadium atom. Atoms C(12), C(13), C(15), and C(16) are displaced from the least-squares plane by distances ranging from 0.011 to 0.020 Å toward the vanadium atom. This form of "boatlike" distortion has been previously observed, e.g., $(\eta^6\text{-toluene})Mo(CH_3)_2L_2$[18] (L = phosphine) (in which the arene carbons exhibit more pronounced deviations of 0.07 and 0.08 Å from the least-squares plane). The distortion is thought to have both an electronic and steric origin.[19]

The methyl group of the toluene ligand C(17) is displaced by 0.129 Å from the arene ring (away from the vanadium atom). This corresponds to the C(14)–C(17) bond being bent by 4.9° from the plane of the arene ring. The hydrogen atoms of the toluene were not located from difference-Fourier maps but rather were placed in calculated positions. Presumably, they are bent slightly toward the vanadium if this structure is consistent with other similarly bonded species.[19] The vanadium to centroid distance, V(1)–X1, is 1.825 Å. This distance is slightly shorter than the centroid–vanadium distance reported in the $[(\eta^6\text{-}C_6H_2Me_4\text{-}1,2,4,5)V(CO)_4]^+$ cation (1.87 Å),[20] a V(I) species. The distance is significantly longer than that of 1.66 Å reported for $(\eta^6\text{-}C_6H_6)_2V$,[19] consistent with trends seen when sandwich structures are compared to piano stool structures for other metals, e.g. Cr···centroid = 1.606(1) Å in $(\eta^6\text{-}C_6H_6)_2Cr$ vs 1.73 Å in $(\eta^6\text{-}C_6H_6)_2Cr$ vs 1.73 Å in $(\eta^6\text{-}C_6H_6)_2Cr(CO)_3$ or 1.72 Å in $(\eta^6\text{-}C_6H_5CH_3)Cr(CO)_3$.[19]

The C–C bond lengths within the toluene ring are not precisely equivalent. The bonds between the ortho and meta positions are significantly longer than the remaining four C–C bonds (C(12)–C(13) = 1.413(7) Å and C(15)–C(16) = 1.401(9) Å, versus values of 1.370(8) to 1.390(7) Å, average 1.380 Å, for the remaining C–C bonds). The longer bonds are those which are eclipsed (or bisected) by carbonyl ligands when viewed down the metal–metal axis (see Figure 2). The lengthening of arene carbon–carbon bonds which are eclipsed by carbonyls has been reported previously.[19]

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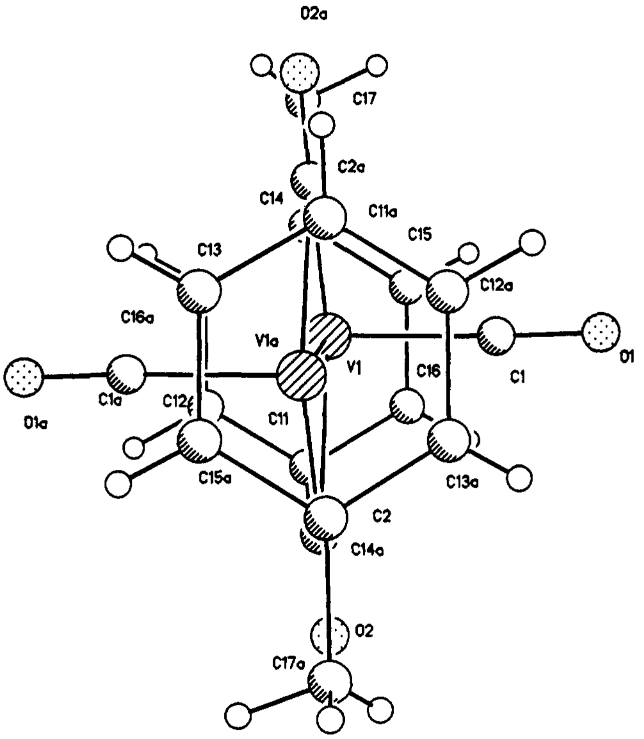

Figure 2. $[(\eta^6\text{-}C_6H_5CH_3)V(CO)_2]_2$ molecule viewed from a direction slightly offset from the V(1A)–V(1) bond and showing the relative orientation of the carbonyl and η^6-toluene ligands.

Table V. Comparison of Metric Parameters for $(\eta^6\text{-}C_6H_5CH_3)_2V_2(CO)_4$ with Those of Isoelectronic $Cp_2Cr_2(CO)_4$ and Related Complexes[a]

complex	M–M (Å)	cent–M–M (deg)	M–C–O (deg)	M–M–CO (deg)
$(\eta^6\text{–}C_6H_5CH_3)_2V_2(CO)_4$	2.388	161	171, 173	71, 75
$Cp_2Cr_2(CO)_4$	2.200	159	171, 173	75, 75
	2.230	165	171, 168	72, 72
$Cp^*{}_2Cr_2(CO)_4$	2.276	159	171, 175	73, 79
$Cp_2Mo_2(CO)_4$	2.448	180	176	67
$(C_6H_6)_2Cr_2(CO)_3$	2.22			

[a] This compilation follows that by: Winter, M. J. *Adv. Organomet. Chem.*, **1989**, *29*, 101.

A well-studied example is $(C_6H_6)Cr(CO)_3$;[21] this molecule has a staggered conformation in the crystalline state and the three eclipsed C–C bonds are significantly longer than the other three C–C bonds (1.423(1) Å as compared to 1.406(1) Å).

The vanadium–carbon bond lengths are not unusual and vary as expected given the elongated boat shape of the toluene. In increasing order they are as follows: V(1)–C(12) = 2.268(4), V(1)–C(16) = 2.268(6), V(1)–C(13) = 2.277(4), V(1)–C(15) = 2.286(5), V(1)–C(11) = 2.314(5), and V(1)–C(14) = 2.347(5) Å.

Carbonyl Ligands. The carbonyl ligands are bent over the metal–metal bond, forming asymmetric bridges.[22] The more strongly bridging exhibits a V(1)–C(2A)–O(2A) angle of 171.5(3)° with V(1)–C(2A) = 1.896(5) Å and V(1A)···C(2A) = 2.509(5) Å. The C(2A)–O(2A) distance is 1.174(7) Å. The remaining carbonyl is associated with the angle V(1)–C(1)–O(1) = 173.6(4) Å and the distances V(1)–C(1) = 1.954(5) Å and V(1A)···C(1) = 2.660(5) Å. The C(1)–O(1) distance is 1.141(6) Å. Using Curtis' "asymmetry parameter", α (where $\alpha = (d_2 - d_1)$; d_2 is the longer M–C distance, d_1 is the shorter; $\alpha = 0$ for a symmetric bridge), to describe the semibridging nature[4] of the carbonyl ligands yields α(C(1)–O(1)) = 0.36 and α(C(2A)–O(2A)) = 0.32. These values are similar to those found for $Cp_2Cr_2(CO)_4$ (0.29[4] and $Cp_2V_2(CO)_5$ (0.24).[23] The origin of close-to-linear semibridging carbonyl ligands has been attributed to both steric and electronic influences.[3,4,23,24] It is noteworthy that in this structure the more strongly bridging carbonyl ligand (C(2A)–O(2A)) is in a position eclipsing the methyl group of the toluene ligand. Each carbonyl ligand and its symmetry related carbonyl ligand necessarily generate a perfect plane. The two such planes are nearly perpendicular to each other, forming an angle of 89.6°. One of these planes bisects the two long arene C–C bonds (vide supra), while the other eclipses the ipso and para carbons of the toluene ligand. The eclipsing of electron-donating substituents on arenes by carbonyl ligands has been widely discussed in "piano stool" complexes and has been explained by the increased negative charge at the ortho and para positions of the arene.[19] The explanations of the nonequivalence of the carbonyl ligands may be similar to those invoked for $[(dmCh)(CO)_2Mo]_2$,[5] a complex which contains both terminal and semibridging carbonyl ligands. C(2A)–O(2A) is essentially trans to the less strongly bound carbon atoms of the toluene ligand and so experiences greater σ-bonding and π-back-bonding, causing a more pronounced bridge.[22] Additionally, steric effects would favor a bridging mode since the ligand C(2A)–O(2A) eclipses the methyl group of the toluene ligand.

Vanadium–Vanadium Bond. The V–V bond length is 2.388(2) Å. This is considerably longer (0.188 Å) than that observed for $V_2(DMP)_2$ (2.200(2) Å; DMP = 2,6-dimethoxyphenyl);[13] it is, however, shorter (0.051 Å) than that reported for (μ-COT)V_2Cp_2 (2.439(1) Å; COT = cyclooctatetrene). Given the lower oxidation state of the vanadium atoms in $[(\eta^6\text{-}C_6H_5CH_3)V(CO)_2]_2$, a longer bond is expected; however, it has been noted that there is not a strict correlation between bond length and bond order.[1] Coordination number, oxidation state, and the presence and nature of bridging ligands all dramatically influence metal–metal bond length. Overall, the structure of $[(\eta^6\text{-}C_6H_5CH_3)V(CO)_2]_2$ is very similar to that of the isoelectronic species $Cp_2Cr_2(CO)_4$. Table V compares some significant parameters in these and related molecules. We are pursuing studies of the reactivity of $(CH_3C_6H_5)_2V_2(CO)_4$, which we expect to parallel that of $Cp_2Cr_2(CO)_4$.

Acknowledgment. T.S.J. wishes to thank the Research Corp. (Award D-152) and the National Science Foundation for a Research Opportunity Award (Grant No. CHE-9015897). The purchase of a Siemens R3m/V diffractometer was made possible by a grant from the Chemical Instrumentation Program of the National Science Foundation (Grant No. 89-13733).

Supplementary Material Available: Listings of anisotropic thermal parameters and H-atom positions (1 page). Ordering information is given on any current masthead page.

OM920532R

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