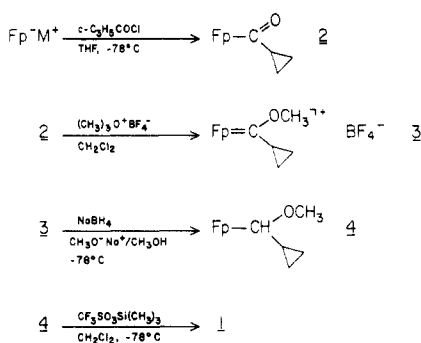


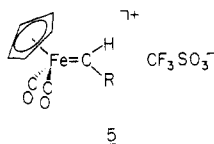
Scheme I



the solution of **3** directly into a cold ($-78\text{ }^{\circ}\text{C}$), stirred solution of NaBH_4 in basic methanol gives the alkylidene precursor $\text{FpCH}(\text{OCH}_3)(\text{c-C}_3\text{H}_5)$ (**4**) (50%).¹² Yellow crystals of **4** (hexane, $-60\text{ }^{\circ}\text{C}$) are stable only for short periods at room temperature but may be kept indefinitely under nitrogen below $0\text{ }^{\circ}\text{C}$.

The cyclopropylmethylidene complex **1** was generated by treatment of **4** in CD_2Cl_2 at $-78\text{ }^{\circ}\text{C}$ with a slight excess of trimethylsilyl triflate. The identification of **1** was based on ^1H and ^{13}C NMR data.¹³ The ^1H resonance at 16.7 ppm and the ^{13}C resonance at 365 ppm are most indicative of the carbene structure and are consistent with those observed for other $(\text{CO})(\text{L})\text{CpFe}=\text{CHR}^+$ complexes.²⁻⁵ Variable-temperature ^1H NMR indicated that decomposition of **1** began at -30 to $-40\text{ }^{\circ}\text{C}$ and was complete on warming to $0\text{ }^{\circ}\text{C}$, based on the total disappearance of the resonance at 16.7 ppm. The decomposition products are complex and were not characterized.

The thermal stability of **1** clearly surpasses that of other monosubstituted Fp^+ -alkylidene complexes and rivals the stability of Fp^+ -arylidene complexes. Fp^+ -ethylidene (**5a**)

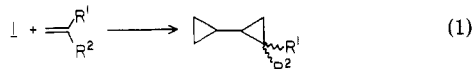


a, $\text{R} = \text{CH}_3$; b, $\text{R} = \text{CH}_2\text{CH}_3$; c, $\text{R} = \text{CH}(\text{CH}_3)_2$; d, $\text{R} = \text{c-C}_4\text{H}_7$; e, $\text{R} = \text{C}_6\text{H}_5$, $p\text{-C}_6\text{H}_4\text{CH}_3$, $p\text{-C}_6\text{H}_4\text{OCH}_3$

and Fp^+ -propylidene (**5b**) complexes cannot be spectroscopically observed and their transient existence is only implied by the transfer of the alkylidene moiety to an olefinic substrate.² The lifetimes of **5c**^{2g} and **5d**¹⁴ are even shorter and transfers are unsuccessful. Fp^+ -arylidene complexes **5e** are spectroscopically observable and, depending on the aryl substituents, may be stable at room temperature.^{2b} Fp^+ -arylidene stability is a consequence of the delocalization of the positive charge into the aryl

ring. This property should be shared by the cyclopropyl substituent whose ability to stabilize adjacent carbocation centers is similar to that of the aryl substituent.¹⁵

Complex **1** transfers $\text{c-C}_3\text{H}_7\text{CH}$: to alkenes to give di-cyclopropyl derivatives (eq 1). In a typical procedure



trimethylsilyl triflate (1 equiv) is added to a stirred solution of **4** (1 equiv) and alkene (2 equiv) in CH_2Cl_2 at $-78\text{ }^{\circ}\text{C}$ and then warmed slowly to room temperature. Neutralizing the burgundy solution with aqueous K_2CO_3 and standard workup^{2e} yields clear colorless hexane solutions of the cyclopropanes. Purification and isomer separation is achieved by preparative GLC ($1/4$ in. \times 19 ft 20% QF-1 on 80/100 Chromosorb W). The reaction of **1** with 2-ethyl-1-butene gives a 64% yield of 2,2-diethyldicyclopropyl¹⁶ while the reaction with styrene gives a 66% yield of *cis*- and *trans*-2-phenyldicyclopropyl (3.4:1 *trans*:*cis* ratio).¹⁷ This *trans* selectivity contrasts with the approximately 4:1 *cis* selectivity typically observed for the reaction of **5a** with styrenes.

Acknowledgment is made to the U.S. Army Research Office and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

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(16) ^1H NMR (250 MHz, CDCl_3): δ -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), 0.85 (t, 3 H), 0.96 (t, 3 H), CH_2CH_3 , 1.16 (q, 2 H), 1.41 (q, 2 H, CH_2CH_3).

(17) ^1H NMR (250 MHz, CD_3NO_2): *cis* isomer, δ 0.1-0.4 (b m, 5 H), 0.8-1.1 (b m, 3 H), 2.14 (dt, $J = 6.5, 8.6, 8.6$ Hz, 1 H, PhCH), 7.17 (m, 1 H), 7.29 (m, 4 H); *trans* isomer, δ 0.22 (m, 2 H), 0.45 (m, 2 H), 0.81 (m, 2 H) 0.99 (m, 1 H), 1.15 (m, 1 H), 1.72 (dt, $J = 7.8, 5.2, 5.2$ Hz, 1 H, PhCH), 7.10 (b m, 3 H), 7.28 (b m, 2 H). *Cis* and *trans* geometries in the products may be assigned on the basis of observed vicinal coupling constants and on the chemical shift of the benzylic cyclopropyl hydrogen, with the resonance for the *cis* isomer appearing at lower fields.^{2g}

Photoinduced Ring Expansion of a Cyclopropyliron σ -Complex to a Metallacyclopentenone: An Example of Alkyl Group Rearrangement from Carbon to Iron To Generate a Carbene Complex

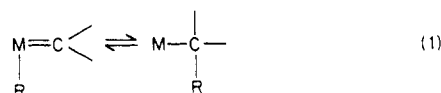
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Summary: Photolysis of acyl complex **1** or σ -complex **2** results in formation of the ring-expanded carbene complex **6**, presumably via the metallacyclobutene complex **4**. The proposed mechanism involves migration of alkyl from carbon to 16-electron coordinately unsaturated iron, thus generating the carbene complex **4** which subsequently ring expands to give **6**.

On the basis of extended Hückel calculations, Hoffmann and co-workers have made the interesting prediction that the interconversion of metal alkyl and metal carbene complexes should be facile (eq 1).^{1,2} Indeed, there have



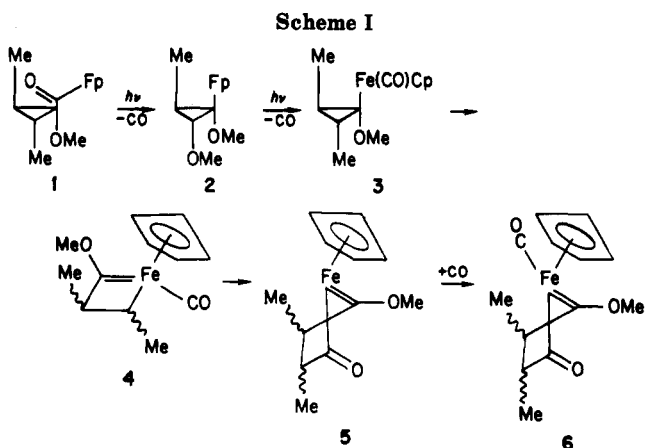
(10) IR (CH_2Cl_2): $\nu_{\text{C=O}}$ 2015, 1955 cm^{-1} ; $\nu_{\text{C-O}}$ 1630 cm^{-1} . ^1H NMR (100 MHz, C_6D_6): δ 0.39 (m, 2 H), 1.12 (m, 2 H), 2.33 (m, 1 H), 4.22 (s, 5 H). ^{13}C NMR (62.89 MHz, off-resonance decoupled, C_6D_6): δ 10.5 (t), 39.4 (d), 86.2 (d), 215.1 (s), 250.0 (s). Anal. Found (Calcd): C, 53.35 (53.70); H, 4.10 (4.10).

(11) IR (CH_2Cl_2): $\nu_{\text{C=O}}$ 2060, 2012 cm^{-1} .

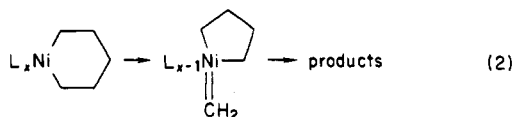
(12) IR (CH_2Cl_2): $\nu_{\text{C=O}}$ 1998, 1936 cm^{-1} . ^1H NMR (100 MHz, C_6D_6): δ 0.6 (b m, 4 H), 1.3 (b m, 1 H), 3.18 (s, 3 H), 4.18 (d, $J = 8$ Hz, 1 H), 4.27 (s, 5 H). ^{13}C NMR (62.89 MHz, off-resonance decoupled, C_6D_6): δ 7.0 (t), 10.2 (t), 26.5 (d), 57.6 (q), 86.3 (d), 87.4 (d), 217.7 (s), 218.2 (s).

(13) ^1H NMR (250 MHz, $-50\text{ }^{\circ}\text{C}$, CD_2Cl_2): δ 2.61 (m, 2 H), 2.79 (m, 2 H, CH_2CH_2), 4.15 (m, 1 H, CHCH_2CH_2), 5.70 (s, 5 H, C_6H_5), 16.73 (d, 1 H, $J = 13$ Hz, $\text{Fe}=\text{CH}$). ^{13}C NMR (62.89 MHz, off-resonance decoupled, $-50\text{ }^{\circ}\text{C}$, CD_2Cl_2): δ 37 (t, CH_2CH_2), 62 (d, CHCH_2CH_2), 92 (d, C_6H_5), 207 (s, $\text{C}=\text{O}$), 365 (d, $\text{Fe}=\text{CH}$).

(14) Unpublished results.



recently appeared a number of clear cases of the forward reaction, i.e., alkyl rearrangement from metals to carbene carbons to give new metal alkyls.³⁻⁵ However, the reverse of this reaction has been considerably more elusive.⁶ In fact, to date eq 2 is the only case to our knowledge in which strong evidence is provided for such a rearrangement.¹⁴



Cooper and Green have suggested that the reason rearrangements from saturated carbon to metal to give carbene complexes have not been more frequently encountered may be thermodynamic in origin;⁷ the primary advantage of the right side of eq 1 resting on the C-C vs. C-M bond strength. This would suggest that systems might be designed to favor the carbene side of the equilibrium, in which case the reverse rearrangement might be observed.

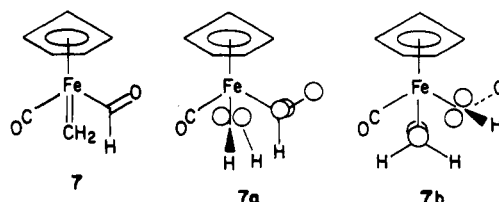
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- (3) Thorn, D. L.; Tulip, T. H. *J. Am. Chem. Soc.* **1981**, *103*, 5984.
- (4) van Leeuwen, P. W. N. M.; Roobeek, C. F.; Huis, R. *J. Organomet. Chem.* **1977**, *142*, 243.
- (5) Threlkel, R. S.; Bercaw, J. E. *J. Am. Chem. Soc.* **1981**, *103*, 2650.
- (6) Analogous hydride shifts are also predicted to be facile, and indeed, a number of well-documented examples of such rearrangements in both directions have appeared in recent years.^{7,8} Such rearrangements have also been postulated as key steps in such important reactions as olefin metathesis⁹ (rearrangement of hydride from saturated carbon to metal to generate the catalyst; however, other mechanisms have recently been provided¹⁰) and the Fischer-Tropsch reaction¹¹ (rearrangement of hydride, or alkyl, from metal to carbene carbon). The carbene producing step in Schrock's now classic preparation of Ta and Nb carbene complexes¹² (and the analogous Pt complex of Whitesides¹³) also most certainly involve at least the early stages of hydride migration from saturated carbon to metal. However, in these cases it is not clear whether the migration is complete before the hydrogen is abstracted by alkyl.
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At this time, we report the photoinduced rearrangement of 2 to 6 (Scheme I) which is believed to go via the carbene complex 4.¹⁵ This example of the reverse of eq 1 apparently occurs because the normal thermodynamic advantage for the metal alkyl is offset by methoxy stabilization of the carbene side of the equation and ring strain destabilization of the metal alkyl side.

The acyl complex 1 was prepared for another purpose, and its synthesis and properties have been reported elsewhere.¹⁶ Photolysis of a benzene solution of 1 under a nitrogen atmosphere with a 450-W Hanovia medium-pressure lamp followed by chromatography over silica gel (230-400 mesh; ethyl acetate-hexane 10:90 v/v) gave 6 (30%) as red crystals, mp 79.5-80.0 °C. The structure assignment rests on chemical analysis, IR and ¹H and ¹³C NMR.¹⁷ Of particular importance in this structural assignment are the ¹³C resonances at 216.8 (terminal CO), 269.2 (bridging CO), and 348.1 (carbene carbon) ppm.

The stereochemistry of the two methyl groups in 6 is unknown. In principle, rearrangement of 2 to 6 could give four enantiomeric pairs of diastereomers; two with methyl groups cis and two with methyls trans. In fact, although 6 was isolated in only 30% yield, from the ¹H NMR of the crude reaction mixture the isolated stereoisomer is formed in large preponderance with, at most, only traces of minor isomers. The fact that deuterium exchange in 6 occurred without isomerization^{18a} and the expectation that rearrangement of 3 to 4 and 4 to 5 would both be stereospecific with retention make it likely that the two methyls are trans. It should also be noted that a preponderance of one isomer (regardless of stereochemistry) requires either a highly regioselective rearrangement of 3 to 4^{18b} or product equilibration by racemization at the iron center. Both of these questions will be addressed.

The preferred conformation of the carbene complex is interesting because 6 corresponds to an "upright"¹⁹ conformation of the carbene while 8 corresponds to a "bisecting"¹⁹ conformation. EHMO calculations on model systems 7a and 7b predict 7a to be favored by 8.1 kcal/



mol²⁰⁻²² which leads to the expectation that conformation

- (15) Rosenblum has prepared a somewhat analogous five-membered metallocycle carbene by treatment of cyclohexene oxide with KFe(CO)₂Cp and subsequent methylation of an equilibrium mixture of the anionic σ and carbene complexes. Klemarczyk, P.; Price, P.; Priester, W.; Rosenblum, M. *J. Organomet. Chem.* **1977**, *139*, C25.

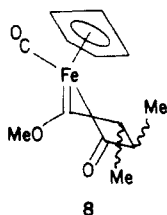
- (16) Lisko, J. R.; Jones, W. M. *Organometallics*, in press.
- (17) IR (KBr) 2950 (3), 1950(s), 1625(m), 1450(w), 1360(m), 900(m), 730(m) cm⁻¹; ¹H NMR (300 MHz, benzene-d₆) δ 0.936 (d, 3 H, ³J_{HH} = 6.89 Hz), 1.085 (d, 3 H, ³J_{HH} = 7.01 Hz), 1.926 (p, 1 H, ³J_{HH} = 7.01 Hz), 2.109 (p, 1 H, ³J_{HH} = 7.18 Hz), 3.739 (s, 3 H), 4.353 (s, 5 H); ¹³C NMR (75 MHz, benzene-d₆) δ 15.8244 (CH₃), 16.7991 (CH₃), 63.8712 (CH), 66.2104 (OC-H₃), 69.0369 (CH), 86.4801 (Cp), 216.783 (C=O), 269.249 (C=O), 348.088 (carbene C); mass spectrum, *m/e* 276 (M⁺). Anal. Calcd for C₁₃H₁₆O₃Fe: C, 56.44; H, 5.84. Found: C, 56.29; H, 5.91.

- (18) (a) Treatment of 6 with D₂O under basic conditions resulted in signal loss for the methine hydrogen (δ 2.109) and collapse of the methyl doublet (δ 1.085) to a singlet, with all other resonances remaining unchanged. Epimerization, with its concomitant chemical shift changes, would be expected if 6 were a higher energy isomer (cis-dimethyl). (b) High diastereoselectivity has been in related iron systems: Lennon, P.; Priester, W.; Rosan, A.; Mádharao, M.; Rosenblum, M. *J. Organomet. Chem.* **1977**, *139*, C29.

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6 would be favored over 8. Consistent with this prediction was an observed NOE effect between Cp and OCH₃ and the absence of such an effect between Cp and either methyl.^{23,24}



The facility of the rearrangement of 2 to 6 is striking and probably results from a combination of methoxy acceleration and relief of strain. Thus, the methoxy group can do little to stabilize 2 while conjugation with the p orbital in the carbene should have a significant impact on the energy of 4. It is more difficult to assess the contribution of strain relief to this reaction because even though there would be little question that ring strain on the cyclopropane side of the equilibrium is about 25 kcal/mol,²⁵ the strain on the metallacyclobutene side is not known. Were the rearrangement to a carbocycle, strain would slightly favor the cyclopropane; however, small ring metallocycles are probably much less strained than their carbocyclic analogues.²⁶ However, it is unlikely that relief of ring strain, alone, is sufficient to induce the rearrangement since photolysis of cyclopropyl σ -complexes with α -hydrogens showed no reaction.²⁷

Attempts to obtain evidence for the intermediacy of 3 in the rearrangement sequence by studying the effect of added CO on the rate of rearrangement were inconclusive due to the photoinduced decomposition of 6 which was retarded by the presence of CO. However, the mechanism in Scheme I is probably correct in view of the known photobehavior of Fp-alkyl complexes²⁸ as well as our successful isolation of the primary rearrangement product (corresponding to 4) from rearrangement of cyclobutyl²⁹ and cyclobutenyl³⁰ complexes. These results as well as anticipated mechanisms studies on the rearrangement of 2 to 6 will be provided in future papers.

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Cyclopentadienylvanadium(III) and -vanadium(II) Methyl, Phenyl, and Borohydride Compounds

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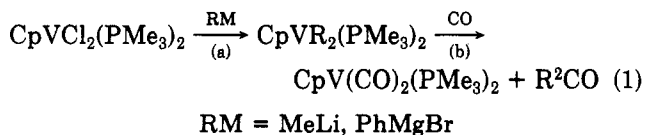
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Summary: Reaction of CpVCl₂(PMe₃)₂ with MeLi and PhMgBr yields CpVMe₂(PMe₃)₂ and CpVPh₂(PMe₃)₂, respectively. Conproportionation of CpVCl₂(PMe₃)₂ and CpVMe₂(PMe₃)₂ gives selective conversion to CpVMe(CI)(PMe₃)₂. These paramagnetic compounds show isotropic ¹H NMR shifts of the P-Me protons. CpVMe₂(PMe₃)₂ reacts rapidly with CO to give acetone and *diag*-CpV(CO)₂(PMe₃)₂. Borohydride converts CpVCl(Me₂PCH₂CH₂PMe₂) to CpV(η^2 -BH₄)(dmpe), shown to have one unpaired electron, two less than its chloride precursor. Conversion of this monochloride to CpVR(dmpe) occurs with MeLi and PhMgBr. The monomethyl compound has a low VC-H stretching frequency (2750 cm⁻¹), but the crystal structure shows no agostic hydrogen to be involved. Crystal data (-158 °C): *a* = 12.526 (3) Å, *b* = 9.285 (2) Å, *c* = 12.772 (3) Å, *Z* = 4 in space group *P*2₁2₁2₁.

Complexes of the early transition metals containing one η^5 -C₅H₅ ligand are currently under study¹⁻⁶ since they are less sterically encumbered and offer more metal orbitals for transformations of coordinated ligands than do their bis(η^5 -C₅H₅) relatives. Among early transition metals, representatives of the first transition series are particularly interesting since they offer a situation atypical in organometallic chemistry, that of isolable paramagnetic compounds. For example, all monomeric CpV²⁺ compounds, although d², contain two unpaired electrons.^{7,8} We report here the synthesis of methyl and phenyl compounds of the CpV²⁺ and CpV⁺ fragments, as well as their characterization by selected physical methods and reactivity studies.

As summarized in eq 1a, purple-blue CpVCl₂(PMe₃)₂ can be converted, in Et₂O at -30 °C, to red CpVR₂(PMe₃)₂, R = Me and Ph.⁹ Both air-sensitive compounds can be



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