spectra. M.C. also thanks NSERC Canada for partial funding of the diffractometer. Acknowledgment is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of the work done at Calvin College on the Fenske–Hall calculations.

Registry No. **1**, 14243-23-3; **2**, 22364-22-3; **3a**, 75249-93-3; **3b**, 75249-92-2; **4**, 116888-32-5; **8**, 116888-33-6; **13**, 69657-52-9; **14**, 116888-35-8; (η^5-C_5H_5)Co(CO)$_2$, 12078-25-0; (η^5-C_5Me_5)Co(CO)$_2$, 12129-77-0; (PPh$_3$)$_4$Pt, 14221-02-4; (PPh$_3$)$_4$Pd, 14221-01-3; (diphos)Ni(CO)$_2$, 15793-01-8; Cp$_2$Ti(CO)$_2$, 12129-51-0; Co$_2$(CO)$_8$, 10210-68-1; Fe$_2$(CO)$_9$, 15321-51-4; S$_2$Fe$_3$(CO)$_9$, 22309-04-2; (μ-Me$_5$C$_5$CoS$_2$)Fe$_2$(CO)$_6$, 116888-34-7.

Supplementary Material Available: Tables of anisotropic thermal parameters, idealized hydrogen parameters, bond lengths and angles within the carbonyl and Cp* groups, and weighted least-squares planes (9 pages); listings of observed and calculated structure amplitudes (23 pages). Ordering information is given on any current masthead page.

Synthesis and Spectral Characterization of a Series of Iron and Ruthenium Benzylidene Complexes, Cp(CO)(L)M=CH(C$_6$H$_4$R)$^+$ (M = Fe, Ru; L = CO, PPh$_3$; R = *p*-H, *p*-F, *p*-CH$_3$, *p*-OCH$_3$). Barriers to Aryl Rotation and Benzylidene Transfer Reactions

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Received March 29, 1988

The α-ether complexes Cp(CO)$_2$Fe–CH(OCH$_3$)C$_6$H$_4$R (**7a**, R = H; **7b**, R = *p*-F; **7c**, R = *p*-CH$_3$; **7d**, R = *p*-OCH$_3$; **7e**, R = *m*-OCH$_3$; **7f**, R = *p*-CF$_3$), Cp(CO)$_2$Ru–CH(OCH$_3$)C$_6$H$_4$R (**10a**, R = H; **10b**, R = *p*-F; **10c**, R = *p*-CH$_3$; **10d**, R = *p*-OCH$_3$), and Cp(CO)(PPh$_3$)M–CH(OCH$_3$)C$_6$H$_4$R (**11a–d**, M = Fe; **15a–d**, M = Ru; **a**, R = H; **b**, R = *p*-F; **c**, R = *p*-CH$_3$; **d**, R = *p*-OCH$_3$) were synthesized by methylation of the corresponding benzoyl complexes followed by hydride reduction. Treatment of the α-ether complexes with trimethylsilyl triflate gave the series of benzylidene complexes Cp(CO)$_2$M=CH(C$_6$H$_4$R)$^+$ (**1**, M = Fe; **2**, M = Ru) and Cp(CO)(PPh$_3$)M=CH(C$_6$H$_4$R)$^+$ (**3**, M = Fe; **4**, M = Ru) which were characterized by ^{1}H and ^{13}C NMR spectroscopy. Barriers to aryl ring rotation were measured by dynamic ^{1}H NMR methods and found to be 9.4 (**1a**), 10.2 (**1b**), 10.7 (**1c**), 13.5 (**1d**), 10.6 (**2b**), 10.9 (**2c**), 14.5 (**2d**), 9.0 (**3b**), 9.0 (**3c**), 10.9 (**3d**), 9.1 (**4b**), 9.2 (**4c**), and 11.1 (**4d**) kcal/mol. Barriers vary in the expected way with arene substituents and a reasonable Hammett σ^+/ρ correlation exists for **1** (ρ = ca. +5). The nearly identical barriers observed for Fe and Ru analogues suggest similar positive charge densities at C$_\alpha$ in these analogues. Benzylidene transfers to propene to give 1-aryl-2-methylcyclopropanes were carried out by using **1a–f**. The cis/trans isomer ratios are all ca. 8 except for **1d** where cis/trans = 2. Mechanistic implications of this data are considered.

Electrophilic transition-metal carbene complexes L$_n$M=CHR (R = H, alkyl, aryl) are much less stable than classical, Fischer-type heteoatom-substituted carbene complexes, especially where the organometallic fragment is not electron-rich. For example, the complexes Cp(CO)$_2$Fe=CH$_2^+$[1] and Cp(CO)$_2$Fe=CHCH$_3^+$[2-4] (Cp = η^5-C$_5$H$_5$) are implicated as reactive intermediates but have escaped direct observation by usual spectroscopic techniques.[5] Analogues of these highly electrophilic species may be stabilized either by substitution of better donor ligands for the π-acid CO ligands or by substitution of hydrocarbon substituents at the carbene carbon which are effective at delocalizing positive charge. Hence, the phosphine-substituted derivatives Cp(Ph$_2$PCH$_2$CH$_2$PPh$_2$)Fe=CH$_2^+$[6] and Cp(CO)(PPh$_3$)Fe=CHCH$_3^+$[2] have been characterized spectroscopically at low temperatures and aryl-, vinyl-, and cyclopropyl-substituted complexes (CO)$_5$W=CHPh,[7] Cp(CO)$_2$Fe=CHPh$^+$,[8] Cp(CO)$_2$Fe=CHCH=C(CH$_3$)$_2^+$,[9,10] and Cp(CO)$_2$Fe=CH-*c*-C$_3$H$_5^+$[11] have been described. These complexes are sufficiently

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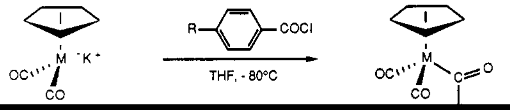
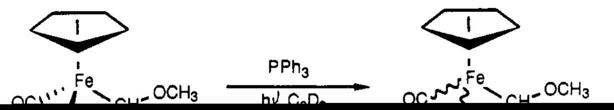
Scheme I



Scheme II



[redacted]

Table I. ^1H NMR Data for Carbene Complexes (CD_2Cl_2, δ in ppm versus TMS)

a. $CpM(CO)_2{=}CH(p\text{-}C_6H_4R)^+$ (M = Fe (**1**), Ru (**2**))

complex	R	C_5H_5	M=C*H*	*o*-Ar	*m*-Ar	R	temp, K
1a	H	5.87 (s)	16.86 (s)	7.70–8.13 (complex)			248
1b	F	5.92 (s)	16.78 (s)	8.22 (d)	7.41 (d)		253
1c	CH_3	5.90 (s)	16.61 (s)	8.01 (b s)	7.57 (b t)	2.53 (s)	273
1d	OCH_3	5.67 (s)	15.24 (s)	8.27/7.59 (d/d)	7.29/7.05 (d/d)	4.10 (s)	253
2a	H	6.05 (s)	16.32 (s)	7–8 (complex)			213
2b	F	6.13 (s)	16.34 (s)	8.53/8.05 (b s/b s)	7.53/7.33 (b t/b t)		193
2c	CH_3	6.12 (s)	16.07 (s)	8.31/7.75 (d/d)	7.67/7.50 (d/d)	2.48 (s)	193
2d	OCH_3	5.98 (s)	14.86 (s)	8.32/7.75 (dd/dd)	7.33/7.10 (dd/dd)	4.10 (s)	243

b. $CpM(CO)(PPh_3){=}CH(p\text{-}C_6H_4R)^+$ (M = Fe (**3**), Ru (**4**))

complex	R	C_5H_5	M=C*H*	$(C_6H_5)_3P$/*o*-Ar	*m*-Ar	R	temp, K
3a	H	5.4 (s)	17.48 (b s)	7.1–7.6 (complex)			253
3b	F	5.32 (s)	17.20 (b s)	7.1–7.9 (b m)	6.90 (b m)		233
3c	CH_3	5.28 (s)	16.93 (s)	7.1–7.7 (b m)	7.09 (b s)	2.36 (s)	273
3d	OCH_3	5.26 (s)	16.62 (s)	7.2–7.6 (b m)	6.75 (d)	3.96 (s)	298
					(6.84/6.41) (d/d)		(213)
4a	H	5.68 (s)	16.90 (s)	6.9–7.7 (complex)			233
4b	F	5.73 (s)	16.89 (s)	7.1–7.6 (b m)	6.87 (m)		233
4c	CH_3	5.64 (s)	16.41 (s)	7.1–7.6 (b m)	7.01 (m)	2.32 (s)	253
4d	OCH_3	5.60 (s)	15.91 (s)	7.1–7.6 (m)	6.75 (d)	2.95 (s)	273

only very slowly in solution.

We were unable to convert the α-ether complexes **10** to their phosphine-substituted derivatives using photochemical methods, so an alternative route to α-ether complexes **15** was sought (Scheme III). The cationic complex $CpRu(PPh_3)(CO)_2{}^+PF_6{}^-$ (**12**) was found to react with excesses of arylmagnesium bromides to give acyl complexes **13** in good yields. Alkylation and reduction was accomplished as already described to give stable α-ether complexes **15** as mixtures of diastereomers.[13]

Generation of Carbene Complexes. Treatment of CD_2Cl_2 solutions of α-ether complexes **7**, **10**, **11**, or **15** with electrophiles at low temperatures results in abstraction of the methoxy group and formation of carbene complexes **1**–**4**. The iron carbene complexes **1** and **3** gave orange to red-orange solutions; the colorless solutions of the ruthenium α-ethers **10** and **15** yielded bright yellow solutions of carbene complexes **2** and **4**.[14] Triflic acid (CF_3SO_3H) may be used as the electrophile, but interfering resonances associated with the acid system often appear in the low-field carbene region of the ^1H NMR spectrum. Therefore, in most cases trimethylsilyl triflate was used as the abstracting electrophile. Occasionally, and especially for **3**, the ^1H spectra were broadened to such an extent due to paramagnetic impurities that assignment of aryl signals was difficult. In those cases use of triflic acid was found to attenuate line broadening and permit dynamic NMR studies.

The stability of the arylcarbene complexes **1**–**4** depends on the ancillary ligand L and the aryl substituent R. The dicarbonyl complexes **1a**,**b** and **2a**,**b** (R = H, F) are stable at −80 °C but decompose rapidly on warming, while the *p*-methoxy derivatives **1d** and **2d** survive for several hours at 25 °C. All of the phosphine-substituted arylcarbene complexes **3** and **4** have half-lives on the order of days at 25 °C. All complexes are more stable in the solid state. The orange salt of **1a** and the burgundy salt of **3a** were obtained from the reaction of their α-ether precursors with $PhC_3{}^+AsF_6{}^-$ in CH_2Cl_2, followed by precipitation with pentane or hexane. The yellow salt of ruthenium complex **2d** (R = OCH_3) was obtained from the reaction of α-ether **10d** with HBF_4 in ether solution. Solutions of the isolated salts were spectroscopically identical with those of carbene complexes generated in situ.

The ^1H and ^{13}C NMR resonances of the series of carbene complexes **1**–**4** are summarized in Tables I and II. A few general observations are noted. Each of the carbene complexes **1**–**4** exhibits a resonance at 14–17 ppm in its ^1H NMR spectrum (H_α) and at 290–360 ppm in its ^{13}C NMR spectrum (C_α), typical of electrophilic carbene complexes. The ^1H and ^{13}C resonances for the cyclopentadienyl ligand and the aryl group are consistently shifted to lower fields relative to the resonances observed in the α-ether precursors, an indication of the charge development in the carbene complex.

Of particular interest are the chemical shifts of the ortho and para carbons of the aryl groups which are useful for assessing the extent of positive charge delocalization into the aromatic ring.[21] The para shifts should be insulated from any effects of the Cp(CO)(L)M group, and chemical shifts should reflect relative charge densities. The para shift in **1a**, 141.5 ppm, is close to that in Ph_3C^+ of 144 ppm[15] and suggests similar charge densities. For comparison, the para shift in $(CO)_5W{=}CPh_2$ is 131.4 ppm[16] and indicates much less positive charge density at C_{para} in this neutral diphenyl-substituted carbene complex. A comparison of aryl ^{13}C chemical shifts between the iron and ruthenium analogues, **1** versus **2** and **3** versus **4**, shows the differences in analogous ^{13}C shifts are small, suggesting a similar positive charge density at the carbene carbon and thus little difference in the electrophilic character of C_α in analogous iron and ruthenium carbene complexes. (This is supported by similar values for rotational barrier measurements (vide infra).)

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[14] At low temperatures carbene formation may be slow enough that side reactions become important. When **10d** was treated with (TMS)OTf at −80 °C, a 1:1 mixture of methoxycarbene complex and *p*-methoxybenzyl complex was obtained, presumably the result of intermolecular hydride transfer. When the reaction was run at 0 °C and then cooled to −80 °C, only **2d** was obtained.

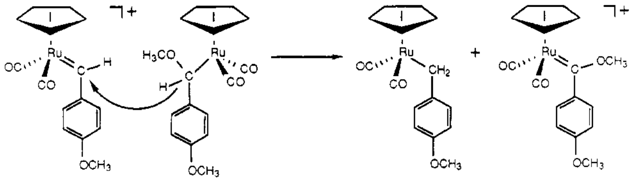

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Table II. ^{13}C NMR Chemical Shifts of Carbene Complexes (CD_2Cl_2, δ in ppm versus TMS)

$CpM(CO)_2{=}CH(p\text{-}C_6H_4jR)^+$ (M = Fe (**1**), Ru (**2**))

complex	R	CO	C_5H_5	M=C*H*	*i*-Ar	*o*-Ar	*m*-Ar	*p*-Ar	R	temp, K
1a	H	206.5	93.2	342.4	151.8	134.5	130.0	141.5		233
1b	F	207.9	94.0	338.8	150.8	139.7	118.5	170.7		253
1c	CH_3	208.3	93.5	335.5	152.1	136.1	131.5	157.4	23.4	253
1d	OCH_3	209.0	92.0	310.0	149.6	141.1/140.4	119.6/113.4	172.9	57.7	253
2a	H	194.0	94.9	323.5	151.5	128–134 (complex)[a]				213
2b	F	195.0	95.0	322.0	151.0	142.0	116.0	171.0		224
2c	CH_3	196.8	96.9	320.0	152.9	139.9	134.0	161.1	25.5	243
2d	OCH_3	195.8	94.2	294.9	158.0	144.0	113.0	175.0	58.0	298

b. $CpM(CO)_2{=}CH(p\text{-}C_6H_4R)^+$ (M = Fe (**3**), Ru (**4**))[b]

complex	R	CO	C_5H_5	M=C*H*	$^2J_{PC}$, Hz	*i*-Ar	*o*-Ar	*m*-Ar	*p*-Ar	R	temp, K
3a	H	215.5	93.5	342.0	23	153.1	complex				253
3b	F	215.5	93.3	334.3	20	149.9	135.0	116.5	166.8		233
3c	CH_3	215.7	93.0	336.4	22	151.0	complex		152.5	22.6	273
3d	OCH_3	216.4	92.0	323.6	23	149.3	136.0	114.7	167.8	56.7	253
4a	H	201.7	95.4	321.3	(br)	151.4	complex				233
4b	F	201.9	95.4	317.6	(br)	148.6	136.5	116.7	167.6	23.3	253
4c	CH_3	202.1	95.9	315.3	(br)	150.7	complex		151.9	23.3	253
4d	OCH_3	202.6	94.2	303.8	12	147.3	138.2	115(br)	168.7	58.6	253

[a] Impurities formed during carbene generation coupled with line broadening preclude precise assignments. [b] Resonances for the $P(C_6H_5)_3$ ligand are found in the supplementary material.

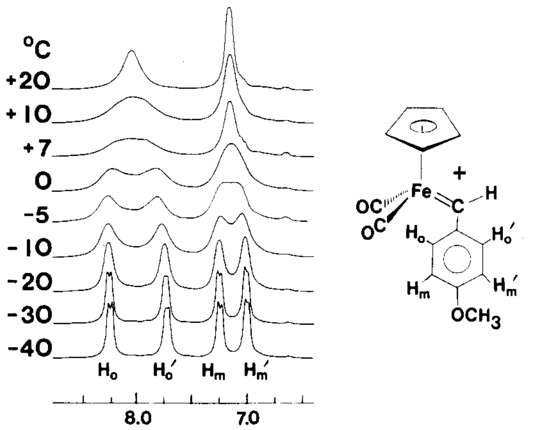


Figure 1. Variable-temperature ^1H NMR spectrum of **1d** in the aromatic region.

Dynamic Studies. For effective charge delocalization into the arene ring, the p orbital at C_α must be aligned with the ring π-system which requires that the aryl ring be coplanar with the $M–C_\alpha–C_{ipso}$ plane. This condition is reflected in the ^1H NMR spectra of complexes **1–4** at low temperatures, where aryl rotation is slow on the NMR time scale. The ortho and meta hydrogens appear as a set of four distinct but sometimes overlapping multiplets at 6.7–8.5 ppm (see Figure 1).

On the basis of known[6] and calculated[17,18] geometries for complexes $CpL_2Fe{=}CH_2^+$, the carbene ligand in complexes **1** and **2** (L = CO) was expected to display the vertical orientation **V-1,2** where the $H_\alpha–C_\alpha–C_{ipso}$ plane bisects the

Table III. $\Delta G^{\ddagger}_{rot}$ (kcal mol^{-1}) for Complexes 1–4

complex	1	2	3	4
a, R = H	9.4			
b, R = F	10.2	10.6	9.0	9.1
c, R = CH_3	10.7	10.9	9.0	9.2
d, R = OCH_3	13.5	14.5	10.9	11.1

vations by Gladysz for $Cp(NO)(PPh_3)Re{=}CHPh^+$[20] suggest that complexes **3** and **4** adopt a conformation wherein the $H_\alpha–C_\alpha–C_{ipso}$ plane is aligned with the M–CO plane.

Barriers to aryl rotation can be obtained for these species by observing broadening and coalesence of the ortho pairs of resonances and/or the meta pairs of resonances at higher temperatures. The variable-temperature spectrum of **1d** is shown in Figure 1. In complexes **1b–d** and **2b–d** both sets could be analyzed but generally more accurate data could be obtained by using the ortho (to C_α) resonances, which differed more in chemical shift. In **3** and **4** the broad, complex aryl signals due to PPh_3 normally overlapped at least one of the ortho signals and line-shape analysis was carried out only on the meta set of signals which appeared upfield of PPh_3.

The barriers to rotation determined from the variable-temperature experiments are summarized in Table III. The most complete set of data is available for **1**; the unsubstituted systems **2a–4a** could not be analyzed. Several points should be noted. First, aryl substituents have an impact on $\Delta G^{\ddagger}_{rot}$ values consistent with their ability to delocalize positive charge. Thus for **1** $\Delta G^{\ddagger}_{rot}$ are in in the order *p*-H, *p*-F < *p*-CH_3 < *p*-OCH_3. In fact, a reasonable Hammett-type correlation exists between log k_{rot} and σ^+ with a ρ value of ca. +5. These correlations and the strong sensitivity to para substituents indicate that the barrier

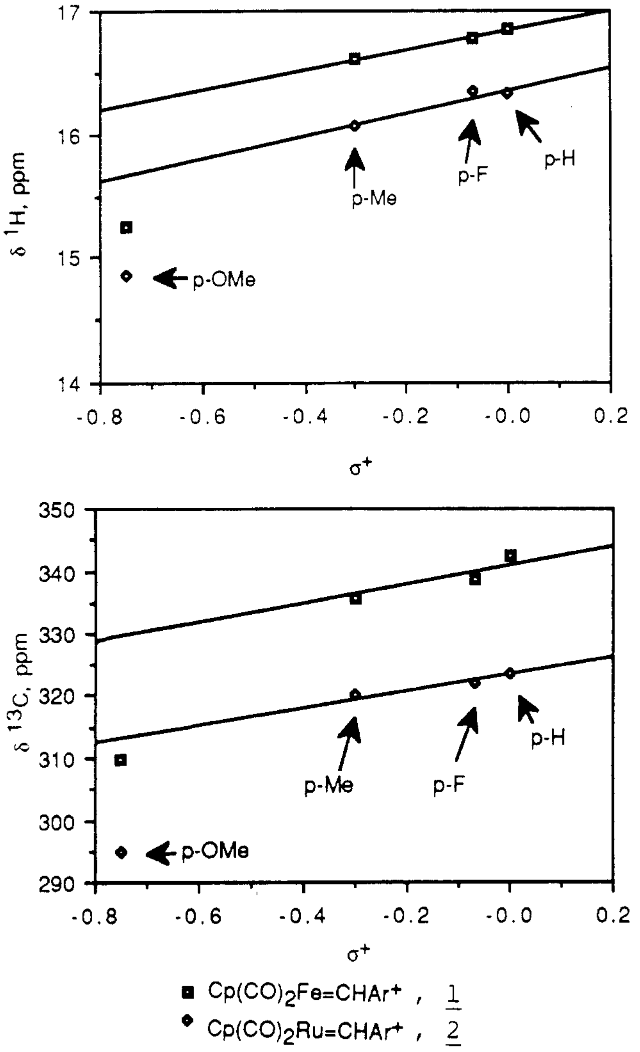


Figure 2. a. Correlation of ^{1}H chemical shifts of H_α for complexes **1a–d** and **2a–d** with Hammett σ^+ constants. b. Correlation of ^{13}C chemical shifts of C_α in complexes **1a–d** and **2a–d** with Hammett σ^+ constants.

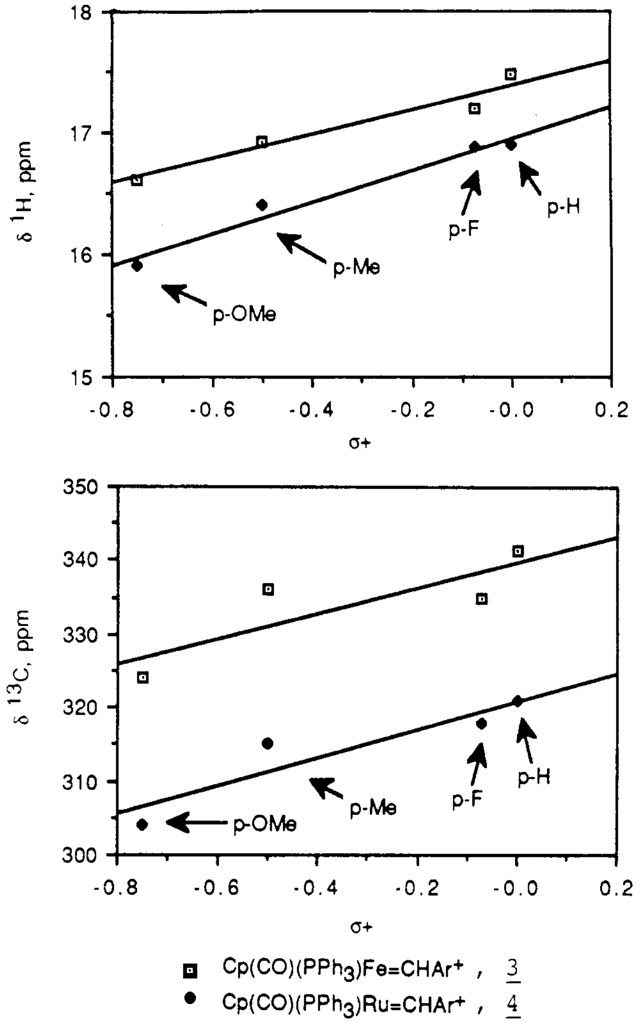
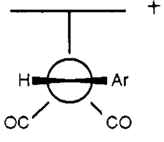


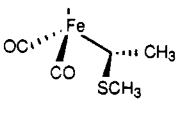
Figure 3. a. Correlation of ^{1}H chemical shifts of H_α for complexes **3a–d** and **4a–d** with Hammett σ^+ constants. b. Correlation of ^{13}C chemical shifts of C_α for complexes **3a–d** and **4a–d** with Hammett σ^+ constants.

charge densities at C_α between iron and ruthenium analogues.

Analysis of chemical shifts suggests that **1d** and **2d** may possess structures different from **1a–c** and **2a–c**. We expected a Hammett-type correlation of σ^+ with $^{13}C_\alpha$ and $^1H_\alpha$ chemical shifts of **1–4**.[21] For complexes **3** and **4** this proves to be the case as shown in Figure 2. However, for species **1** and **2**, surprisingly, the ^{13}C and ^{1}H shifts of the p-OCH_3 derivatives **1d** and **2d** are apparently out of range (Figure 2). A possible explanation of the anomalous behavior of **1d** and **2d** is that these two derivatives adopt different conformations in which the H_α–C_α–C_{ipso} plane is rotated 90° from that in **V-1d,2d** into a horizontal conformation, **H-1d,2d**, or that there is an equilibrium between **V-1d(2d)** and **H-1d(2d)** and that **H-1d(2d)** is significantly populated.[22] Previous observations lend support to this possibility. For compounds that contain strongly electron-donating substitutents at C_α, namely, **16**[23] and **17**,[24] the



H - 1d, 2d



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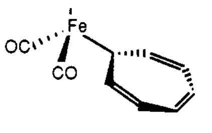

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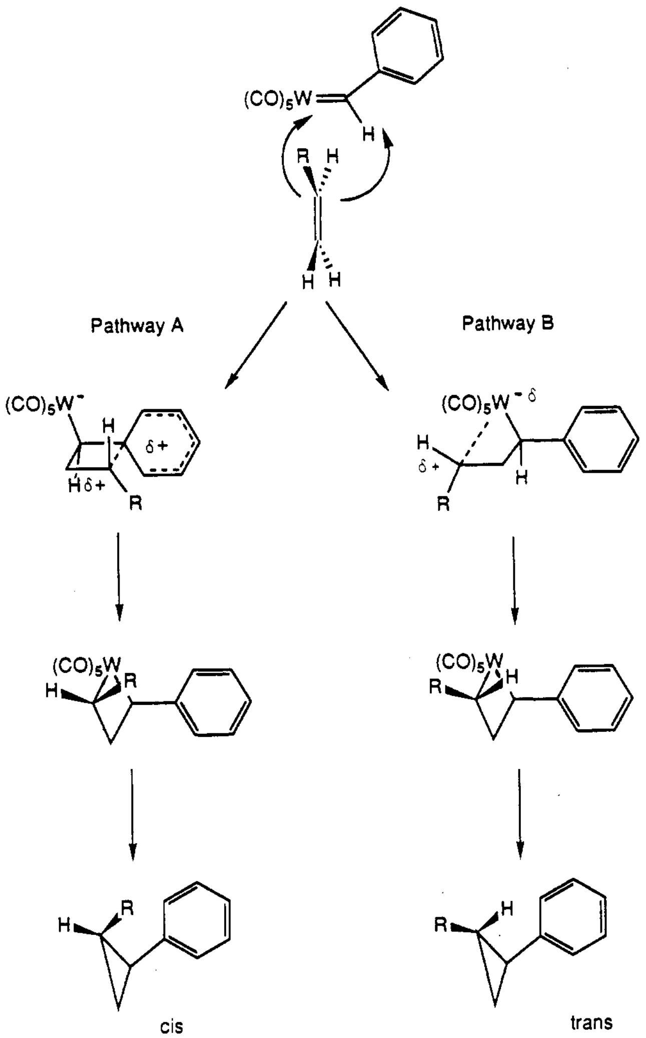
[21] (a) Ray, G. J.; Kurland, R. J.; Colter, A. K. *Tetrahedron* **1971**, *27*, 735. (b) Olah, G. A.; Porter, R. S.; Jeuell, C. L.; White, A. M. *J. Am. Chem. Soc.* **1972**, *94*, 2044. (c) Ehrenson, S.; Brownlee, R. T. C.; Taft, R. W. *Prog. Phys. Org. Chem.* **1973**, *10*, 1.

[22] A reviewer has suggested that acceptable straight lines can be drawn through all four points in parts a and b of Figure 2 and that the vertical conformation is highly questionable. We agree that the data does not firmly establish the presence of **H-1d** or **H-2d** or a mixture of **V-1d(2d)** and **H-1d(2d)**. However in view of the *apparent* deviation of the p-OMe-substituted systems in Figure 2 relative to similar plots in Figure 3 for **3**, **4**, and the anomolous *cis*/*trans*-cyclopropane isomer ratios observed upon transfer of p-methoxybenzylidene from **1d** to propene (see later), we believe it is worth considering that **H-1d** is significantly populated and that transfer reactions could proceed from this isomer. In conformation **H-1d** the carbonyl ligands are nonequivalent. Low-temperature (−120 °C) ^{13}C NMR experiments show only a single CO resonance. On the basis of other systems, the Fe–C_α rotational barrier in **1d** is expected to be very low, and the inability to "freeze out" this rotation does not rule out **H-1d**.

[23] Knors, C.; Kuo, G.-H.; Lauper, J. W.; Eigenbrot, C.; Helquist, P. *Organometallics* **1987**, *6*, 988.

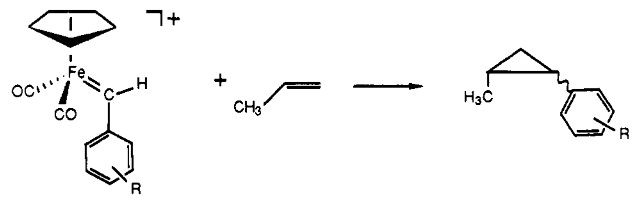
Scheme IV



preferred conformation is one in which the carbene moiety assumes the "horizontal" geometry. The vertical conformation is electronically most favorable for back-bonding from M to C_α,[17] and, apparently, the horizontal conformation is sterically most favorable. Since C_α of **16** and **17** contains strongly electron-donating substituents, back-bonding from iron is less important and steric effects dominate to dictate the horizontal conformation. This analysis would be consistent with a change in configuration going from **1a–c** to **1d** and **2a–c** to **2d** as the *p*-methoxyphenyl group is strongly electron-donating.[21] However, because **1d** and **2d** are monosubstituted (no synclinal group interacting with Cp), the relief of steric strain in going from a vertical to a horizontal conformation may be less than for **16** or **17**.

Carbene-Transfer Reactions. As outlined in the Introduction, phenylcarbene transfer from **1** to a variety of alkenes has been carried out. Our results parallel those reported by Casey[7] using $(CO)_5W{=}CHPh$, and we originally suggested that the mechanism proposed for the reactions of $(CO)_5W{=}CHPh$ might also apply to the iron systems.[8b] Specifically, this mechanism involves two competitive pathways, shown as A and B in Scheme IV, whose relative rates are largely determined by steric effects. Pathway B involves interaction of the developing charge at C_α with the metal center and yields *trans*-cyclopropanes.

Table IV



	yield,[a] %	cis/trans
1a, R = *p*-H	90	7.8
1b, R = *p*-F	80	9.4
1c, R = *p*-CH_3	60	9.0
1d, R = *p*-OCH_3	85	2.0
1e, R = *m*-OCH_3	81	9.6
1f, R = *p*-CF_3	67	7.3

[a] Reaction conditions and workup as described in the text.

Pathway A involves stabilization of the developing positive charge at C_α by interaction in the transition state with the C_{ipso} carbon of the aryl ring. For monosubstituted alkenes reacting via pathway A, the cis isomer would be preferred due to a preference for substituents to lie trans to $(CO)_5W$. For example, in the reaction with propene (cis/trans = 2) the major product is presumed to arise via pathway A.

To test the applicability of this mechanism in the iron system we carried out a series of transfers of substituted phenylcarbenes to propene and observed the cis/trans ratios of the resulting 1-aryl-2-methylcyclopropanes **18**. The transfers were accomplished by generating the carbene complex in situ in the presence of propene. Typically, a propene-saturated CH_2Cl_2 solution at 0 °C containing precursor **7** and 0.1 equiv of triethylamine[25] was treated with a slight excess of trimethylsilyl triflate. After 5 h at 0 °C, base quench, and standard workup the cis/trans ratios were assessed by GC analysis. Results are summarized in Table IV. As is apparent all cis/trans ratios are similar (ca. 8.5) with the exception of the *p*-methoxyphenyl derivative (cis/trans = 2.0).

The results appear to rule out the mechanism shown in Scheme IV as applied to the iron system. If competitive pathways obtained, the relative proportion of the reaction proceeding through pathway A should be quite sensitive to the aryl substituents since the aryl ring is called upon for charge stabilization in the transition state and substantial charge develops, especially at the ortho and para positions. The strongly electron-withdrawing substituent *p*-CF_3 would be expected to disfavor pathway A and show a higher fraction of trans isomer than electron-donating substituents such as *p*-CH_3 or *p*-OCH_3. This is not the case. The similarity of the ratios for R = *p*-H, *p*-F, *p*-CH_3, *p*-CF_3, and *m*-OCH_3 suggests these transition-state geometries for formation of cis and trans geometries are quite similar. Isomer ratios are dictated by steric interactions and are relatively insensitive to electronic effects. The structures of the transition states are unclear, but other models have been proposed.[12] The only major deviation to be noted is for *p*-OCH_3 where the cis/trans isomer ratio is a low 2.0. This low value for the reaction of only **1d** is consistent with the speculation that the conformation of **1d** may differ from the other species as noted above, although other explanations are possible.[26]

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(24) Riley, P. E.; Davis, R. E.; Allison, N. T.; Jones, W. M. *J. Am. Chem. Soc.* **1980**, *102*, 2458.

(25) Triethylamine is added to prevent any acid-catalyzed ring opening of cyclopropanes. Products were stable under reaction and workup conditions.

Summary

(1) The ^{13}C chemical shifts and the observed C_α–aryl rotational barriers in the set of complexes **1**–**4** indicate there is substatial positive charge at C_α.

(2) Aryl rotational barriers are quite sensitive to aryl substituents at the para position, and in **1a**–**d** barriers correlate reasonably well with σ^+ ($\rho = -5$). Consistent with electronic considerations, barriers are reduced by substitution of PPh_3 for CO.

(3) Ruthenium and iron analogues exhibit almost identical rotational barriers and aryl ^{13}C chemical shifts which indicates little charge difference at C_α between iron and ruthenium pairs.

(4) Transfer of substituted arylcarbenes from $Cp(CO)_2Fe{=}CHC_6H_4R^+$ to propene gives cyclopropanes which show very similar cis/trans ratios (ca. 8.5) with the exception of R = *p*-OCH_3 (2.0). These results are inconsistent with a transfer mechanism involving C_α–C_{ipso} interaction in the transition state to account for the cis stereoselectivity as previously invoked.[8b] The result for **1d** (R = *p*-OCH_3) may be due to reaction from a different (horizontal) conformation as suggested by chemical shift anomalies in **1d** and **2d**.

Experimental Section

General Data. All reactions were carried out under a dry nitrogen atmosphere using standard Schlenk techniques. All solvents were dried and distilled under nitrogen. Other reagents were commercial grade and were used as received. Infrared spectra were obtained in CH_2Cl_2 solution. Complexes **7a**–**d**, **8a**–**d**, **10a**,**c**,**d**, **11a**,**c**,**d**, **13c**,**d**, and **15a**,**c**,**d** gave satisfactory elemental analyses. The fluorine-containing complexes **7f**, **10b**, **11b**, and **15b** were relatively unstable, and satisfactory analyses could not be obtained. ^{13}C NMR data for complexes **9**, **14**, **16**, **18**, **20**, and **22** appears as supplementary material.

$Cp(CO)_2Fe(CO)(C_6H_4R)$ (5a–f). General Procedure. $Cp(CO)_2Fe^-K^+$ (1–2 g, 5–10 mmol)[11b] was stirred in 100–200 mL of THF at −80 °C, and 1 equiv of RC_6H_4COCl was added. After 5 min the product solution was warmed to room temperature and the solvent was evaporated at reduced pressure. The brown residue was extracted into hexanes and filtered through Celite to give a yellow solution which on cooling overnight at −50 °C gave yellow-orange crystals. **5a**: yield 70%; IR 2020, 1970, 1610 cm^{-1}; ^{1}H NMR (C_6D_6) δ 7.35 (m, 5 H), 4.85 (s, 5 H). **5b**: yield 56%; IR 2020, 1968, 1597 cm^{-1}; ^{1}H NMR (C_6D_6) δ 6.84–7.44 (m, 4 H), 4.37 (s, 5 H). **5c**: yield 62%; IR 2016, 1957, 1611, 1592 cm^{-1}; ^{1}H NMR ($(CD_3)_2CO$) δ 7.44 (d, J = 12 Hz, 2 H), 7.18 (d, J = 12 Hz, 2 H), 5.07 (s, 5 H), 2.32 (s, 3 H). **5d**: yield 77%; Ir 2012, 1963, 1609, 1585 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.57 (d, J = 8 Hz, 2 H), 6.84 (d, J = 8 Hz, 2 H), 4.90 (s, 5 H), 3.82 (s, 3 H). **5e**: yield 80%; IR 2019, 1959, 1624, 1591 cm^{-1}; ^{1}H NMR (C_6D_6) δ 7.05–7.31 (m, 3 H), 6.84 (d, J = 8 Hz, 1 H), 3.96 (s, 5 H), 3.31 (s, 3 H). **5f**: yield 50%; IR 2018, 1969, 1619, 1585 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.44–7.74 (m, 4 H), 4.94 (s, 5 H).

$CpFe(CO)_2CH(OCH_3)(C_6H_4R)$ (7a–f). General Procedure. The acyl complex **5** (1–2 g) and 2–3 equiv of $(CH_3)_3O^+BF_4^-$ were stirred in 50 mL of CH_2Cl_2. When the IR absorption bands due to CO stretching in **5** had completely disappeared (typically 24 h), the supernatant solution containing the heterocarbene **6** was transferred via cannula into a solution of 2 equiv of $NaBH_4$ and 4 equiv ov $NaOCH_3$ (from the reaction of Na metal with solvent) in 200 mL of CH_3OH at −80 °C. After being stirred for 15–30 min, the mixture was poured into 500 mL of 0.5 M aqueous K_2CO_3 and extracted three times with CH_2Cl_2. The combined organic fractions were dried over K_2CO_3, concentrated, and chromatographed on alumina, eluting with 9:1 hexanes/ethyl acetate. Cooling hexane solutions of the product gave yellow-orange cyrstals. **9a**: yield 70%; IR 2004, 1953 cm^{-1}; ^{1}H NMR (C_6D_6) δ 7.37 (m, 2 H), 7.22 (m, 2 H), 7.00 (m, 1 H), 5.77 (s, 1 H), 4.04 (s, 5 H), 3.21 (s, 3 H). **9b**: yield 35%; IR 2007, 1949 cm^{-1}; ^{1}H NMR ($(CD_3)_2CO$) δ 7.24 (m, 2 H), 6.96 (m, 2 H), 5.89 (s, 1 H), 4.78 (s, 5 H), 3.17 (s, 3 H). **9c**: yield 72%; IR 2001, 1953 cm^{-1}; ^{1}H NMR (C_6D_6) δ 7.30 (d, J = 7 Hz, 2 H), 7.05 (d, J = 7 Hz, 2 H), 5.82 (s, 1 H), 4.09 (s, 5 H), 3.04 (s, 3 H), 2.20 (s, 3 H). **9d**: yield 77%; IR 2000, 1951 cm^{-1}; ^{1}H NMR ($(CD_3)_2CO$) δ 7.17 (d, J = 13 Hz, 2 H), 6.78 (d, J = 13 Hz, 2 H), 5.88 (s, 1 H), 4.73 (s, 5 H), 3.75 (s, 3 H), 3.15 (s, 3 H). **9e**: yield 75%; IR 2010, 1954 cm^{-1}; ^{1}H NMR (C_6D_6) δ 6.98–7.30 (m, 3 H), 6.68 (m, 1 H), 5.82 (s, 1 H), 4.12 (s, 5 H), 3.56 (s, 3 H), 3.27 (s, 3 H). **9f**: yield 86%; IR 2002, 1947 cm^{-1}; ^{1}H NMR (C_6D_6) δ 7.48 (d, J = 8 Hz, 2 H), 7.24 (d, J = 8 Hz, 2 H), 5.61 (s, 1 H), 4.01 (s, 5 H), 3.17 (s, 3 H). IR of methoxycarbene complexes (cm^{-1}): **6a**, 2055, 2010; **6b**, 2064, 2020; **6c**, 2058, 2018; **6d**, 2054, 2014; **6e**, 2065, 2030; **6f**, 2058, 2018.

$Cp(CO)(P(C_6H_5)_3)Fe{-}CH(OCH_3)(C_6H_4R)$ (11a–d). General Procedure. The appropriate α-ether complex **7** (0.5–1.0 g) and a slight molar excess of triphenylphosphine in 150 mL of degassed benzene were bubbled with nitrogen and irradiated with a 450-W quartz-filtered mercury vapor lamp for 2 h, during which time the solution turned from yellow to deep red. The solution was then filtered through Celite and concentrated to a brown oil. A solid product could be obtained by dissolving the oil in CH_2Cl_2/heptane and slowly evaporating the CH_2Cl_2. Repetition generally gave adequate purification. **11a**: yield 78%; IR 1903 cm^{-1}; ^{1}H NMR (C_6D_6) δ 7.72 (m), 7.57 (m), 6.9–7.3 (m, 20 H), 5.20 (d, J = 9 Hz, 1 H), 4.14 (s, 5 H), 2.76 (s, 3 H). **11b**: yield 40%; IR 1902 cm^{-1}; ^{1}H NMR (CD_2Cl_2) δ 7.4–7.8 (m, 15 H), 7.13 (m, 2 H), 6.86 (m, 2 H), 4.77 (d, J = 9 Hz, 1 H), 4.06 (s, 5 H), 2.56 (s, 3 H). **11c**: yield 60%; IR 1901 cm^{-1}; ^{1}H NMR (C_6D_6) δ 7.96 (m), 7.53 (d, J = 8 Hz), 7.09 (m, 19 H), 5.25 (d, J = 10 Hz, 1 H), 4.20 (s, 5 H), 2.83 (s, 3 H), 2.23 (s, 3 H). **11d**: yield 30%; IR 1902 cm^{-1}; ^{1}H NMR (D_6D_6) δ 7.77 (m), 7.09 (m), 15 H), 7.50 (d, J = 8 Hz, 2 H), 6.90 (d, J = 8 Hz, 2 H), 5.24 (d, J = 10 Hz, 1 H), 4.23 (s, 5 H), 3.45 (s, 3 H), 2.84 (s, 3 H).

$CpRu(CO)_2{-}C(O)(C_6H_4R)$ (8a–d). General Procedure. The procedure is identical with that described for the preparation of complexes **5**, using $CpRu(CO)_2^-K^+$ (ref 11b) instead of $CpFe(CO)_2^-K^+$. Recrystallizing from hexanes gave light yellow needles. Yields are for the recrystallized products. **8a**: yield 39%; IR 2030, 1970, 1610 cm^{-1}; ^{1}H NMR ($(CD_3)_2CO$) δ 7.4 (b m, 5 H), 5.54 (s, 5 H). **8b**: yield 43%; IR 2032, 1975, 1608 cm^{-1}; ^{1}H NMR (C_6D_6) δ 7.57 (dd, J = 9, 6 Hz, 2 H), 6.89 (dd, J = 9, 9 Hz, 2 H), 4.58 (s, 5 H). **8c**: yield 23%; IR 2028, 1970, 1609 cm^{-1}; ^{1}H NMR ($(CD_3)_2CO$) δ 7.44 (d, J = 8 Hz, 2 H), 7.19 (d, J = 8 Hz, 2 H), 5.64 (s, 5 H), 2.34 (s, 3 H). **8d**: yield 77%; IR 2026, 1970, 1620, 1590 cm^{-1}; ^{1}H NMR ($(CD_3)_2CO$) δ 7.58 (d, J = 9 Hz, 2 H), 6.92 (d, J = 9 Hz, 2 H), 5.54 (s, 5 H), 3.84 (s, 3 H).

$CpRu(CO)_2{-}CH(OCH_3)(p\text{-}C_6H_4R)$ (10a–d). General Procedure. The procedure is identical with that described for the preparation of complexes **7**, using acyl complexes **8**. α-Ether complexes **10** were recrystallized from hexanes to give beige blocks. Yields are for the recrystallized products. **10a**: yield 60%; IR 2020, 1960 cm^{-1}; ^{1}H NMR ($(CD_3)_2CO$) δ 6.84–7.30 (b m, 5 H), 6.04 (s, 1 H), 5.23 (s, 5 H), 3.16 (s, 3 H). **10b**: yield 23%; IR 2019, 1958 cm^{-1}; ^{1}H NMR (C_6D_6) δ 7.14 (dd, J = 9, 5 Hz, 2 H), 6.86 (dd, J = 9, 9 Hz, 2 H), 5.85 (s, 1 H), 4.46 (s, 5 H), 3.15 (s, 3 H). **10c**: yield 56%; IR 2010, 1950 cm^{-1}; ^{1}H NMR ($(CD_3)_2CO$) δ 7.14 (d, J = 8 Hz, 2 H), 7.01 (d, J = 8 Hz, 2 H), 6.03 (s, 1 H), 5.23 (s, 5 H), 3.15 (s, 3 H). **10d**: yield 46%; IR 2002, 1950 cm^{-1}; ^{1}H NMR δ 7.16 (d, J = 9 Hz, 2 H), 6.79 (d, J = 9 Hz, 2 H), 6.03 (s, 1 H), 5.23 (s, 5 H), 3.75 (s, 3 H), 3.14 (s, 3 H).

$CpRu(P(C_6H_5)_3)(CO)_2^+PF_6^-$ (12). $CpRu(P(C_6H_5)_3)(CO)Cl$[27] (2.5 g), 2.3 g of NH_4PF_6, and 400 mL of CH_3OH were placed in a 1-L autoclave, heated to 100 °C, and stirred under 1000 psi of

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(26) Other possibilities include the following: (1) Reduction of the electrophilicity of C_α in **1d** to such an extent that the transition state now occurs quite late and resembles products, favoring a shift to smaller cis/trans ratios. This is made less plausible by the total lack of any similar trend in the cis/trans ratios of all other derivatives. (2) Closure to a metallacyclobutane which, in the case of R = *p*-OCH_3, can reopen prior to cyclopropane formation to give a stabilized *p*-anisyl carbocation. The cis:trans stereochemical relationship between CH_3 and $C_6H_4OCH_3$ can then be altered via bond rotation prior to reclosure. We note that the cis/trans ratio is *not* the same as that produced from transfer of ethylidene from $Cp(CO)_2Fe{=}CHCH_3^+$ to *p*-methoxystyrene (0.9:1), which rules out a common intermediate for these two transfers.

(27) Brookhart, M.; Kegley, S. E.; Husk, G. R. *Organometallics* **1984**, *3*, 650.

CO for 4 days. After the autoclave had been cooled and the pressure released, the solution was removed and the solvent was evaporated at reduced pressure. The residue was extracted into CH_2Cl_2 and filtered to give a yellow-green solution, which was washed with water and separated. Adding one volume hexanes with stirring precipitated a pale yellow solid which was filtered then redissolved in CH_2Cl_2. Repeating the last step precipitated 1.89 g of fine white needles (52%). The IR spectrum (CH_2Cl_2, ν_{CO} 2067, 2020 cm^{-1}) was consistent with the reported values.[28]

$CpRu(P(C_6H_5)_3)(CO)–C(O)(C_6H_4R)$ (13a–d). General Procedure. **12** (0.73 g, 1.0 mmol) was stirred in 50 mL of THF under nitrogen at −78 °C, and a twofold excess of RC_6H_4MgBr (ether solution, Aldrich) was added. The mixture was allowed to warm slowly until a clear solution was obtained, at which time several drops of water were added to quench the excess Grignard reagent. The solvent was evaporated at reduced pressure, leaving a yellow residue which was chromatographed on basic alumina, eluting with 4:1 hexanes/ethyl acetate. Evaporation of the solvent at reduced pressure yielded a yellow solid. **13a**: yield 0.52 g (92%); IR 1926, 1598, 1580, 1568 cm^{-1}; ^{1}H NMR (C_6D_6) δ 7.68 (m), 7.22 (m), 7.02 (m, 20 H), 4.83 (s, 5 H). **13b**: yield 0.50 g (86%); IR 1930, 1594, 1568 cm^{-1}; ^{1}H NMR (C_6D_6) δ 7.66 (m), 7.00 (m, 15 H), 7.49 (dd, J = 9, 6 Hz, 2 H), 6.86 (dd, J = 9, 9 Hz, 2 H), 4.81 (s, 5 H). **13c**: yield 0.22 g (39%); IR 1928, 1601, 1577 cm^{-1}; ^{1}H NMR (C_6D_6) δ 7.70, 7.03 (m, 17 H), 7.61 (d, J = 7 Hz, 2 H), 4.85 (s, 5 H), 2.13 (s, 3 H). **13d**: yield 0.27 g (46%); IR 1927, 1600, 1577 cm^{-1}; ^{1}H NMR (C_6D_6) δ 7.73, 7.02 (m, 17 H), 6.82 (d, J = 9 Hz, 2 H), 4.86 (s, 5 H), 3.32 (s, 3 H).

$CpRu(P(C_6H_5)_3)(CO)–CH(OCH_3)(C_6H_4R)$ (15a–d). General Procedure. The procedure is identical with that describe for the preparation of complexes **7** and **10**, using acyl complexes **13**. α-Ether complexes **15** were recrystallized from hexanes to give small, beige-yellow crystals. **15a**: yield 68%; IR 1913 cm^{-1}; ^{1}H NMR (C_6D_6) major isomer, δ 7.73 (m), 7.51 (m), 7.05 (m, 20 H), 5.41 (d, J = 6 Hz, 1 H), 4.52 (s, 5 H), 2.73 (s, 3 H), minor isomer, 6.8–7.7 (m, 20 H), 5.46 (d, J = 6 Hz, 1 H), 4.37 (s, 5 H), 2.60 (s, 3 H); isomer ratio ca. 5:1. **15b**: yield 50%; IR 1919 cm^{-1}; ^{1}H NMR (C_6D_6) major isomer, δ 7.72 (m), 7.07 (m, 15 H), 7.28 (m, 2 H), 6.88 (m, 2 H), 5.30 (d, J = 7 Hz, 1 H), 4.50 (s, 5 H), 2.68 (s, 3 H), minor isomer, 7.53 (m), 7.07 (m), 6.88 (m, 19 H), 5.36 (d, J = 6 Hz, 1 H), 4.36 (s, 5 H), 2.55 (s, 3 H); isomer ratio 3:1. **15c**: yield 20%; IR 1911 cm^{-1}; ^{1}H NMR (C_6D_6) major isomer, δ 7.79 (m), 7.49 (m), 7.10 (m, 19 H), 5.46 (d, J = 7 Hz, 1 H), 4.59 (s, 5 H), 2.63 (s, 3 H), 2.22 (s, 3 H), minor isomer, 7.60 (m), 7.38 (d), 7.10 (m, 19 H), 5.50 (d, J = 6 Hz, 1 H), 4.43 (s, 5 H), 2.80 (s, 3 H), 2.24 (s, 3 H); isomer ratio 10:1. **15d**: yield 54%; IR 1912 cm^{-1}; ^{1}H NMR (C_6D_6) major isomer, δ 7.76 (m), 7.07 (m, 15 H), 7.44 (d, J = 9 Hz, 2 H), 6.87 (d, J = 9 Hz, 2 H), 5.42 (d, J = 7 Hz, 1 H), 4.59 (s, 5 H), 3.40 (s, 3 H), 2.78 (s, 3 H), minor isomer, 7.57 (m), 7.07 (m, 15 H), 7.33 (d, J = 9 Hz, 2 H), 6.85 (d, J = 9 Hz, 2 H), 5.47 (d, J = 6 Hz, 1 H), 4.44 (s, 5 H), 3.42 (s, 3 H), 2.63 (s, 3 H), isomer ratio 4:1.

Generation of Carbene Complexes 1–4 for Spectroscopic Study. The appropriate α-ether complex **7**, **10**, **11**, or **15** (20–50 mg) was dissolved in 0.75 mL of CD_2Cl_2 in a 5-mm NMR tube and cooled to −80 °C. Trimethylsilyl triflate (1+ equiv) or triflic acid (2+ equiv) was then added, and the tube was shaken vigorously to ensure complete mixing of the contents. At −78 °C the tube could be evacuated without danger of the solvent bumping, and the tubes were sealed in vacuo at that temperature.

Reactions of 1a–f with Propene. Synthesis of 1-Methyl-2-phenylcyclopropanes (18a–f). General Procedure. The appropriate α-ether precursor **7** (1–2 mmol) was dissolved in 15 mL of CH_2Cl_2 at 0 °C, and the solution was saturated with propene. Trimethylsilyl triflate (1.1 equiv) and triethylamine (0.1 equiv) were then added to the stirred solution, and the solution was bubbled with propene for an additional 30 min. The deep red solution was stirred for 5 h at 0 °C, then 5 mL of 1 M aqueous $NaHCO_3$ was added, and the mixture was stirred vigorously for 5–10 min and was extracted with 5 × 10 mL of 2-methylbutane. The resulting reddish solution was filtered through a plug of neutral alumina, and the solvent was evaporated at reduced pressure to give a yellowish oil. Isolated yields reported in Table IV are for the crude product. Isomer ratios were determined by analytical gas chromatography using a 12 ft × $^1/_8$ in. stainless-steel column packed with 25% QF-1 on 80/100 Chrom W. Identical response ratios for cis and trans isomers were assumed. Cis and trans isomers were purified for spectroscopic study by preparative gas chromatography using a 14 ft × $^1/_4$ in. stainless-steel column packed with 25% QF-1 on 60/80 Chrom. W. Cis and trans geometries were assigned on the basis of established precedents using coupling constants of the benzylic hydrogen.[29] ^{1}H NMR ($CDCl_3$): **18a**, identical with published spectra;[29a] **18b** (cis isomer), δ 7.15 (dd, J = 4, 7 Hz, 2 H), 7.02 (t, J = 7 Hz, 2 H), 2.01 (dt, J = 5.6, 8.4 Hz, 1 H), 1.10 (m, 1 H), 0.96 (dt, J = 4.7, 8.4 Hz, 1 H), 0.74 (d, J = 6 Hz, 3 H), 0.49 (dt, J = 5.4, 6 Hz, 1 H); **18b** (trans isomer), δ 1.52 (dt, J = 8.4, 5 Hz, 1 H), 1.16 (d, J = 6 Hz, 3 H), other resonances obscured by major isomer; **18c** (cis isomer); δ 7.45–7.07 (m, 4 H), 2.32 (s, 3 H), 2.02 (dt, J = 6.3, 8.4 Hz, 1 H), 1.10 (m, 1 H), 0.93 (dt, 4.7, 8.5 Hz, 1 H), 0.77 (d, J = 6.6 Hz, 3 H), 0.52 (dt, J = 5, 6 Hz, 1 H); **18c** (trans isomer); δ 2.28 (s, 3 H), 1.52 (dt, J = 8.4, 4.8 Hz, 1 H), 1.16 (d, J = 6.1 Hz, 3 H), other resonances obscured by major isomer; **18d** (cis isomer); δ 7.08 (d, J = 7.5 Hz, 2 H), 6.80 (d, J = 7.5 Hz, 2 H), 3.78 (s, 3 H), 2.00 (dt, J = 6, 8.5 Hz, 1 H), 1.06 (m, 1 H), 0.94 (dt, J = 5, 8.5 Hz, 1 H), 0.78 (d, J = 6 Hz, 3 H), 0.48 (dt, J = 5, 6 Hz, 1 H); **18d** (trans isomer); δ 6.96 (d, J = 8 Hz, 2 H), 6.78 (d, J = 8 Hz, 2 H), 3.76 (s, 3 H), 1.52 (dt, J = 9, 5 Hz, 1 H), 1.16 (d, J = 6 Hz, 3 H), 0.96 (m, 1 H), 0.79 (dt, J = 5, 9 Hz, 1 H), 0.66 (dt, J = 5, 9 Hz, 1 H); **18e** (cis isomer; δ 7.16 (dd, J = 7.5, 7.0 Hz, 1 H), 6.73 (m, 3 H), 3.79 (s, 3 H), 2.05 (dt, J = 6, 8.8 Hz, 1 H), 1112 (m, 1 H), 0.97 (dt, J = 5.2, 8.8 Hz, 1 H), 0.80 (d, J = 6.4 Hz, 3 H), 0.56 (dt, J = 5.2, 6 Hz, 1 H); **18e** (trans isomer); δ 7.15 (t, J = 7.5 Hz, 1 H), 6.62 (m, 3 H), 3.78 (s, 3 H), 1.54 (dt, J = 8, 5 Hz, 1 H), 1.18 (d, J = 6.8 Hz, 3 H), 1.06 (m, 1 H), 0.84 (dt, J = 5, 8 Hz, 1 H), 0.74 (dt, J = 5, 8 Hz, 1 H); **18f** (cis isomer); δ 7.50 (d, J = 8 Hz, 2 H), 7.26 (d, J = 8 Hz, 2 H), 2.10 (dt, J = 6.1, 8.4 Hz, 1 H), 1.18 (m, 1 H), 1.04 (dt, J = 4.7, 8.4 Hz, 1 H), 0.77 (d, J = 6.1 Hz, 3 H), 0.62 (dt, J = 5, 6 Hz, 1 H); **18f** (trans isomer); δ 7.46 (d, J = 8 Hz, 2 H), 7.09 (d, J = 8 Hz, 2 H), 1.60 (dt, J = 8.4, 4.7 Hz, 1 H), 1.20 (d, J = 6.6 Hz, 3 H), other resonances obscured by major isomer.

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Registry No. **1a**, 64494-44-6; **1b**, 117040-74-1; **1c**, 75250-24-7; **1d**, 95763-51-2; **1e**, 117040-75-2; **1f**, 117040-76-3; **2a**, 117040-77-4; **2b**, 117040-78-5; **2c**, 117040-29-6; **2d**, 117040-80-9; **3a**, 64494-46-8; **3b**, 117040-81-0; **3c**, 117040-82-1; **3d**, 117040-83-2; **4a**, 117040-84-3; **4b**, 117040-85-4; **4c**, 117040-86-5; **4d**, 117040-87-6; **5a**, 12154-94-8; **5b**, 117040-88-7; **5c**, 117040-89-8; **5d**, 66485-15-2; **5e**, 117040-90-1; **5f**, 117040-91-2; **6a**, 74171-09-8; **6b**, 117024-17-6; **6c**, 117024-18-7; **6d**, 117024-19-8; **6e**, 117024-20-1; **6f**, 117024-21-2; **7a**, 64494-50-4; **7b**, 117024-22-3; **7c**, 88994-68-7; **7d**, 117024-23-4; **7e**, 117024-24-5; **7f**, 117024-25-6; **8a**, 117024-26-7; **8b**, 117040-92-3; **8c**, 117024-27-8; **8d**, 117024-28-9; **10a**, 117024-29-0; **10b**, 117024-30-3; **10c**, 117024-31-4; **10d**, 117024-32-5; **11a**, 64494-48-0; **11b**, 117024-33-6; **11c**, 117024-34-7; **11d**, 117024-35-8; **12**, 91482-99-4; **13a**, 117024-36-9; **13b**, 117024-37-0; **13c**, 117040-93-4; **13d**, 117040-94-5; **14a**, 117040-95-6; **14b**, 117040-96-7; **14c**, 117040-97-8; **14d**, 117040-98-9; **15a** (isomer 1), 117040-99-0; **15a** (isomer 2), 117141-86-3; **15b** (isomer 1), 117041-00-6; **15b** (isomer 2), 117141-87-4; **15c** (isomer 1), 117041-01-7; **15c** (isomer 2), 117141-88-5; **15d** (isomer 1), 117041-02-8; **15d** (isomer 2), 117141-89-6; *cis*-**18a**, 4866-54-0; *trans*-**18a**, 5070-01-9; *cis*-**18b**, 89321-46-0; *trans*-**18b**, 89321-47-1; *cis*-**18c**, 4076-60-2; *trans*-**18c**, 4076-61-3; *cis*-**18d**, 77525-89-4; *trans*-**18d**, 77525-88-3; *cis*-**18e**, 77525-85-0; *trans*-**18e**, 77525-84-9; *cis*-**18f**, 89321-48-2; *trans*-**18f**, 89321-49-3; $K^+Cp(CO)_2Fe$, 60039-75-0; C_6H_5COCl, 98-88-4; *p*-FC_6H_4COCl, 403-43-0; *p*-$CH_3C_6H_4COCl$, 874-60-2; *p*-$CH_3OC_6H_4COCl$, 100-07-2; *m*-

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$CH_3OC_6H_4COCl$, 1711-05-3; *p*-$CF_3C_6H_4COCl$, 329-15-7; $CpRu(CO)_2^-K^+$, 84332-45-6; $CpRu(P(C_6H_5)_3)(CO)Cl$, 32613-25-5; C_6H_5MgBr, 100-58-3; *p*-FC_6H_4MgBr, 352-13-6; *p*-$CH_3C_6H_4MgBr$, 4294-57-9; *p*-$CH_3OC_6H_4MgBr$, 13139-86-1; trimethylsilyl triflate, 27607-77-8; propene, 115-07-1.

Supplementary Material Available: ^{13}C NMR data for **9a–d**, **14a–d**, **16a–d**, **18a–d**, **20a–d**, **22a–d**, ^{13}C NMR data for PPh_3 ligand in **3a–d**, **4a–d**, **13a–d**, **11a–d**, and **15a–d**, and analytical data for **7a–d**, **8a–d**, **10a,c,d**, **11a,c,d**, **13c,d**, and **15a,c,d** (5 pages). Ordering information is given on any current masthead page.

Electrochemical Activation of Dinuclear Thiolato-Bridged Molybdenum Complexes $[Mo_2Cp_2(CO)_4(\mu\text{-}SR)_2]^{0/2+}$ (R = Me, Ph) toward Carbonyl Substitution Reactions. Electrochemical and Chemical Syntheses of Substituted Derivatives. The X-ray Crystal Structure of $[Mo_2Cp_2(CO)_3(MeCN)(\mu\text{-}SPh)_2](BF_4)_2$[†,‡]

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The dinuclear thiolato-bridged molybdenum complexes $[Mo_2Cp_2(CO)_{4-n}(L)_n(\mu\text{-}SR)_2]^{2+}$ (L = *t*-BuNC, n = 1 or 2, R = Me or Ph; L = MeCN, n = 1, R = Me or Ph) are obtained from the tetracarbonyl species $[Mo_2Cp_2(CO)_4(\mu\text{-}SR)_2]^z$ via a substitution process which is either oxidatively induced (z = 0) or catalyzed according to an electron transfer chain (ETC) mechanism (z = 2+). The results demonstrate that the reactive species involved in the substitution of *t*-BuNC or MeCN for CO is an unstable radical cation, intermediate in a single-step two-electron transfer. The nature or R is shown to have a pronounced effect on the substitution lability of the complexes, and this suggests that the substitution takes place according to a bridge-opening process. X-ray analysis of $[Mo_2Cp_2(CO)_3(MeCN)(\mu\text{-}SPh)_2](BF_4)_2$ reveals that the dimeric structure of the cation is based on a butterfly $Mo_2(\mu\text{-}S)_2$ core. The complex crystallizes in the space group $P2_1/n$ with a = 19.145 (3) Å, b = 11.583 (3) Å, c = 13.894 (4) Å, β = 96.62 (2)°, and Z = 4; R = 0.064 for refinement of 356 parameters with 2356 unique observations.

Introduction

Polynuclear transition-metal compounds have been extensively investigated in the past few years, owing to their interest as models for catalysis at metal surfaces.[2] Dinuclear complexes, the simplest models of clusters, are also very attractive, and among these compounds, species where bridging (or capping) groups are designed to maintain the metal centers close to each other throughout the reaction sequence of catalytic processes are particularly interesting.[3–12] In this respect, thiolate or sulfide ligands have been widely used to bridge, for example, molybdenum, tungsten, iron, copper, vanadium, or manganese centers in homo- or hetero(di)nuclear complexes.[4–13]

In the course of an electrochemical study of thiolato-bridged dinuclear molybdenum compounds, we observed that the simple $[Mo_2Cp_2(CO)_4(\mu\text{-}SR)_2]^z$ complexes presented the interesting property to form substituted derivatives via oxidatively induced (z = 0) *and* electron transfer chain (ETC)[14] catalyzed (z = 2+) processes. Many reactions of that type, which may or may not be catalytic,[14b] have now been reported for mono-,[15–17] di-,[18–21] and polynuclear[22–26] complexes. Transition-metal complexes[27a–d] or oxides[27e,f] are also used to catalyze substitution reactions.

Table I. Cyclic Voltammetry Data[a] Concerning the First Reduction of the $[Mo_2Cp_2(CO)_{4-x}(L)_x(\mu\text{-}SR)_2]^{2+}$ Complexes in Nonaqueous Solvents

R	x	L	solv	$E^{1/2}$ red.1,[b] V/Fc
Me	0		THF	−0.54[c]
Me	0		MeCN	−0.52[c]
Me	1	MeCN	MeCN	−0.91 (−0.87)
Me	1	*t*-BuNC	THF	−0.84
Me	2	*t*-BuNC	THF	-1.10
Ph	0		THF	−0.44[c]
Ph	0		MeCN	−0.41[c]
Ph	1	MeCN	THF	−0.76 (−0.71)
Ph	1	MeCN	MeCN	−0.76 (−0.72)
Ph	1	*t*-BuNC	THF	−0.71
Ph	2	*t*-BuNC	THF	−0.97

[a] $E^{1/2}$, E_p, and $E_{p/2}$ are obtained at 0.2 V s^{-1} unless stated otherwise. [b] For irreversible systems, the potentials given are E_p ($E_{p/2}$). [c] See ref 1.

The work reported here is concerned with the substitution of nitrile (MeCN) and isocyanide (*t*-BuNC) for CO

[†] Part 4 of "Electrochemistry of Dinuclear, Thiolato-Bridged Transition-Metal Compounds". See ref 1 for part 3.

[‡] Throughout this paper, Cp stands for (η^5-C_5H_5).

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