(on the high side) by up to 40% for χ_i and 20% for Δa. To the extent that these errors exist, our conclusion regarding the very close structural similarity between MLCT singlet and triplet excited states will need to be modified.

Concluding Remarks

Despite the caveats, the preresonance technique in combination with the time-dependent analysis appears to provide a powerful and reliable approach to charge-transfer structural measurements. Normal-coordinate distortions derived from preresonance Raman agree reasonably well with those that can be inferred from other methods. For the $Ru(NH_3)_4(bpy)^{2+}$ case, the precision and sensitivity are nothing short of remarkable. Separate studies with $(NC)_5Ru(CN)Ru(NH_3)_5^-$ tend to reinforce these conclusions.[24] Clearly, it will be necessary, however, to examine additional systems before the hoped-for generality of the new approach can be firmly established. Of particular interest in such an effort will be studies of symmetrical mixed-valence systems, outer-sphere (ion-paired) systems, and systems featuring spin-orbit allowed triplet transitions.

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Alkoxy and Aryloxy Derivatives of (Pentamethylcyclopentadienyl)ruthenium. X-ray Crystal Structures of $[(\eta^5\text{-}C_5Me_5)Ru(\mu\text{-}OMe)]_2$, $[(\eta^5\text{-}C_5Me_5)(CO)Ru(\mu\text{-}OEt)]_2$, and $(\eta^5\text{-}C_5Me_5)Ru(\eta^5\text{-}2,6\text{-}{}^tBu_2C_6H_3O)$ and Molecular Orbital Analysis of $[(\eta^5\text{-}C_5H_5)Ru(\mu\text{-}OMe)]_2$

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Abstract: Ruthenium methoxide dimer $[Cp^*Ru(\mu\text{-}OMe)]_2$ (**1**, $Cp^* = \eta^5\text{-}C_5Me_5$) is produced by reaction of $[Cp^*RuCl_2]_2$ or $Cp^*RuCl_2(pyr)$ with NaOMe in methanol or by reaction of $Cp^*(PCy_3)RuCl$ with LiOMe in methanol. Compound **1** is best prepared in pure form (in 84% yield) by reaction of the tetranuclear cluster $[Cp^*RuCl]_4$ with 4 equiv of LiOMe in methanol. An X-ray crystallography study revealed that **1** has a dimeric structure with bridging methoxy ligands. The dimer is folded along the O⋯O axis, with a fold angle of 124.3°. Complex **1** crystallizes in the monoclinic space group $C2/c$ with $a = 15.821$ (8) Å, $b = 6.659$ (3) Å, $c = 21.51$ (1) Å, $\beta = 103.32$ (3)°, $Z = 8$, $V = 2205$ (2) Å^3, and $R_F = 2.17\%$. Ethoxide dimer $[Cp^*Ru(\mu\text{-}OEt)]_2$ (**2**), prepared from $[Cp^*RuCl]_4$ and LiOEt in ethanol, combines with carbon monoxide to form the adduct $[Cp^*(CO)Ru(\mu\text{-}OEt)]_2$ (**3**). Compound **3** crystallizes in tetragonal space group $P\bar{4}2_1c$ with $a = 26.22$ (2) Å, $c = 8.709$ (5) Å, $Z = 8$, $V = 5986$ (6) Å^3, and $R_F = 5.68\%$. An analogous adduct of **1**, $[Cp^*(CO)Ru(\mu\text{-}OMe)]_2$ (**4**), is observed by ^1H NMR but is unstable in solution, eventually decomposing to $[Cp^*Ru(CO)(\mu\text{-}CO)]_2$. Reaction of $LiO\text{-}2,6\text{-}{}^tBu_2C_6H_3$ with $[Cp^*RuCl]_4$ in toluene gives the η^5-oxocyclohexadienyl complex $Cp^*Ru(\eta^5\text{-}2,6\text{-}{}^tBu_2C_6H_3O)$ (**5**), which was crystallograpically characterized. Compound **5** crystallizes in space group $P2_1/n$ with $a = 12.203$ (3) Å, $b = 10.028$ (3) Å, $c = 18.414$ (4) Å, $\beta = 99.11$ (2)°, $Z = 4$, $V = 2225$ (1) Å^3, and $R_F = 3.03\%$. The electronic structure of an analogue of **1**, $[CpRu(\mu\text{-}OMe)]_2$ (**1′**, $Cp = \eta^5\text{-}C_5H_5$), was investigated by using Fenske–Hall molecular orbital calculations. These studies show that the folded C_{2v} structure of **1** is due to electronic preferences of the bridging alkoxide ligands. Upon folding, lone-pair orbitals of appropriate symmetry on the bridging oxygen atoms maximize their donation into the unoccupied Ru orbitals.

Recent interest in the preparation and study of noble metal (Ru, Os, Rh, Ir, Pd, and Pt) alkoxide and aryl oxide derivatives stems from the paucity of examples and what appears to be an inherently rich reaction chemistry.[1] Currently alkoxide or aryl oxide derivatives of all of these metals have been described, but there are relatively few investigations of the chemistry of these species.[1-12,15-17] In an attempt to obtain a ruthenium alkoxide, Wilkinson and co-workers studied the reaction of $RuHCl(PPh_3)_3$ with sodium methoxide. This investigation showed that methoxide complexes in this system are thermally unstable and that decomposition products include formaldehyde, formyl, and carbonyl derivatives.[2]

A number of bonding modes for alkoxy and aryloxy ligands on ruthenium have now been identified. Yamamoto prepared the terminal alkoxide $RuH[OCH(CF_3)Ph](PPh_3)_3$ by insertion of trifluoromethyl phenyl ketone into the Ru–H bond of RuH_2-

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$(PPh_3)_4$.[3] Other terminal Ru–OR derivatives are the aryl oxide $Ru(CO)(PPh_3)_2(\eta^2\text{-}OC_6H_4NO)(m\text{-}OC_6H_4NO_2)$,[4] porphyrin complexes such as Ru(OEP)(NO)(OMe),[5a] $[Ru(TPP)(p\text{-}OC_6H_4Me)]_2O$[5b] and Ru(TPP)(OEt)(ETOH)·2EtOH,[5b] and the ruthenium(III) alkoxides *trans*-$[RuCl(OR)(pyr)_4]^+$ (R = Me, Et, ^{n}Pr, and ^{i}Pr).[6] Bridging OR groups are observed in the diruthenium complexes $[(\eta^6\text{-arene})Ru(\mu\text{-}OR)_3Ru(\eta^6\text{-arene})]^+$,[7] $[(^tBuNC)_4Ru(\mu\text{-}OR)_2Ru(CN^tBu)_4]^{2+}$,[8] and $[(^tBu_3P)(CO)_2Ru(\mu\text{-}OMe)]_2$[9] and in ruthenium clusters.[10] Aryl oxide ligands have also been found to π-bond to ruthenium through the aromatic ring.[11] Thus, the hydride $RuH_2(PPh_3)_4$ reacts with phenol to afford $RuH(\eta^5\text{-}C_6H_5O)(PPh_3)_2$, which was obtained as the unsolvated complex and in various solvated forms.[11a] Bennett and Matheson have reported $[Ru(\eta^6\text{-}C_6H_3Me_3)(\eta^6\text{-}C_6H_5OH)](BF_4)_2$, which is readily deprotonated to $[Ru(\eta^6\text{-}C_6H_3Me_3)(\eta^6\text{-}C_6H_5O)]BF_4$.[11b] Finally, in a variety of complexes, alkoxy and aryloxy Ru–O–C linkages are present as part of a chelating ligand.[11d,12]

Our interest in reactive late-transition-metal alkoxide and aryl oxide derivatives has led us to attempt syntheses of electron-deficient Ru–OR complexes. The pentamethylcyclopentadienyl derivatives $[Cp^*RuCl]_4$ and $Cp^*Ru(PR_3)Cl$ ($Cp^* = \eta^5\text{-}C_5Me_5$; R = ^{i}Pr, cyclohexyl) seemed to be promising starting materials for this work, since these species are convenient sources of Cp^*Ru[13] and $Cp^*(PR_3)Ru$[14] fragments. Here we report methoxy, ethoxy, and 2,6-di(*tert*-butyl)phenoxy derivatives derived from these systems and the crystal structures of $[Cp^*Ru(\mu\text{-}OMe)]_2$ (**1**), $[Cp^*(CO)Ru(\mu\text{-}OEt)]_2$ (**3**), and $Cp^*Ru(\eta^5\text{-}2,6\text{-}^tBu_2C_6H_3O)$ (**5**). In addition, the unusual folded structure of **1** has been examined via molecular orbital calculations. The pentamethylcyclopentadienyl derivatives $Cp^*(PMe_3)_2RuOPh$[15] and $Cp^*(CO)_2RuOMe$[16] have previously been reported. Recently, Koelle and Kossakowski described an alternate synthesis of $[Cp^*Ru(\mu\text{-}OMe)]_2$ and conversions of this complex to $[Cp^*Ru(\mu\text{-}OMe)]_2(\mu\text{-}Ph_2PCH_2PPh_2)$, $Cp^*Ru(Ph_2PCH_2PPh_2)OMe$, and $Cp^*Ru(bpy)OMe$.[17]

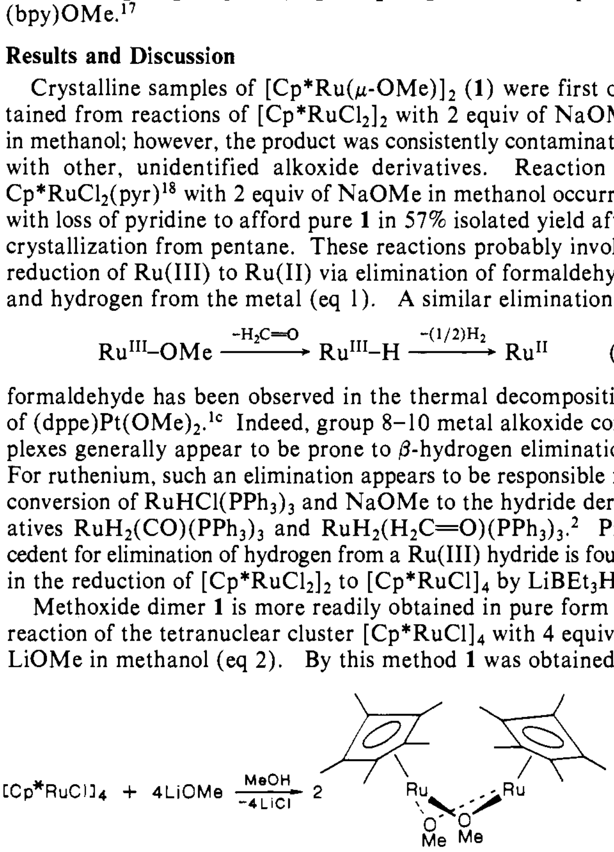
Results and Discussion

Crystalline samples of $[Cp^*Ru(\mu\text{-}OMe)]_2$ (**1**) were first obtained from reactions of $[Cp^*RuCl_2]_2$ with 2 equiv of NaOMe in methanol; however, the product was consistently contaminated with other, unidentified alkoxide derivatives. Reaction of $Cp^*RuCl_2(pyr)$[18] with 2 equiv of NaOMe in methanol occurred with loss of pyridine to afford pure **1** in 57% isolated yield after crystallization from pentane. These reactions probably involve reduction of Ru(III) to Ru(II) via elimination of formaldehyde and hydrogen from the metal (eq 1). A similar elimination of

$$Ru^{III}\text{–}OMe \xrightarrow{-H_2C=O} Ru^{III}\text{–}H \xrightarrow{-(1/2)H_2} Ru^{II} \qquad (1)$$

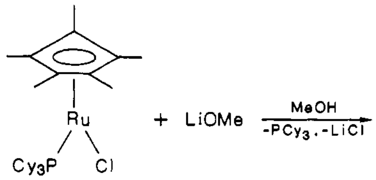
formaldehyde has been observed in the thermal decomposition of $(dppe)Pt(OMe)_2$.[1c] Indeed, group 8–10 metal alkoxide complexes generally appear to be prone to β-hydrogen elimination. For ruthenium, such an elimination appears to be responsible for conversion of $RuHCl(PPh_3)_3$ and NaOMe to the hydride derivatives $RuH_2(CO)(PPh_3)_3$ and $RuH_2(H_2C{=}O)(PPh_3)_3$.[2] Precedent for elimination of hydrogen from a Ru(III) hydride is found in the reduction of $[Cp^*RuCl_2]_2$ to $[Cp^*RuCl]_4$ by $LiBEt_3H$.[13]

Methoxide dimer **1** is more readily obtained in pure form by reaction of the tetranuclear cluster $[Cp^*RuCl]_4$ with 4 equiv of LiOMe in methanol (eq 2). By this method **1** was obtained in 84% yield as maroon crystals from diethyl ether. The structure of **1** was determined by an X-ray crystal structure determination (vide infra). Compound **1** is also formed in the reaction of 16-electron complex $Cp^*Ru(PCy_3)Cl$ with LiOMe (eq 3). In the latter reaction products of β-H elimination, e.g., $Cp^*Ru(PCy_3)(H_2C{=}O)(H)$, were not observed. Thus, both $[Cp^*RuCl]_4$ and $Cp^*Ru(PCy_3)Cl$ function as sources of "Cp*RuCl" in formation of these alkoxide derivatives. The ethoxide analogue $[Cp^*Ru(\mu\text{-}OEt)]_2$ (**2**) was prepared by the method of eq 2 from $[Cp^*RuCl]_4$ and LiOEt. On the basis of a molecular weight determination (cryoscopy in dichloromethane), this complex is dimeric and presumably has a structure analogous to that for **1**.



1

(2)



(3)

On the basis of the crystal structure of **1** and molecular orbital calculations (vide infra), which suggest that the ruthenium atoms are coordinatively unsaturated, we expected **1** and **2** to be reactive toward donor species. Indeed, reaction of 2 equiv of ethanol with **1** (benzene-d_6, 25 °C) results in rapid establishment of an equilibrium that interconverts **1** and **2** (eq 4). The methoxide

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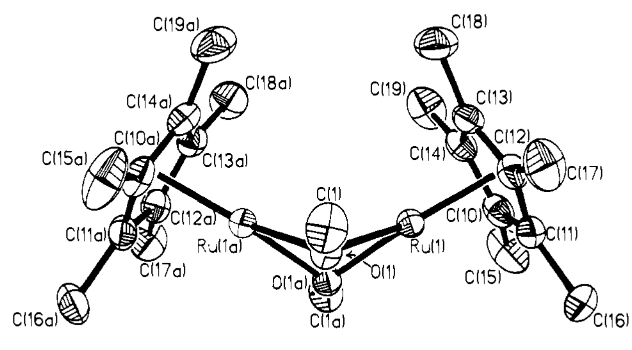
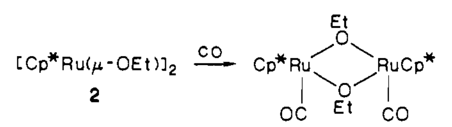


Figure 1. ORTEP view of 1 with atom-labeling scheme.

complex is favored in this equilibrium, as shown by the equilibrium constant of 0.3, obtained by integration of ^1H NMR spectra.

$$\underset{\mathbf{1}}{[Cp^*Ru(\mu\text{-}OMe)]_2} + 2EtOH \xrightleftharpoons{K=0.3} \underset{\mathbf{2}}{[Cp^*Ru(\mu\text{-}OEt)]_2} + 2MeOH \quad (4)$$

Pentane solutions of **2** react with carbon monoxide (20 psi) to form the yellow, crystalline adduct $[Cp^*(CO)Ru(\mu\text{-}OEt)]_2$ (**3**), which was obtained in 55% yield after crystallization from pentane (eq 5). The chemical shift for the methylene protons of the ethoxy



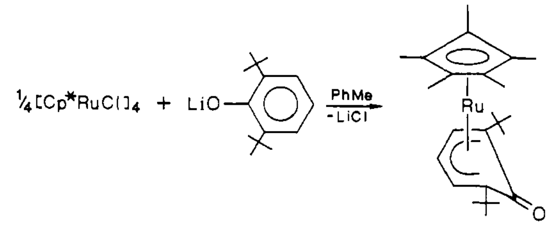
2

3

(5)

ligands in **3**, δ 3.36, is at significantly higher field than the analogous shift for the methylene protons for **2**, at δ 4.99. The structure of **3** was determined unambiguously with X-ray crystallography (vide infra). As reported previously by others,[17] we observe that methoxide **1** reacts with carbon monoxide to give the ruthenium(I) dimer $[Cp^*Ru(CO)(\mu\text{-}CO)]_2$. Monitoring this reaction by ^1H NMR in benzene-d_6 using 1 atm of CO revealed a quantitative conversion that proceeds through an intermediate species **4**. On the basis of the chemical shift of the methoxy protons for this intermediate (δ 3.53), we suggest that it has a structure analogous to **3**, $[Cp^*(CO)Ru(\mu\text{-}OMe)]_2$. Koelle and Kossakowski have also reported a diphosphine adduct analogous to **4**, the dimer $[Cp^*Ru(\mu\text{-}OMe)]_2(\mu\text{-}Ph_2PCH_2PPh_2)$.[17]

In attempts to stabilize a monomeric structure, we have carried out reactions between $[Cp^*RuCl]_4$ and bulky alkoxide reagents. The reaction with LiO-2,6-$^tBu_2C_6H_3$ is shown in eq 6. Yellow



(6)

5

crystals of **5** are readily obtained by slow cooling of concentrated pentane solutions. The η^5-oxocyclohexadienyl ligand was characterized spectroscopically and by X-ray crystallography (vide infra). The large upfield shift of the ring protons of the η^5-2,6-$^tBu_2C_6H_3O$ ligand (to 3.87 and 4.85 ppm) upon coordination to ruthenium is consistent with observations for related ruthenium complexes.[11] An intense infrared stretching frequency at 1542 cm^{-1}, attributed to the carbonyl group of **5**, is similar to corresponding values reported for $RuH(\eta^5\text{-}C_6H_5O)(PPh_3)_2$ (1577 cm^{-1})[11a] and $Rh(\eta^5\text{-}2,6\text{-}^tBu_2\text{-}4\text{-}MeC_6H_2O)(PPh_3)_2$ (1548 cm^{-1}).[19]

Table I. Crystal, Data Collection, and Refinement Parameters for **1**, **3**, and **5**

	1	3	5
	(a) Crystal Parameters		
formula	$C_{11}H_{18}ORu$	$C_{26}H_{40}O_4Ru_2$	$C_{24}H_{36}ORu$
crystal size, mm	0.15 × 0.30 × 0.40	0.25 × 0.30 × 0.40	0.30 × 0.40 × 0.40
crystal system	monoclinic	tetragonal	monoclinic
space group	$C2/c$	$P\bar{4}2_1c$	$P2_1/n$
a, Å	15.821 (8)	26.22 (2)	12.203 (3)
b, Å	6.659 (3)	26.22 (2)	10.028 (3)
c, Å	21.51 (1)	8.709 (5)	18.414 (4)
β, deg	103.32 (3)		99.11 (2)
V, Å^3	2205 (2)	5986 (6)	2225 (1)
Z	8	8	4
ρ(calcd), g cm^{-3}	1.61	1.37	1.32
μ, mm^{-1} (Mo Kα)	1.36	1.01	0.70
F(000)	1088	2528	928
	(b) Data Collection		
diffractometer	Nicolet R3m/V	Nicolet R3m/V	Nicolet R3m/V
radiation	Mo Kα (λ = 0.71073 Å)	Mo Kα (λ = 0.71073 Å)	Mo Kα (λ = 0.71073 Å)
temp, °C	23	23	23
monochromator	ordered graphite crystal	ordered graphite crystal	ordered graphite crystal
scan type	$\theta/2\theta$	$\theta/2\theta$	$\theta/2\theta$
2θ scan range, deg	$3 \le 2\theta \le 48$	$3 \le 2\theta \le 45$	$3 \le 2\theta \le 55$
scan speed, deg/min	variable, 1.5–15	variable, 1.5–15	variable, 1.5–15
index ranges	$0 \le h \le 18$ $0 \le k \le 7$ $-24 \le l \le 23$	$0 \le h \le 28$ $0 \le k \le 28$ $0 \le l \le 9$	$0 \le h \le 14$ $0 \le k \le 11$ $-21 \le l \le 21$
std rflns	3 std/50 rflns	3 std/75 rflns	3 std/66 rflns
rflns collected	3963	4416	5683
unique rflns	1739 (R_{int} = 0.84%)	2219 (R_{int} = 2.20%)	5141 (R_{int} = 1.29%)
obsd rflns	1544 ($F > 6.0\sigma(F)$)	1736 ($F > 6.0\sigma(F)$)	3917 ($F > 6.0\sigma(F)$)
absorption corr	semiempirical	semiempirical	semiempirical
min/max trans	0.752/1.000	0.515/0.540	0.550/0.570
	(c) Refinement		
R_F, %	2.17	5.68	3.03
R_{wF}, %	2.92	8.00	3.90
GOF	1.85	1.58	1.76
largest Δ/σ	0.003	0.004	0.001
data/param	13.0	11.7	15.7
largest $\Delta(\rho)$, e/Å^3	0.42	0.77	0.41

Table II. Selected Bond Distances (Å) and Angles (Deg) for **1**[a]

(a) Bond Distances			
Ru(1)–Ru(1a)	2.961 (1)	Ru(1)–CNT	1.748
Ru(1)–O(1)	2.070 (2)	O(1)–C(1)	1.389 (4)
Ru(1)–O(1a)	2.065 (2)		
(b) Bond Angles			
Ru(1a)–Ru(1)–O(1)	44.2 (1)	Ru(1a)–Ru(1)–CNT	150.0
Ru(1a)–Ru(1)–O(1a)	44.3 (1)	Ru(1)–O(1)–C(1)	124.3 (2)
O(1)–Ru(1)–O(1a)	71.8 (1)	Ru(1a)–O(1)–C(1)	125.1 (2)
O(1)–Ru(1)–CNT	144.3	Ru(1)–O(1)–Ru(1a)	91.5 (1)
O(1a)–Ru(1)–CNT	143.7		

[a] CNT denotes the centroid of the η^5-C_5Me_5 ring.

Description of the Structure of 1. The structure of **1** is depicted in Figure 1 with the atom-labeling scheme. Crystal and data collection parameters for all three structure determinations are summarized in Table I. Relevant geometrical parameters for **1** are listed in Table II. The structure of **1** consists of discrete dimers with no abnormally short intermolecular contacts. The molecule possesses a C_2 axis perpendicular to the ruthenium–ruthenium vector and relates the two Cp*RuOMe units of the dimer. In addition, there are approximate (noncrystallographic) mirror planes that bisect the dimer, one containing the bridging methoxide ligands and the other containing the two ruthenium atoms (Figure 2).

Interestingly, **1** adopts a dimeric structure rather than a tetrameric, distorted cube analogous to $[Cp^*RuCl]_4$[13] and $[(\eta^6\text{-}C_6H_6)Ru(OH)]_4[SO_4]_2\cdot 12H_2O$.[20] This could be for steric reasons,

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(20) Gould, R. O.; Jones, C. L.; Robertson, D. R.; Stephenson, T. A. *J. Chem. Soc., Chem. Commun.* **1977**, 222.

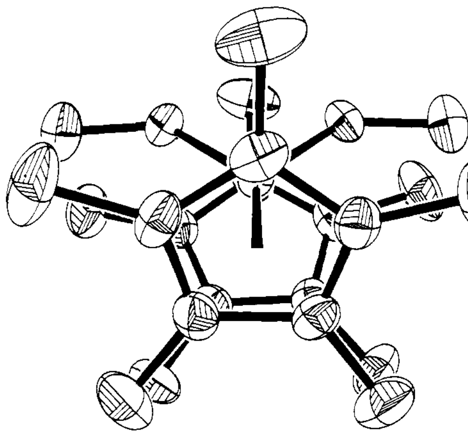

Figure 2. View of **1** down the Ru–Ru vector.

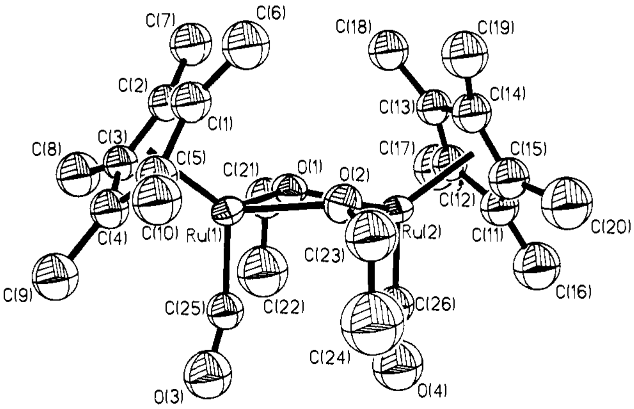

Figure 3. ORTEP view of **3** with atom-labeling scheme.

since the Cp* ligand may be too large to participate in such a tetrameric structure with the relatively small oxygen donors as bridging groups. The two independent Ru-O distances of 2.070 (2) and 2.065 (2) Å are quite similar to the observed average Ru-O distance in $[(\eta^6\text{-}C_6H_6)Ru(\mu\text{-}OMe)_3Ru(\eta^6\text{-}C_6H_6)][BPh_4]$, 2.060 (8) Å.[7b] Also, the Ru–O–Ru angle at the bridging oxygen atoms, 91.5 (1)°, is consistent with values reported for the latter compound (93.9 (3), 94.6 (3), and 92.6 (3)°). The O(1)···O(1a) distance of 2.43 Å, like the comparable distance in $[(\eta^6\text{-}C_6H_6)Ru(OH)]_4[SO_4]_2\cdot 12H_2O$ (2.62 Å),[20] is less than the O···O van der Waals contact distance of 2.80 Å.[21]

The coordination environment about the ruthenium center is very nearly trigonal planar, if the Cp* ligand is considered to occupy a single coordination site. The Ru_2O_2 core is not planar but is bent in a butterfly fashion resulting in a fold angle of 124.3° (angle between the two RuO_2 planes). This bending results in a Ru-Ru separation of 2.961 (1) Å, which is comparable to the nonbonding distance observed in $[(\eta^6\text{-}C_6H_6)Ru(\mu\text{-}OMe)_3Ru(\eta^6\text{-}C_6H_6)][BPh_4]$, 3.005 (2) Å.[7b] This distance is significantly longer than typical Ru-Ru single bonds, e.g., 2.738 (4) Å in $Ru_2O_2(CH_2SiMe_3)_6$[22] and 2.85–2.86 Å in $Ru_3(CO)_{12}$.[23] Bending of the molecule results in rather close contacts between methyl groups of the two Cp* ligands, as evidenced by the C(18)–C(19a) and C(19)–C(18a) separations of 3.83 Å, which are less than the van der Waals contact distance of 4.0 Å.[21] Overall, the geometry of **1** resembles that previously reported for $[(CO)_2Rh(\mu\text{-}Cl)]_2$, which is bent along the Cl–Cl axis (fold angle 124°) with a Rh-Rh distance of 3.12 Å.[24]

Table III. Selected Bond Distances (Å) and Bond Angles (Deg) for **3**[a]

(a) Bond Distances			
Ru(1)–O(1)	2.10 (1)	Ru(2)–CNT(2)	1.86
Ru(1)–O(2)	2.12 (1)	Ru(2)–C(11)	2.19 (2)
Ru(1)–C(25)	1.82 (2)	Ru(2)–C(12)	2.19 (2)
Ru(1)–CNT(1)	1.86	Ru(2)–C(13)	2.26 (2)
Ru(1)–C(1)	2.31 (2)	Ru(2)–C(14)	2.29 (2)
Ru(1)–C(2)	2.26 (2)	Ru(2)–C(15)	2.18 (2)
Ru(1)–C(3)	2.20 (2)	O(3)–C(25)	1.20 (2)
Ru(1)–C(4)	2.18 (2)	O(4)–C(26)	1.20 (3)
Ru(1)–C(5)	2.20 (2)	O(1)–C(21)	1.44 (2)
Ru(2)–O(1)	2.12 (1)	C(21)–C(22)	1.50 (4)
Ru(2)–O(2)	2.12 (1)	O(2)–C(23)	1.37 (3)
Ru(2)–C(26)	1.82 (2)	C(23)–C(24)	1.46 (4)
(b) Bond Angles			
O(1)–Ru(1)–O(2)	72.2 (4)	C(26)–Ru(2)–CNT(2)	123.8
O(1)–Ru(1)–C(25)	97.4 (6)	Ru(1)–O(1)–Ru(2)	106.6 (5)
O(1)–Ru(1)–CNT(1)	124.8	Ru(1)–O(1)–C(21)	126 (1)
O(2)–Ru(1)–C(25)	96.6 (7)	Ru(2)–O(1)–C(21)	120 (1)
O(2)–Ru(1)–CNT(1)	125.5	Ru(1)–O(2)–Ru(2)	105.9 (5)
C(25)–Ru(1)–CNT(1)	125.9	Ru(1)–O(2)–C(23)	120 (1)
O(1)–Ru(2)–O(2)	71.8 (4)	Ru(2)–O(2)–C(23)	124 (1)
O(1)–Ru(2)–C(26)	98.3 (7)	O(1)–C(21)–C(22)	108 (2)
O(1)–Ru(2)–CNT(2)	127.0	O(2)–C(23)–C(24)	120 (2)
O(2)–Ru(2)–C(26)	97.3 (7)	Ru(1)–C(25)–O(3)	165 (2)
O(2)–Ru(2)–CNT(2)	125.0	Ru(2)–C(26)–O(4)	172 (2)

[a] CNT denotes the centroid of the $\eta^5\text{-}C_5Me_5$ ring.

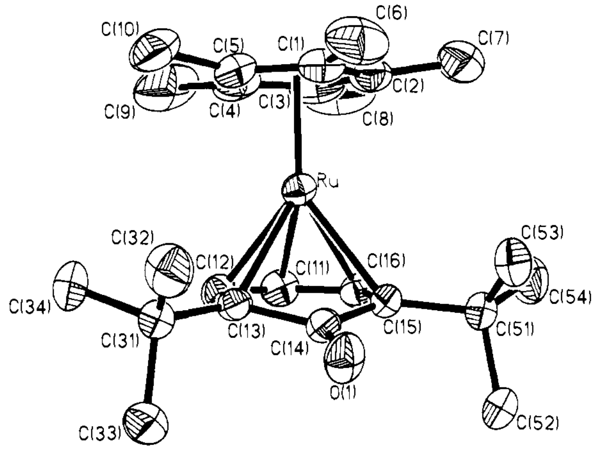

Figure 4. ORTEP view of **5** with atom-labeling scheme.

Description of the Structure of 3. An ORTEP view of **3** is given in Figure 3, and a list of distances and angles in the molecule is given in Table III. The dimers are bisected by two approximate (noncrystallographic) mirror planes, one containing the ruthenium atoms and carbonyl ligands, and the other containing the ethoxy groups. The Ru_2O_2 core of **3** is puckered by 162.5° (angle between the two RuO_2 planes) and is therefore more "flattened" than the Ru_2O_2 core of **1**. In contrast to **1**, bending at the oxygen–oxygen vector is in the direction of the Cp* ligands. This geometry results in Ru-O-Ru angles, 106.6 (5) and 105.9 (5)°, that are larger than the one found in **1**, 91.5 (1)°. However, the O–Ru–O angles found in **3**, 71.8 (4) and 72.2 (4)°, are not significantly different from the value of 71.8 (1)° observed for **1**. The Ru-Ru separation (3.39 Å) is too long to be consistent with the presence of a Ru-Ru bond. The coordination geometry at each ruthenium may be described as a somewhat distorted "three-legged piano stool" (see angles at Ru(1) and Ru(2)). There appears to be no significant steric interaction between Cp* ligands of the dimer, since the smallest carbon-carbon separation involving these Cp* ligands is 4.15 Å, between C(19) and C(6). As might be expected based on differences in coordination numbers, the Ru-O distances in **3**, 2.10 (1)–2.12 (1) Å, are slightly larger than the corresponding distances in **1**. Also consistent with the higher coordination number in **3**, the Ru-Cp*(centroid) distance (1.86 Å) is greater than the analogous distance in **1** (1.75 Å).

Description of the Structure of 5. Compound **5** (Figure 4) is an 18-electron ruthenium sandwich complex containing an η^5-oxocyclohexadienyl ligand. The molecule possesses an approximate

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(22) Tooze, R. P.; Wilkinson, G.; Motevalli, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1986**, 2711.

(23) Churchill, M. R.; Hollander, F. J.; Hutchinson, J. P. *Inorg. Chem.* **1977**, *16*, 2655.

(24) (a) Dahl, L. F.; Martell, C.; Wampler, D. L. *J. Am. Chem. Soc.* **1961**, *83*, 1761. (b) Norman, J. G., Jr.; Gmur, D. J. *Ibid.* **1977**, *99*, 1446.

Table IV. Selected Bond Distances (Å) and Bond Angles (Deg) for **5**[a]

(a) Bond Distances

Ru–C(11)	2.183 (3)	Ru–CNT	1.833	C(13)–C(14)	1.471 (4)
Ru–C(12)	2.192 (3)	O(1)–C(14)	1.256 (4)	C(14)–C(15)	1.463 (4)
Ru–C(13)	2.295 (3)	C(11)–C(12)	1.397 (5)	C(15)–C(16)	1.418 (4)
Ru–C(15)	2.300 (3)	C(11)–C(16)	1.404 (5)	C(13)–C(31)	1.548 (4)
Ru–C(16)	2.196 (3)	C(12)–C(13)	1.418 (4)	C(15)–C(51)	1.535 (4)

(b) Bond Angles

C(13)–C(14)–O(1)	122.3 (3)	C(16)–C(15)–C(14)	119.5 (3)
C(15)–C(14)–O(1)	122.6 (3)	C(16)–C(15)–C(51)	119.9 (3)
C(13)–C(14)–C(15)	114.8 (3)	C(14)–C(15)–C(51)	118.8 (3)
C(12)–C(11)–C(16)	119.2 (3)	C(11)–Ru–CNT	137.2
C(11)–C(12)–C(13)	121.4 (3)	C(12)–Ru–CNT	139.0
C(11)–C(16)–C(15)	121.6 (3)	C(13)–Ru–CNT	142.8
C(12)–C(13)–C(14)	119.7 (3)	C(15)–Ru–CNT	142.8
C(12)–C(13)–C(31)	120.1 (3)	C(16)–Ru–CNT	139.3
C(14)–C(13)–C(31)	118.5 (3)		

[a] CNT denotes the centroid of the η^5-C_5Me_5 ring.

mirror plane through Ru, O(1), C(1), C(6), C(11), and C(14). The mean deviation from a least-squares plane calculated for these atoms is 0.04 Å, with the maximum deviation being 0.08 Å for C(6).

The pentadienyl nature of the 2,6-${}^tBu_2C_6H_3O$ group is clearly demonstrated by the bonding parameters (Table IV). Generally, distances and angles for the η^5-2,6-${}^tBu_2C_6H_3O$ ligand of **5** are comparable to corresponding parameters in Rh(η^5-2,6-${}^tBu_2$-4-MeC_6H_2O)$(PPh_3)_2$.[19] Ring carbon–carbon distances within the pentadienyl fragment are shorter (1.397 (5)–1.418 (4) Å) than the carbon–carbon bonds to C(14) (1.463 (4), 1.471 (4) Å). The C(14)–O distance of 1.256 (4) is clearly consistent with double-bond character and is similar to analogous distances reported for Rh(η^5-2,6-${}^tBu_2$-4-MeC_6H_2O)$(PPh_3)_2$ (1.28 Å)[19] and RuH(η^5-C_6H_5O)$(PPh_3)_2$·MeOH (1.277 Å).[11a] Also consistent with the structure of Rh(η^5-2,6-${}^tBu_2$-4-MeC_6H_2O)$(PPh_3)_2$, the para carbon of the oxocyclohexadienyl ligand is bound most closely to the metal (Ru–C(11) = 2.183 (3) Å), followed by the meta (Ru–C(12) = 2.192 (3), Ru–C(16) = 2.196 (3) Å) and ortho (Ru–C(13) = 2.295 (3), Ru–C(15) = 2.300 (3) Å) carbons. The Ru–C(14) distance, 2.554 (3) Å, is quite long and reflects the absence of a significant bonding interaction.

Puckering in the 2,6-${}^tBu_2C_6H_3O$ ligand is evident from examination of least-squares planes. Atoms C(11), C(12), C(13), C(15), and C(16), corresponding to the pentadienyl fragment, define a reasonably good plane with a mean deviation of 0.008 Å. The maximum deviation from this plane is 0.013 Å by C(11), toward the ruthenium atom. The carbonyl carbon C(14) and O(1) lie 0.26 and 0.57 Å, respectively, out of this plane. The angle between the latter plane and the one defined by C(13), C(14), and C(15) is 19.1°. Finally, the two carbocyclic ligands bound to ruthenium are not quite parallel, since the plane of C(11), C(12), C(13), C(15), and C(16) makes an angle of 7.2° with the plane defined by C(1)–C(5) of the Cp* ligand.

Molecular Orbital Analysis of [CpRu(μ-OMe)]$_2$. In order to investigate the unusual geometry of **1** and its diamagnetism in the apparent absence of a Ru–Ru bond, we have investigated the electronic structure of [CpRu(μ-OMe)]$_2$ (**1′**) by using Fenske–Hall molecular orbital calculations.[25] The analysis will be similar to that which we have used previously on piano stool dimer systems.[26] We will initially consider the hypothetical pseudo-D_{2h} conformer in which the dihedral angle between the two RuO_2 planes is 180°.

The frontier orbitals of a typical CpM fragment have, of course, been analyzed in detail by several authors.[27] The interaction of the Cp ligand with the metal atom occurs principally through donation from the e_1'' Cp orbitals into the M dπ orbitals, leading to the d-orbital energetic ordering dδ (x^2–y^2, xy) < dσ (z^2) ≪ dπ (xz, yz). In a d^6 $CpRu^+$ fragment, the dδ and dσ orbitals will be fully occupied and the "dπ" orbitals (which are Cp–Ru antibonding) will be empty. We now allow two $CpRu^+$ fragments to interact to form $[CpRu\cdots RuCp]^{2+}$ at a Ru–Ru distance of 2.96 Å. At this distance, the Ru–Ru interaction is weaker than the splitting induced by the Cp ligands, and a nonbonded $\sigma^2\delta^4\delta^{*4}\sigma^{*2}$ configuration results, as shown in Figure 5. Neither the destabilization of the Ru–Ru σ^* orbital nor the stabilization of the Ru–Ru π orbital is great enough to lead to net Ru–Ru bonding.

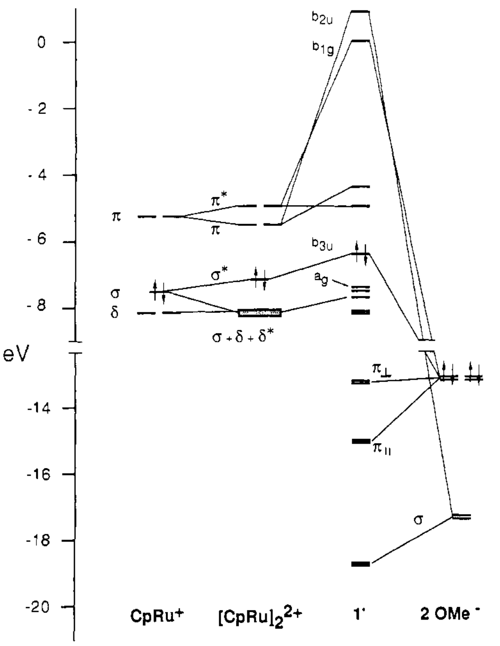

Figure 5. Molecular orbital diagram showing the formation of $[CpRu\cdots RuCp]^{2+}$ from $CpRu^+$ and its interaction with $2OMe^-$ to form **1′**. The Cp-based orbitals of **1′** are not shown. The arrows indicate the HOMO of each species.

Two OMe^- ligands will now be allowed to interact with $[CpRu\cdots RuCp]^{2+}$ to generate a conformer of **1′** in which the two Ru atoms and the two O atoms are coplanar. The important donor orbitals of an alkoxide ligand are the σ lone pair on the oxygen atom (Oσ), and the two π lone pairs on O, which will be designated Oπ_{par} (parallel to Ru–Ru axis) and Oπ_{perp} (perpendicular to the Ru–Ru axis). From overlap considerations, it would be expected that the ordering of interaction of the alkoxide lone pairs with the Ru atoms would be Oπ_{par} > Oσ > Oπ_{perp}. It is seen in Figure 5 that, indeed, the strongest interactions are donation from the b_{1g} combination of Oπ_{par} into the Ru–Ru π^* orbital of appropriate symmetry and from the b_{2u} combination of Oσ into the in-plane Ru–Ru π orbital. These two interactions compose a delocalized four-center, four-electron bonding scheme similar to that which we have discussed in other piano stool dimer systems.[26]

The other interactions between the OMe^- ligands and the diruthenium unit are less productive with regard to Ru–O bonding. The symmetric (a_g) combination of the Oσ orbitals can, and does, interact strongly with the Ru–Ru σ orbital. Likewise, the b_{3u} combination of the Oπ_{par} orbitals interacts well with both the Ru–Ru σ^* and one of the δ^* orbitals. These filled–filled interactions contribute nothing to net bonding within the Ru_2O_2 core. The Oπ_{perp} orbitals interact only weakly with the appropriate Ru–Ru δ and π orbitals; because of poor overlap, these have little consequence on the Ru–O bonding.

Will the Ru–O bonding strengthen or weaken as the molecule is distorted into a folded C_{2v} structure such as that observed for **1**? The answer will depend on the influence of the geometric distortion on the donation from the alkoxide ligands into empty orbitals of the Ru_2 fragment. We have chosen a distortion coordinate in which the Ru–Ru distance does not change, so that Ru–Ru bonding should not be affected by the distortion. We have also constrained the Cp(centroid)–Ru vectors to bisect the O–O vector, a feature evident in the structure of **1**. As the dihedral angle between the two O–Ru–O planes is varied from 180°

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(25) Hall, M. B.; Fenske, R. F. *Inorg. Chem.* **1972**, *11*, 768.

(26) See, for example: (a) Bursten, B. E.; Cayton, R. H.; Gatter, M. G. *Organometallics* **1988**, *7*, 1342. (b) Bursten, B. E.; Cayton, R. H. *Ibid.* **1988**, *7*, 1349. (c) Bursten, B. E.; Cayton, R. H. *Polyhedron* **1988**, *7*, 943.

(27) Burdett, J. K.; Albright, T. A.; Whangbo, M.-H *Orbital Interactions in Chemistry*; Wiley: New York, 1985; Chapter 20 and references therein.

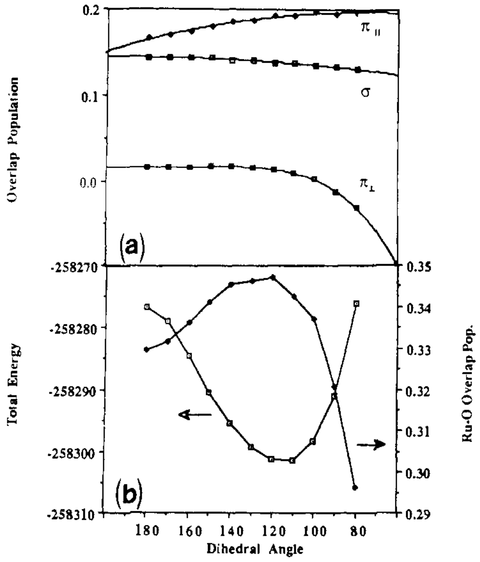
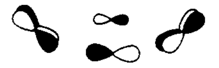


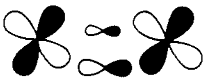
Figure 6. (a) Plots of the overlap populations between the Ru atoms and the $O\sigma$, $O\pi_{par}$, and $O\pi_{perp}$ orbitals in **1′** as a function of the dihedral angle between the two O–Ru–O planes. (b) Plots of the Fenske–Hall total energy (□) and the total Ru–O overlap population (♦) as a function of the dihedral angle.

(planar, "D_{2h}") to 80° (folded, C_{2v}), we observe the following effects on the Ru–O overlap populations (Figure 6a): (1) As expected, the $O\sigma$ donation, which should be the most omnidirectional of the interactions, is largely invariant to the folding. (2) The small $O\pi_{perp}$ donation is also invariant to the folding down to ca. 100°, at which point the two $O\pi_{perp}$ orbitals start strongly repelling one another. (3) The folding has its major influence on the donation from the $O\pi_{par}$ orbitals, with an increase in the O to Ru donation as the dihedral angle decreases.

The increased $O\pi_{par}$ to Ru donation upon folding is due primarily to an increase in the overlap of the $O\pi_{par}$ a_2 combination with the antisymmetric $d\pi$ orbital combination that has its origin in the in-plane π^* orbital:



The b_1 combination of the $O\pi_{par}$ orbitals, which participated in a filled–filled interaction with one of the δ^* orbitals in the planar conformation (and donation into the higher lying Ru 5s and 5p orbitals), can now, by symmetry, interact with the other antisymmetric $d\pi$ combination:



While this would allow donation into an acceptor orbital that was not utilized in the planar arrangement, we find very little such donation; the poor overlap of the "vertical" $d\pi$ orbitals with the $O\pi_{par}$ orbitals mitigates against a good interaction. This is consistent with the availability of these vertical $d\pi$ orbitals as acceptors for incoming nucleophiles. That the donation from the a_2 combination dominates the donation from the $O\pi_{par}$ orbitals is evident from a transformation of the 120° calculation onto the canonical orbitals of the $[OMe]_2^{2-}$ fragment. The Mulliken populations of the a_2 and b_1 $O\pi_{par}$ combinations (1.55 and 1.66, respectively) indicate the predominance of donation from the former.

Figure 6b shows plots of the total Ru–O overlap population and the Fenske–Hall total energy[28] of **1′** as a function of the dihedral angle. These two plots are nearly mirror images of one another, and the minimum total energy and maximum overlap population are both achieved at an angle of about 120°, in excellent agreement with the observed structure of **1**. We believe that the close relationship between the Ru–O overlap population, the total energy, and the experimental observation provide strong support for the folding of **1** being due to the electronic influence of the alkoxide ligands. We see no appreciable direct Ru–Ru interaction and do not believe that metal–metal bonding can be responsible for the observed structure.

These conclusions have both similarities to and differences from those reached for other folded and bridged dinuclear systems. Norman and Gmur[24b] used the $X\alpha$–SW method to advance an explanation for the bent structure of $Rh_2Cl_2(CO)_4$, a molecule that, like **1**, has a long (3.12 Å) metal–metal separation. They conclude that the bridging Cl ligands induce an enhanced Rh–Rh interaction, a somewhat different explanation than that reached here. Burdett has examined the bridging-ligand effects on the dihedral angle in a series of $Fe_2(CO)_6(\mu\text{-}AX_2)_2$ complexes.[29] These d^7–d^7 dimers generally have Fe–Fe bond lengths consistent with a single Fe–Fe bond, and the variation of the dihedral angle is attributed to a balance between the metal–metal bonding and metal–ligand antibonding in the HOMO of the complexes. The analogue of this orbital is unoccupied in the d^6–d^6 systems, and hence the explanations must be somewhat different for the two types of molecules. Burdett does note that for a d^6–d^6 system of the same *ilk* (none of which were structurally characterized at the time) no metal–metal bond would be expected.

The analysis presented here also seems consistent with the observed structure of another $[CpM(\mu\text{-}OR)]_2$ species, namely, $[CpCr(\mu\text{-}O^tBu)]_2$ (**6**).[30] This d^4–d^4 dimer has a Cr–Cr bond length of 2.65 Å, indicative of a Cr–Cr single bond. With reference to the MO diagram in Figure 5, it is expected that the σ^* orbital, which was occupied in **1′**, will be empty in **6**, leading to a net Cr–Cr σ bond. Two more electrons must necessarily be removed from the remaining closely spaced manifold of metal-based orbitals and will lead to a more complicated picture of metal–alkoxide bonding. The molecule is paramagnetic and nonplanar,[30] evidence for partial occupation of at least two of these orbitals. A complete comparison of the electronic structures of **1′** and **6** will not be presented here.

In summary, the diamagnetism of **1** can be attributed to the strong d-orbital splitting induced by the Cp* ligands; this nicely separates the Ru π orbitals from the σ and δ and leaves six lower lying Ru-based orbitals in which to house the 12 Ru-based electrons. The folded C_{2v} structure of **1** is due to the electronic preferences of the bridging alkoxide ligands; the folding allows the $O\pi_{par}$ orbitals of these ligands to maximize their donation into the unoccupied Ru orbitals.

Experimental Section

General. Manipulations were conducted under an atmosphere of nitrogen or argon using standard Schlenk techniques and/or a Vacuum Atmospheres glovebox. Rigorously dried, oxygen-free solvents were employed throughout. Elemental analyses were performed by Mikroanalytisches Labor Pascher. Infrared spectra were recorded on a Perkin-Elmer 1330 instrument. NMR spectra were obtained with either a GE QE-300 instrument at 300 (^1H) and 75.5 (^{13}C) MHz or a Varian EM 390 (90 MHz, ^1H). The starting materials $[Cp^*RuCl_2]_2$,[31] $[Cp^*RuCl]_4$,[13] and $Cp^*Ru(PCy_3)Cl$[14a] were prepared by literature procedures. Lithium methoxide was prepared by slow addition of pieces of lithium wire to methanol and was isolated by removal of excess methanol under vacuum. $LiO\text{-}2,6\text{-}{}^tBu_2C_6H_3$ was prepared by reaction of ^nBuLi with $HO\text{-}2,6\text{-}{}^tBu_2C_6H_3$ in hexane.

$[Cp^*Ru(\mu\text{-}OMe)]_2$ (1). (a) At room temperature methanol (50 mL) was added to a flask containing both LiOMe (0.043 g, 1.13 mmol) and $[Cp^*RuCl]_4$ (0.20 g, 0.18 mmol). After the resulting mixture was stirred for 36 h, all volatiles were removed in vacuo. The residue was then extracted with diethyl ether (2 × 40 mL, 15 mL). The extracts were combined, concentrated to ca. 20 mL, and cooled to −40 °C to afford maroon crystals (dec > 175 °C) of the product in 84% yield (0.164 g). Anal. Calcd for $C_{22}H_{36}O_2Ru_2$: C, 49.4; H, 6.79. Found: C, 49.6; H, 6.89. IR (Nujol, CsI, cm^{-1}): 2792 w, 1119 s, 1050 br m, 500 w, 460 w, 440 w. ^1H NMR (300 MHz, benzene-d_6, 22 °C): δ 1.62 (s, 15 H,

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C_5Me_5), 4.83 (s, 3 H, OCH_3). $^{13}C\{^1H\}$ NMR (75.5 MHz, benzene-d_6, 22 °C): δ 11.46 (C_5*Me*$_5$), 70.37 (OCH_3), 70.46 (*C*$_5$Me$_5$). UV-vis (pentane, nm, ϵ values in parentheses): 302 (2950), 506 (1210).

(b) At room temperature, methanol (25 mL) was added to a flask containing both LiOMe (0.013 g, 0.36 mmol) and Cp*Ru(PCy_3)Cl (0.20 g, 0.36 mmol). Within minutes the solution turned maroon. After 40 min of stirring, the solvent was removed in vacuo and the crude solid extracted with pentane (2 × 25 mL). The resulting maroon solution was concentrated and cooled to −40 °C to give **1** in 25% yield (0.025 g).

[Cp*Ru(μ-OEt)]$_2$ (2). To [Cp*RuCl]$_4$ (0.30 g, 0.27 mmol) in ethanol (40 mL) was added a solution of LiOEt (0.057 g, 1.10 mmol) in 10 mL of ethanol. The solution began to turn maroon after ca. 5 min. After 3 h the solvent was removed in vacuo and the resulting orange-maroon solid extracted into diethyl ether (2 × 40 mL). Cooling the combined extracts to −40 °C allowed isolation of the product as maroon crystals (did not melt up to 280 °C) in 46% yield (0.14 g). Anal. Calcd for $C_{24}H_{40}O_2Ru_2$: C, 51.2; H, 7.16. Found: C, 51.1; H, 7.21. IR (Nujol, CsI, cm^{-1}): 1360 s, 1340 m sh, 1258 w, 1096 s, 1050 s, 1020 s, 890 m, 778 w, 568 br m, 420 br w. ^1H NMR (300 MHz, benzene-d_6, 22 °C): δ 1.50 (t, 6 H), 1.62 (s, 30 H), 4.99 (q, 4 H). $^{13}C\{^1H\}$ NMR (75.5 MHz, benzene-d_6, 22 °C): δ 11.47 (C_5*Me*$_5$), 21.20 (OCH_2*C*H_3), 70.2 (*C*$_5$Me$_5$), 76.07 (O*C*H_2CH_3).

[Cp*(CO)Ru(μ-OEt)]$_2$ (3). Compound **2** (0.075 g, 0.13 mmol) was dissolved in pentane (40 mL) at room temperature to give a maroon solution, which was transferred to a pressure bottle. Carbon monoxide (20 psi) was admitted and within 2 min the solution turned yellow. After stirring for 2 h, the solution was degassed and filtered. Concentration and cooling (−40 °C) gave the product as yellow crystals (mp 141–142 °C) in 55% yield (0.040 g). Anal. Calcd for $C_{26}H_{40}O_4Ru_2$: C, 50.5; H, 6.52. Found: C, 50.3; H, 6.38. IR (benzene-d_6 solution, CaF_2, cm^{-1}): 2970 m, 2908 m, 2840 sh m, 2758 sh m, 1912 s, 1653 m, 1445 w br, 1369 m, 1095 m, 1045 m. ^1H NMR (300 MHz, benzene-d_6, 22 °C): δ 1.30 (t, 6 H), 1.45 (s, 30 H), 3.36 (q, 4 H). ^{13}C NMR (75.5 MHz, benzene-d_6, ppm): δ 10.04 (q, *J* = 127 Hz, C_5*Me*$_5$), 18.54 (q, *J* = 125 Hz, OCH_2*C*H_3), 72.83 (t, *J* = 132 Hz, O*C*H_2CH_3), 90.24 (*C*$_5$Me$_5$), 211.25 (Ru*C*O).

Cp*Ru(η^5-2,6-^{t}Bu$_2$C$_6$H$_3$O) (5). At room temperature toluene (40 mL) was added to a flask containing [Cp*RuCl]$_4$ (0.20 g, 0.18 mmol) and LiO-2,6-^{t}Bu$_2$C$_6$H$_3$ (0.157 g, 0.74 mmol). The solution immediately turned orange-brown. After 35 min, solvent was removed in vacuo and the crude residue extracted into pentane (50 mL). Upon concentration and cooling (−40 °C), yellow crystals (mp 227–228 °C) of the product were obtained in 20% yield (0.06 g). No attempt was made to maximize the yield of **5**. Anal. Calcd for $C_{24}H_{36}ORu$: C, 65.3; H, 8.22. Found: C, 65.0; H, 8.22. IR (Nujol, CsI, cm^{-1}): 1542 s, 1353 m, 1251 w, 1107 w, 1074 br w, 1025 m, 884 w, 857 w, 741 m, 633 w. ^1H NMR (300 MHz, benzene-d_6, 22 °C): δ 1.56 (s, 15 H), 1.60 (s, 18 H), 3.87 (t, 1 H), 4.85 (d, 2 H). $^{13}C\{^1H\}$ NMR (75.5 MHz, benzene-d_6, ppm): δ 11.75 (C_5*Me*$_5$), 29.80 (C*Me*$_3$), 34.97 (*C*Me$_3$), 74.02, 74.15, 84.57, 84.84, 102.21 (η^5-2,6-^{t}Bu$_2$H$_3$*C*$_5$C=O), 88.70 (*C*$_5$Me$_5$), 158.68 (η^5-2,6-^{t}Bu$_2$H$_3$C$_5$*C*=O).

Collection and Solution of Diffraction Data. Parameters summarizing the collection and solution of diffraction data for **1**, **3**, and **5** are contained in Table I. Crystals of **1** and **3** were mounted in glass capillary tubes in an inert-atmosphere glovebox and then flame-sealed. Crystals of **5** were mounted in glass capillaries in air. In all cases the data were corrected for absorption by using a semiempirical procedure that refines six parameters defining a pseudoellipsoid. Each structure was solved by direct methods and refined by full-matrix least-squares methods (SHELXTL PLUS computer programs, Nicolet Instrument Corp., Madison, WI).

For **1**, systematic absences could not distinguish between space groups *C*2/*c* and *Cc*. Solution and isotropic refinement were conducted in both space groups, and the choice of *C*2/*c* is based on the results of significance tests on the *R* factor.[32] A 2(*b*) rotation at $a = ^1/_2$, $c = ^3/_4$ relates the two halves of the dimer. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were initially found from a Fourier difference map, refined, and then constrained at a fixed distance (d(C–H) = 0.96 Å) and given a fixed isotropic thermal parameter.

Systematic absences uniquely determined the tetragonal space group for **3**. Due to the limited amount of data, only Ru(1), Ru(2), O(1), and O(2) were refined anisotropically. Hydrogen atoms were placed in fixed, idealized positions and were given a fixed isotropic thermal parameter. The absolute configuration was determined by inverting all atom coordinates, refining the new structure, and comparing *R* factors for the two refinements. The structure described is the correct enantiomorph.

The space group for **5** was also uniquely determined from systematic absences. Of the observed reflections ($F > 6\sigma(F)$), 4 had $\Delta/\sigma > 10$ and were removed from the final refinement. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms of the pentadienyl fragment (H(11), H(12), and H(16)) were located via Fourier difference maps and then fixed (d(C–H) = 0.96 Å) with independent isotropic thermal parameters. The remaining hydrogen atoms were fixed in idealized positions with fixed isotropic thermal parameters.

Calculational Details. Molecular orbital calculations were performed on an IBM 3081-D computer system using the Fenske–Hall approximate MO method.[25] The bond lengths used for [CpRu(μ-OCH$_3$)]$_2$ were taken from the crystal structure of [Cp*Ru(μ-OCH$_3$)]$_2$ and were idealized to C_{2v} symmetry. Local D_{5h} symmetry was invoked upon the cyclopentadienyl rings, and a C–H distance of 1.08 Å was assumed. The remaining metric parameters, as a function of the dihedral angle between the two RuO$_2$ planes, were determined by constraining the Ru–Ru distance to be 2.961 Å, the Ru–O distance to be 2.070 Å, and the Ru–Cp(centroid) distance to be 1.748 Å and by requiring the Ru–Cp(centroid) vector to bisect the O–O vector.

All atomic wave functions were generated by using the method of Bursten, Jensen, and Fenske.[33] Contracted double-ζ representations were used for the Ru 4d AOs and for the C and O 2p AOs. An exponent of 1.16 was used for the hydrogen 1s AO.[34] The basis functions for Ru were derived for the +2 oxidation state (s^{0}d^n) with the 5s and 5p exponents fixed at 2.0.

The calculations were performed by using a fragment approach, as we have done previously.[26] All calculations were converged with a self-consistent-field iterative technique using a convergence criteria of 0.0010 as the largest deviation of atomic orbital populations between successive cycles.

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Supplementary Material Available: Tables of atomic coordinates and isotropic displacement parameters, tables of bond distances and angles, anisotropic thermal parameters, and hydrogen atom coordinates for **1**, **3**, and **5** (19 pages); listings of observed and calculated structure factors for **1**, **3**, and **5** (29 pages). Ordering information is given on any current masthead page.

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