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Iron and Ruthenium Cyclopropylcarbene Complexes $C_5H_5(CO)_2M{=}CH(c\text{-}C_3H_5)^+CF_3SO_3^-$. Cyclopropylcarbene Transfer Reactions

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The α-ether complexes $C_5H_5(CO)_2MCH(OCH_3)(c\text{-}C_3H_5)$ (**4**, M = Fe; **9**, M = Ru) were prepared by methylation and reduction of the acyl complexes $C_5H_5(CO)_2MC(O)(c\text{-}C_3H_5)$. Treatment of **4** and **9** with trimethylsilyl triflate yields the unsubstituted cyclopropylcarbene complexes $C_5H_5(CO)_2M{=}CH(c\text{-}C_3H_5)^+$ (**5**, M = Fe; **10**, M = Ru) which were characterized by ^1H and ^{13}C NMR spectroscopy. The ^{13}C shifts of the ring carbons indicate substantial charge delocalization into the C_3 ring and nearly equal positive charge density at C_α in the Fe and Ru analogues **5** and **10**. Reactions of **5** with styrene and 2-ethyl-1-butene result in cyclopropylcarbene transfer to yield the corresponding cyclopropylcyclopropanes.

Iron carbene complexes of the type $Cp(CO)(L)Fe{=}CRR'$ (L = CO, PR_3; R, R' = H, alkyl; H, vinyl; H, aryl; CH_3, CH_3) are useful reagents for the transfer of a carbene moiety to olefins to form cyclopropanes.[1-7] Such species are of particular interest when the corresponding free carbenes or classical carbenoid reagents are too unstable to be generally synthetically useful. Furthermore, transfers are often selective and give as the major product the sterically more crowded, thermodynamically less favored cyclopropane isomer.

The stability of iron carbene complexes may depend on several factors, such as the back-bonding characteristics of the organometallic fragment, the ability of the carbene substituents R and R' to stabilize an adjacent carbocation, and the accessibility of facile decomposition pathways. For example, the complexes $Cp(CO)_2Fe{=}CH_2^+$ [1] and $Cp(CO)_2Fe{=}CHCH_3^+$ [4b,c,5b,e] have not been characterized in solution and decompose primarily via bimolecular pathways.[9] Phosphine-substituted carbene complexes $Cp(CO)(PR_3)Fe{=}CHCH_3^+$ [4b-d,9] are somewhat stable at room temperatures whereas $Cp(CO)(PPh_3)Fe{=}CHCH_2CH_3^+$ [4c] and $Cp(CO)_2Fe{=}C(CH_3)_2^+$ [6a,c] both decompose rapidly at 0 °C via an intramolecular hydride shift. Arylcarbene complexes $Cp(CO)(L)Fe{=}CH(C_6H_4R)^+$ [10] are stabilized by charge delocalization into the aryl group and may be isolated as stable salts.

Given the propensity of cyclopropyl-substituted carbenes to undergo rapid rearrangements (normally ring expansions to cyclobutenes)[11] and the well-established ability of a

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Table I. Spectroscopic Characterization of Complexes 1-10

complex		IR (CH_2Cl_2), cm^{-1}		^1H NMR, δ vs. Me_4Si					
		C≡O	C=O	C_5H_5	M—CH	OCH_3	$C_\beta H$	$C_\gamma H$	
anion[a]	1 (Fe)	1866, 1772							
	6 (Ru)	1896, 1811							
acyl[b]	2 (Fe)	2006, 1950	1630	4.22 (s)			2.33 (m)	1.12 (m, 2 H)	0.39 (m, 2 H)
	7 (Ru)	2023, 1966	1612	4.68 (s)			2.30 (m)	1.21 (m, 2 H)	0.42 (m, 2 H)
heterocarbene[c]	3 (Fe)	2060, 2012		4.27 (s)		3.39 (s)	(obscured)	1.88 (m, 2 H)	1.60 (m, 2 H)
	8 (Ru)	2068, 2018		4.22 (s)		3.58 (s)	3.20 (m)	1.84 (m, 2 H)	1.57 (m, 2 H)
α-ether[b]	4 (Fe)	1995, 1937		4.35 (s)	4.24 (d, J = 8 Hz)	3.24 (s)	1.18 (m)	0.62 (b m, 3 H)	0.33 (m, 1 H)
	9 (Ru)	2001, 1943		4.74 (s)	4.26 (d, J = 9 Hz)	3.16 (s)	1.36 (m)	0.68 (m, 1 H)	0.58 (m, 2 H) 0.27 (m, 1 H)
carbene[c]	5 (Fe)			5.66 (s)	15.47 (d, J = 14 Hz)		4.09 (m)	2.79 (m, 2 H)	2.63 (m, 2 H)
	10 (Ru)			5.95 (s)	15.35 (d, J = 16 Hz)		4.23 (m)	2.87 (m, 2 H)	2.70 (m, 2 H)

[a] IR in THF. [b] NMR in C_6D_6. [c] NMR in CD_2Cl_2.

Table II. Proton-Decoupled ^{13}C NMR of Complexes 2-5 and 7-10 (δ vs. Me_4Si)

complex		C=O	C_5H_5	M—C	OCH_3	C_β	C_γ
acyl[a]	2 (Fe)	215.2	86.2	250.2		39.4	10.5
	7 (Ru)	201.0	89.2	234.0		40.4	10.1
heterocarbene[b]	3 (Fe)	209.3	87.0	315	60.2	44.3	22.9
	8 (Ru)	195.2	89.9	305.0	61.3	44.2	23.0
α-ether[a]	4 (Fe)	218.2, 217.7	86.4	87.4	57.6	26.6	10.2, 6.9
	9 (Ru)	203.2, 202.8	89.6	81.4	57.2	27.5	10.8, 6.5
carbene[b]	5 (Fe)	207.8	92.3	365.4		61.3	37.2
	10 (Ru)	193.9	93.3	346.0		60.9	37.7

[a] C_6D_6. [b] CD_2Cl_2.

cyclopropyl group to stabilize an adjacent carbocation,[12] we felt it was both feasible and of interest to prepare a stable electrophilic transition-metal complex of a cyclopropyl carbene. In a preliminary communication we reported the synthesis, characterization, and carbene transfer reactions of $Cp(CO)_2Fe{=}CH(c\text{-}C_3H_5)^+$ (**5**).[4e] In this paper we report the full details of this study and further describe the synthesis and characterization of the ruthenium analogue to **5**, $Cp(CO)_2Ru{=}CH(c\text{-}C_3H_5)^+$ (**10**), and examine and compare the charge distributions in these two species in a ^{13}C NMR study.

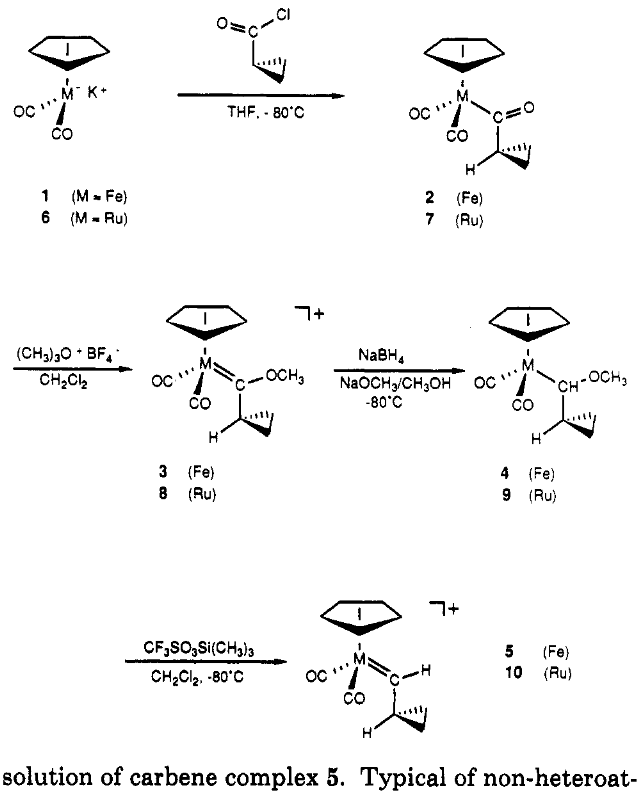
Results and Discussion

Synthesis of Carbene Precursors. The precursors to **5** and **10**, α-methyl ether complexes **4** and **9**, were prepared following well-established methods (Scheme I).[4c] Hence, treatment of $Cp(CO)_2Fe^-K^+$ (**1**) and $Cp(CO)_2Ru^-K^+$ (**6**), with $c\text{-}C_3H_5COCl$ gave acyl complexes **2** and **7** in good yields. Methylation of **2** and **7** with $(CH_3)_3O^+BF_4^-$ gave heterocarbene complexes **3** and **8**, which were not isolated but were reduced directly with basic methanolic $NaBH_4$ to give **4** and **9**. The iron α-ether complex **4**, when very pure, may be obtained as moderately air- and temperature-sensitive crystals, which may be stored cold indefinitely. The ruthenium analogue **9** is more stable and is readily obtained as a light yellow solid.

Generation and Spectroscopic Characterization of Carbene Complexes. Heteroatom carbene complexes **3** and **8** were generated for spectroscopic studies by treating CD_2Cl_2 solutions of acyl complexes **2** and **7** with excess methyl triflate. The ^{13}C NMR resonances at 315 and 305 ppm for **3** and **8**, respectively, are typical for an electrophilic carbene carbon. No decomposition of **3** or **8** was evident by ^1H NMR after the solutions were left standing in sealed tubes for several months at room temperature.

Treatment of CD_2Cl_2 solutions of the iron α-ether complex **4** at −78 °C with trimethylsilyl triflate results in methoxide abstraction and formation of a deep orange solution of carbene complex **5**. Typical of non-heteroatom-stabilized electrophilic carbene complexes were the ^1H NMR resonance at 15.47 ppm and the ^{13}C resonance at 365 ppm. Similarly, the reaction of ruthenium α-ether complex **9** in CD_2Cl_2 with trimethylsilyl triflate gives a bright yellow solution of **10**, with NMR resonances at 15.35 (^1H) and 346 ppm (^{13}C). The complete NMR data for carbene complexes **3**, **5**, **8**, and **10** are included in Tables I and II.

Scheme I



The stability of **5** and **10** and the products resulting from their decomposition is apparently similar. Both are stable in solution up to −40 °C. After a few minutes at 0 °C, ^1H NMR shows no sign of either; the spectra suggest the formation of two principal products in each case and in

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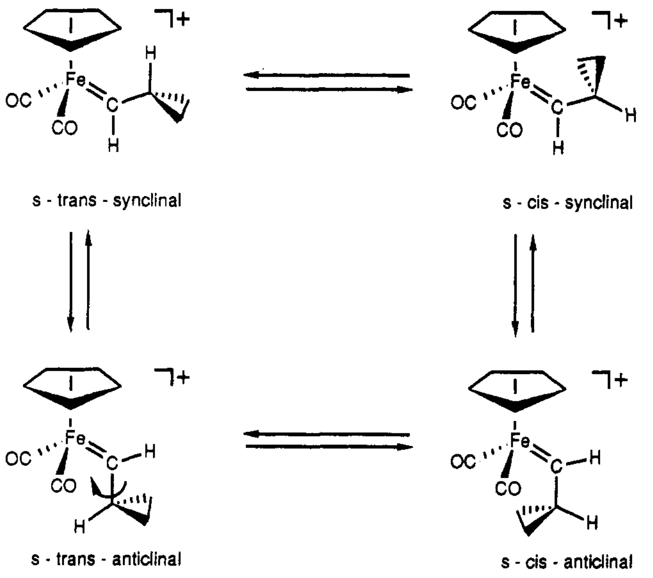
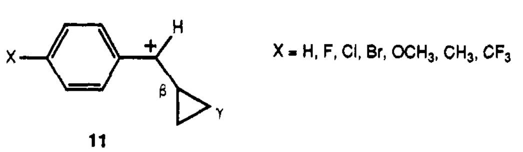


Figure 1.

similar proportions. Rearrangements of cyclopropyl-substituted cations typically result in cyclobutenes or butadienes.[12] A comparison of the ^1H spectral data for solutions of decomposed **5** and **10** with published values for $Cp(CO)_2Fe(\eta^2\text{-butadiene})^+$ [13] and with the data for an authentic sample of $Cp(CO)_2Fe(\eta^2\text{-cyclobutene})^+$ suggests that neither of the latter complexes (nor their ruthenium analogues) were obtained. Attempts to separate and further characterize the decomposition products were unsuccessful.

The 14-Hz vicinal coupling (^1H NMR) between the carbene hydrogen and the cyclopropyl hydrogen in **5** and the 16-Hz coupling in **10** are substantially larger than the 8–9-Hz couplings observed in their progenitors **4** and **9** or the 7.8-Hz coupling in the methylcarbene complex $Cp(CO)(PPh_3)Fe{=}CHCH_3^+$.[4c] They lie well outside the range for coupling constants between vinylic and allylic hydrogens as predicted by the Karplus equation and are in the range where trans-vinylic couplings are generally observed.[14] They suggest that in **5** and **10** the cyclopropyl group and the organometallic fragment assume a trans geometry across the C_α–C_β bond. Such a result would be expected on both steric and electronic grounds. Theoretical[15,16] and experimental[17] results indicate that in the ground states of **5** and **10** the carbene adopts a vertical conformation such that the plane described by Fe=C—H bisects the cyclopentadienyl ring and the CO–M–CO angle. The p_{C_α}–p_σ interaction between C_α and the cyclopropyl ring is at a maximum where the cyclopropyl ring is perpendicular to that same plane. Models suggest that of the four conformations that may then obtain (Figure 1), the one with the lowest energy should be the s-trans-anticlinal. (The barrier to rotation about Fe=C_α is very low. When **5** and **10** are generated and observed by ^1H NMR at −78 °C, there is no evidence of a second isomer, nor is dynamic behavior observed as the complexes are warmed.)

Table III. ^{13}C **NMR of Compounds 11**[a] **(δ vs. Me_4Si)**

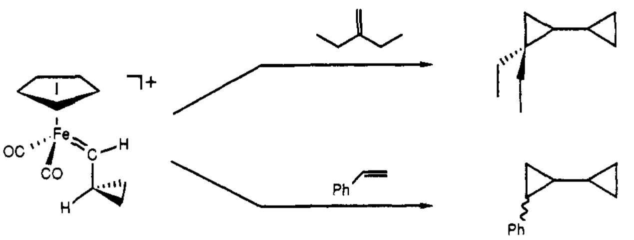


11

X	C+	C_β	C_γ
H	226.3	45.1	45.1
F	222.2	43.4	43.0
Cl	223.1	45.2	45.0
Br	223.6	45.7	45.3
OCH_3	208.6	30.7	29.1
CH_3	221.6	40.0	39.2
CF_3	225.9	54.3	53.8

[a] Taken from ref 18c.

Scheme II



Olah has shown ^{13}C NMR chemical shifts of aryl and cyclopropyl groups to be sensitive probes of charge density in aryl- and cyclopropyl-substituted carbocations.[18] An instructive example taken from the work of Olah is the C_β and C_γ shifts for the series of para-substituted aryl cyclopropyl cations, **11**.[18c] As can be seen from Table III, C_γ shifts are far downfield (29–55 ppm) relative to neutral precursors (0–15 ppm) and both C_β and C_γ shifts are remarkably sensitive to the electron-donating and -withdrawing effects of the para substituent on the aryl group. (In Olah's studies the cyclopropyl carbons were identified as C_α and C_β; to be consistent with our designation of the carbene carbon as C_α, we shall term them C_β and C_γ.)

The ^{13}C chemical shifts for C_β and C_γ in complexes **2–5** and **7–10** are given in Table II, and it is instructive to note the trends and compare the shifts to those in Table III. A progression of $\delta(^{13}C_\gamma)$ to lower fields is apparent on proceeding from neutral acyls **2** and **7** to heteroatom-stabilized carbene complexes **3** and **8** to electrophilic carbene complexes **5** and **10**. These $\Delta\delta(^{13}C_\gamma)$ reflect the increased delocalization of positive charge into the cyclopropyl ring as the sp^2 C_α bears more and more positive charge. The relatively lower $\delta(^{13}C_\gamma)$ for **3** and **8** in comparison with **5**, **10**, and **11** indicate the extent to which charge is delocalized onto the methoxy substituent. Such a result is consistent with the observation that heteroatom-substituted electrophilic carbene complexes are generally more stable and less reactive than their non-heteroatom-substituted analogues. Particularly surprising was the absence of a significant difference in $\delta(^{13}C_\beta)$ or $\delta(^{13}C_\gamma)$ between analogous iron and ruthenium complexes ($\Delta\delta(^{13}C) \leq 0.5$ ppm). This last finding suggests that, contrary to our expectations, the positive charge densities at C_α and thus the net back-bonding characteristics of the organometallic fragments $Cp(CO)_2Fe^+$ and $Cp(CO)_2Ru^+$ are about the same.[19]

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Carbene Transfer Reactions. Iron carbene complex **5** transfers c-C$_3$H$_5$CH: to alkenes to yield bicyclopropyl derivatives (Scheme II). Typically, trimethylsilyl triflate is added to a stirred solution of α-ether complex **4** and alkene in CH$_2$Cl$_2$ at −78 °C then warmed slowly to room temperature. The reaction of **5** with styrene yielded 66% of a 3.4:1 mixture of *trans*- and *cis*-2-phenylbicyclopropyl; **5** plus 2-ethyl-1-butene gave 64% of 2,2-diethyldicyclopropyl. A series of reactions conducted at constant temperatures showed that the reaction of **5** with styrene is sluggish at −78 °C (14% yield after 4 h) but proceeds readily at −50 °C (63%, 1 h). At higher temperatures decomposition is competitive with carbene transfer and yields are diminished accordingly.

cis- and *trans*-2-phenylbicyclopropyl stereochemistries were unambiguously assigned by using ^{1}H NMR.[20] The benzylic hydrogen vicinal coupling pattern $^3J_{H_1,H_2}$, $^3J_{H_1,H_3}$, and $^3J_{H_1,H_{3'}}$ = 5.2, 5.2, and 7.8 Hz, respectively, established the trans isomer as the major product of the reaction of **5** with styrene. Further confirmation of the trans stereochemistry is obtained from the higher field $\delta(^1H_{benzylic})$ of the trans isomer relative to the cis isomer (1.72 vs. 2.14 ppm), typical for 2-substituted phenylcyclopropanes.

In contrast to Cp(CO)$_2$Fe=CHR$^+$ (R = CH$_3$, C$_6$H$_5$),[4] the reaction of **5** with styrene yields the *trans*-cyclopropane as the major isomer. This reversal in stereoselectivity and indeed the factors that control stereoselectivity are presently poorly understood.

Summary

The carbocation-stabilizing ability of the cyclopropyl group can be employed to prepare stable electrophilic cyclopropyl-substituted carbene complexes Cp(CO)$_2$Fe=CH(c-C$_3$H$_5$)$^+$ (M = Fe, Ru). The iron complex is an effective cyclopropyl carbene transfer agent in contrast to free cyclopropyl carbenes which normally undergo rearrangement faster than addition to olefins. Since the preparation of **1** is general, other substituted cyclopropyl systems can no doubt be similarly prepared and transferred. The ^{13}C chemical shifts of the cyclopropyl group (especially C$_\gamma$) are an effective probe of positive charge at C$_\alpha$ and indicate that the Fe and Ru analogues **5** and **10** have almost identical charge densities at C$_\alpha$.

Experimental Section

General Data. All reactions were carried out under a dry nitrogen atmosphere by using standard Schlenk techniques. Solvents were dried and distilled under a nitrogen atmosphere. All other reagents were commercial grade and were used as received. Infrared spectra were recorded on a Beckman 4250 spectrometer and referenced to the polystyrene absorbance at 1601 cm^{-1}. NMR spectra were obtained on a Bruker WM 250 spectrometer equipped with a 5-mm dual ^{1}H/^{13}C probe. Chemical shifts are in ppm vs. tetramethylsilane. Elemental analyses were performed by Galbraith Laboratories (Knoxville, TN) and MicAnal (Tucson, AZ). Gas chromatography was performed on a Hewlett-Packard 5750 gas chromatograph using a thermal conductivity detector.

Cp(CO)$_2$Fe$^-$K$^+$ (1). The entire reaction and workup were carried out under a nitrogen atmosphere in a glovebox. A solution of 21.24 g (0.06 mol) of Cp$_2$Fe$_2$(CO)$_4$ in 850 mL of THF in a 3-L flask was stirred with 4.6 g (0.12 mol of metal + slight excess) of NaK$_{2.8}$ alloy (prepared from the metals). Vigorous mechanical stirring was necessary for complete reaction. After 12–15 h the IR spectrum showed complete disappearance of the carbonyl bands of the starting material and the appearance of two very strong bands at 1772 and 1866 cm^{-1}. Filtration first on a large (600 mL) coarse-fritted Buchner funnel and then on a medium-fritted funnel removed all traces of residual finely divided alkali metal without clogging the filters. Addition of 1–2 volumes of hexane to the anion salt solution precipitated golden platelets that were filtered, washed with hexane, and suction-dried. Yields were typically ca. 25 g (95%). Elemental analysis has shown the counterion to be almost entirely potassium (13.98% K vs. 0.16% Na). Because of the acute air sensitivity of the product, however, a C–H analysis within the standard error limits for C$_7$H$_5$FeKO$_2$ could not be obtained.

Cp(CO)$_2$Ru$^-$K$^+$ (6). The entire reaction and workup was carried out under a nitrogen atmosphere in a glovebox. The procedure parallels that described for **1**. The reaction mixture consisted of 11.10 g (0.025 mol) of Cp$_2$Ru$_2$(CO)$_4$ and 3.6 g (0.1 mol of metal, twofold excess) of NaK$_{2.8}$ alloy in 350 mL of THF. Vigorous mechanical stirring was necessary for complete reaction. After 24 h the IR spectrum showed complete disappearance of the carbonyl bands of the starting material and the appearance of two very strong bands at 1896 and 1811 cm^{-1}. Addition of 1–2 volumes of hexane to the filtered anion salt solution precipitated yellow-green platelets that were filtered, washed with hexane, and suction-dried; yield 11.8 g (91%). Elemental analysis has shown the counterion to be almost entirely potassium (12.68% K vs. 0.04% Na). Because of the acute air sensitivity of the product, however, a C–H analysis within the standard error limits for C$_7$H$_5$RuKO$_2$ could not be obtained.

CpFe(CO)$_2$C(O)(c-C$_3$H$_5$) (2). c-C$_3$H$_5$COCl (1.8 mL, 20 mmol) was added to a stirred solution of 4.22 g (20 mmol) of CpFe(CO)$_2^-$K$^+$ in 200 mL of THF at −80 °C, which was then allowed to warm to room temperature over the course of 2 h. The solvent was evaporated at reduced pressure, leaving a brown residue. The residue was extracted into 100 mL of hexanes and filtered over Celite to give a yellow-orange solution, which on standing at −50 °C yielded 3.37 g (68%) of orange blocks of **2**. IR and ^{1}H NMR: see Table I. ^{13}C NMR: see Table II. Anal. Calcd for C$_{11}$H$_{10}$FeO$_3$: C, 53.70; H, 4.10. Found: C, 53.35; H, 4.10.

NMR Observation of CpFe(CO)$_2$=C(OCH$_3$)(c-C$_3$H$_5$) (3). **2** (26 mg) was dissolved in 0.7 mL of CD$_2$Cl$_2$ in a 5-mm NMR tube. CF$_3$SO$_3$CH$_3$ (50 μL, excess) was added, the solution was cooled to −80 °C, and the tube was evacuated and sealed. After being warmed back to room temperature, the solution was shaken vigorously and allowed to stand for 2 days. The ^{1}H NMR spectrum taken after that time showed only **3** and no sign of starting material. ^{1}H NMR: see Table I. ^{13}C NMR: see Table II.

CpFe(CO)$_2$CH(OCH$_3$)(c-C$_3$H$_5$) (4). **2** (4.92 g, 20 mmol) and 4.4 g (excess) of (CH$_3$)$_3$O$^+$BF$_4^-$ were stirred in 80 mL of CH$_2$Cl$_2$. After 2 days the IR absorption bands due to **2** had disappeared and new bands had appeared at 2060 and 2012 cm^{-1} due to heterocarbene complex **3**. The solution was transferred via cannula into a solution at −78 °C prepared from 200 mL of CH$_3$OH, 0.5 g of Na, and 1.6 g (40 mmol) of NaBH$_4$. The resulting solution was stirred for 15 min and then was poured into 400 mL of degassed 1 M aqueous K$_2$CO$_3$. The organic layer was separated, and the aqueous layer was extracted with 25 mL of CH$_2$Cl$_2$ (3×). The combined organic fractions were dried over anhydrous K$_2$CO$_3$ and filtered, and the solvent was evaporated at reduced pressure. The product oil was chromatographed on neutral alumina with 5:1 hexanes/ethyl acetate; the first and largest band to elute was collected, and the solvent was evaporated at reduced pressure to give a red-orange oil. The oil was dissolved in hexanes and allowed to stand overnight at −50 °C to yield 2.74 g (52%) of **4** as yellow-orange crystals. IR and ^{1}H NMR: see Table I. ^{13}C NMR: see Table II. Anal. Calcd for C$_{12}$H$_{14}$FeO$_3$: C, 54.99; H, 5.38. Found: C, 55.17; H, 5.14.

CpRu(CO)$_2$C(O)(c-C$_3$H$_5$) (7). A solution of 0.5 g (2 mmol) of CpRu(CO)$_2^-$K$^+$ (**6**) in 35 mL of THF at −80 °C was treated with 0.18 mL (2 mmol) of c-C$_3$H$_5$COCl and stirred for 30 min. After the mixture had been warmed to room temperature, the solvent was evaporated at reduced pressure and the residue was extracted into hexanes and filtered. The solvent was again evaporated, and

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[19] A reviewer has pointed out that differences in conformational equilibria between the Ru and Fe systems could affect conclusions based on ^{13}C shifts. We believe the nearly identical ^{13}C shifts of analogous species in these two systems and the identical rotational barriers in Ru and Fe methylene complexes[17] where conformational problems are absent support the simplest interpretation: charge densities at C$_\alpha$ and ground-state conformations are the same.

[20] (a) Closs, G. I.; Moss, R. A. *J. Am. Chem. Soc.* **1964**, *86*, 4042. (b) Moss, R. A. *J. Org. Chem.* **1965**, *30*, 3261.

the oily product was chromatographed on neutral alumina with 4:1 hexanes/ethyl acetate. The first, pale yellow fraction to elute was collected, and the solvent was evaporated at reduced pressure. The pale yellow soild **7** was recrystallized from hexanes at −50 °C to give 0.2 g (35%) of beige needles. IR and ^{1}H NMR: see Table I. ^{13}C NMR: see Table II. Anal. Calcd for $C_{11}H_{10}O_3Ru$: C, 45.36; H, 3.46. Found: C, 45.39; H, 3.42.

NMR Observation of $CpRu(CO)_2{=}C(OCH_3)(c\text{-}C_3H_5)^+CF_3SO_3^-$ (8). A solution of 10 mg of **7** in 0.7 mL of CD_2Cl_2 in a 5-mm NMR tube was treated with 50 μL of $CF_3SO_3CH_3$ and then cooled to −80 °C. The tube was evacuated, sealed, and then warmed back to room temperature, the contents were shaken vigorously. The ^{1}H NMR spectrum after 24 h showed only **8** and no sign of the starting material **7**. ^{1}H NMR: see Table I. ^{13}C NMR: see Table II.

$CpRu(CO)_2CH(OCH_3)(c\text{-}C_3H_5)$ (9). A mixture of 0.2 g (0.7 mmol) of **7** and 0.3 g (2 mmol, excess) of $(CH_3)_3O^+BF_4^-$ was stirred in 15 mL of CH_2Cl_2. After 24 h the IR bands due to **7** (CO stretching in **7**) had disappeared and new bands appeared at 2068 and 2018 cm^{-1} due to the heterocarbene complex **8**. The solution was transferred via cannula to a solution at −78 °C prepared from 25 mL of CH_3OH, 0.2 g of Na, and 0.1 g (2.5 mmol) of $NaBH_4$. The resulting pale yellow solution was stirred for 30 min at −78 °C and then was allowed to warm for 30 min more. It was then poured into 200 mL of aqueous 0.5 M K_2CO_3, and the mixture was extracted with 25 ml of CH_2Cl_2 (3×). The combined organic fractions were dried over anhydrous K_2CO_3 and filtered, and the solvent was evaporated at reduced pressure. The mixture was chromatographed on basic alumina with 10:1 hexanes/ethyl acetate, and the fractions containing the product were combined and evaporated at reduced pressure to give 75 mg (35%) of **9** as a pale yellow powder. IR and ^{1}H NMR: see Table I. ^{13}C NMR: see Table II.

NMR Observation of $CpM(CO)_2{=}CH(c\text{-}C_3H_5)^+CF_3SO_3^-$ (5, 10). General Procedure. A solution of 10–50 μmol of **4** or **9** in 0.7 mL of CD_2Cl_2 in a 5-mm NMR tube was cooled to −78 °C and treated with excess $CF_3SO_3Si(CH_3)_3$. The NMR tube was then evacuated and sealed, and the sample was kept cold until placed in the spectrometer.

Transfer Reactions of $CpFe(CO)_2{=}CH(c\text{-}C_3H_5)^+CF_3SO_3^-$. General Procedure. A solution of 3–5 mmol of **5** and 2 equiv of olefin in 100 mL of CH_2Cl_2 was treated at −78 °C with 1 equiv of $CF_3SO_3Si(CH_3)_3$ and then stirred while slowly being warmed to room temperature over a 3-4-h period. Aqueous 1 M K_2CO_3 (100 mL) was then added to the deep red solution, and the mixture was stirred for 5 min. The organic layer was separated, and the aqueous layer was reextracted with 50 mL of CH_2Cl_2 (2×). The combined organic fractions were evaporated to a red-brown oil, which was taken up in 2-methylbutane and filtered through neutral alumina to give a nearly colorless solution. The latter was reduced in volume to 1–2 mL at reduced pressure, and the internal standard for GC analysis was added.

Purification and Characterization of Transfer Products. (a) Reaction of 5 with Styrene. The product mixture was chromatographed in 50-μL aliquots by using the following GC conditions: column, 20 ft × $^1/_4$ in. 20% QF-1 on Chromosorb W; chromatograph, T_{oven} = 175 °C, T_{inj} = 230 °C, T_{det} = 260 °C, carrier flow = 30 mL min^{-1} He. Independent injections showed retention times for the solvent to be 3 min, for styrene to be 5 min, and for the dodecane standard to be 12 min. Products eluted at 12 and 14$^1/_2$ min and were collected and identified as *cis*- and *trans*-2-phenylbicyclopropyl, **12**, respectively. A second passage of the purified isomers through the column was required for their complete separation. The purified major product was used to calibrate the internal standard (the minor product was assumed to have the same response factor as the major product). ^{1}H NMR (CD_3NO_2, δ vs. Me_4Si): *cis*-**12**, 0.18 (m, 2 H), 0.30 (m, 3 H) (C_3H_5), 0.82 (m, 1 H), 0.90 (m, 1 H), 0.99 (m, 1 H) ($2H_t + 1H_c$), 2.14 (dt, *J* = 6.5, 8.6, 8.6 Hz, 1 H) (PhCH), 7.14 (m, 1 H), 7.29 (m, 4 H) (PhH); *trans*-**12**, 0.22 (m, 2 H), 0.45 (m, 2 H), 0.99 (m, 1 H) (C_3H_5), 0.81 (m, 2 H), 1.15 (m, 1 H) ($1H_t + 2H_c$), 1.72 (dt, *J* = 7.8, 5.2, 5.2 Hz) (PhCH), 7.10 (b m, 3 H), 7.28 (b m, 2 H) (PhH). ^{13}C NMR (CD_3NO_2, off-resonance decoupled): δ 146 (s, ipso-C_{Ar}), 127–131 (m, C_{Ar}), 27 (d, CHPh), 23 (d), 15 (t), 14 (d), 5 (t), 4 (t).

(b) Reaction with 2-Ethyl-1-butene. The product was chromatographed by using the conditions described above, except with T_{oven} = 110 °C. The *n*-nonane internal standard eluted at 6 min and the major product at 9 min. The product was collected and identified as 2,2-diethylbicyclopropyl (**13**). The purified product was then used to calibrate the internal standard and determine the yield. ^{1}H NMR (CD_3NO_2, δ vs. Me_4Si): −0.05 (m, 1 H), 0.12 (m, 2 H), 0.27 (m, 2 H), 0.42 (m, 2 H), 0.58 (m, 1 H) (C_3H_5 + 3 H, α-diethyl); 0.85 (t, 3 H), 0.96 (t, 3 H), 1.16 (q, 2 H), 1.41 (q, 2 H) (diastereotopic CH_2CH_3).

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Registry No. **1**, 60039-75-0; **2**, 32963-18-1; **3**, 107769-64-2; **4**, 95763-46-5; **5**, 95763-43-2; **6**, 84332-45-6; **7**, 107769-65-3; **8**, 107769-67-5; **10**, 107769-70-0; *cis-12*, 95763-54-5; *trans*-**12**, 95763-55-6; **13**, 95763-53-4; $Cp_2Fe_2(CO)_4$, 12154-95-9; $Cp_2Ru_2(CO)_4$, 12132-87-5; c-C_3H_5COCl, 4023-34-1; styrene, 100-42-5; 2-methyl-1-butene, 760-21-4.