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Regio- and Diastereoselectivity in the Rearrangement of Cationic Iron(II) η^1-1-(1-Methylcycloalkyl)methylidenes

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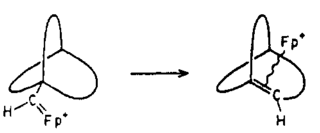
A series of $(CO)(\eta^5\text{-}C_5H_5)(L)Fe\text{-}\eta^1\text{-}\{[-(CH_2)_n-]C(CH_3)CH(OCH_3)\}$ complexes [**7a–d** (n = 2–5, L = CO) and **8a–d** or **9a–d** (n = 2–5, L = $P(OMe)_3$)], when protonated in dichloromethane at −80 to −60 °C, produce $(CO)(\eta^5\text{-}C_5H_5)(L)Fe\text{-}\eta^1\text{-}\{[-(CH_2)_n-]C(CH_3)CH)\}^{+}$'s [**10a–d**$^+$ (n = 2–5, L = CO) or **11a–d**$^+$ (n = 2–5, L = $P(OMe)_3$)] whose rearrangement to iron(II) η^2-olefin complex(es) has been monitored at reduced temperature by NMR. The putative Fp [**10a–d** (n = 2–5, L = CO)] and Fp′ [**11b** (n = 3, L = $P(OMe)_3$)] alkylidenes themselves are too reactive to detect at −80 °C, but the $P(OMe)_3$-ligated (Fp′) alkylidenes **11a,c,d** (n = 2, 4, 5), being less reactive, can be observed by ^{13}C, ^1H, and/or ^{31}P NMR at −80 °C. The resulting Fp′(η^2-olefin) complexes in all cases are appreciably less stable thermally than their Fp counterparts. The thermally unstable η^2-olefin rearrangement products are identified by reduced temperature NMR of the reaction mixtures and by decomplexation with excess tetrabutylammonium iodide followed by capillary GLPC of the resulting olefin(s) **18a–d** and **19d**. These iron(II) η^1-alkylidene rearrangements are highly regioselective: ring enlargement is exclusive in the Fp (**10a–c**) and Fp′ (**11a–c**) cases while methyl migration is prepoderant in the Fp and Fp′ cyclohexyls [**10d** and **11d** (n = 5), respectively]. The rearrangements of the chiral Fp′ alkylidenes **11a–d** are apparently also diastereoselective, producing substantially more of one diastereomeric η^2-olefin complex than of its diastereotopic "epimer". The less stable of the two diastereomeric Fp′ η^2-1-methylcyclobutenes [**14a** or **15a** (n = 2) (and possibly of the others as well)] isomerizes to the more stable under the reaction conditions, thus preventing an assessment of the true kinetic diastereoselectivity of this (and presumably of all these) Fp′ alkylidene rearrangment(s). The relative rates and regiospecificities of these η^1-alkylidene to η^2-olefin rearrangements apparently reflect the strain-energy differences between the starting Fp or Fp′ alkylidene and the rearranged β-Fp or Fp′ carbocation as estimated by molecular mechanics (PCMODEL) with ametallic cations as models for the starting alkylidenes and rearranged olefin complexes.

We have recently shown that some cationic dicarbonyl(η^5-cyclopentadienyl)[η^1-(1-polycycloalkyl)methylidene]iron(II) complexes rearrange to cationic dicarbonyl(η^5-cyclopentadienyl)(η^2-1-homopolycycloalkene)iron(II) complexes by shifting a β-bound carbon to the α-position[1a–d] (eq 1). Similar shifts also occur in acyclic

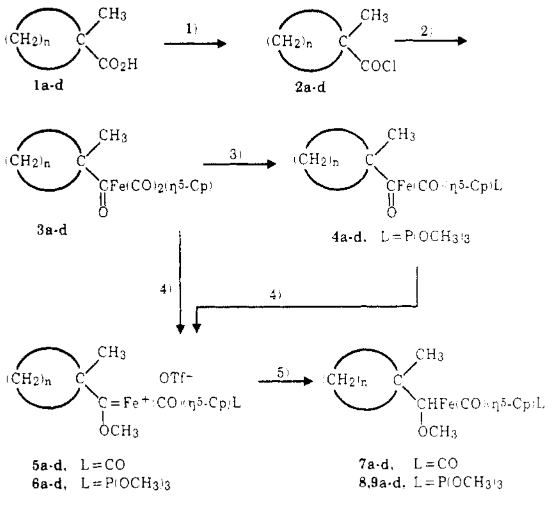


(1)

Fp(η^1-alkylidenes) [Fp = $(CO)_2(\eta^5\text{-}C_5H_5)Fe$], where the relative migratory aptitudes are β-H > β-C_6H_5 > β-CH_3[1e] (eq 2). To extend this reaction to monocyclic *tert*-alkyl-type methylidenes and to examine the effects of ring size and metal ligation upon the relative rates, i.e. regiospecificity, of ring enlargement vs methyl migration, we have prepared a series of Fp- (**7a–d**) and Fp′[η^1-(1-methylcycloalkyl)methoxymethyl] complexes [Fp′ = $(CO)(\eta^5\text{-}C_5H_5)(P(OCH_3)_3)Fe$] (**8a–d** or **9a–d**, respectively) and examined the rearrangement products of the corresponding Fp- and Fp′[η^1-(1-methylcycloalkyl)methylidenes)] (**10a–d** and **11a–d**, respectively), which result when the methoxymethyls **7–9** react in dichloromethane with tetrafluoroboric acid etherate at −20 °C.

(2)

Scheme I



a, $n=2$ b, $n=3$ c, $n=4$ d, $n=5$

1) $(COCl)_2$, C_6H_6 2) $KFe(CO)_2(\eta^5\text{-}Cp)$ 3) hν(pyrex), $P(OCH_3)_3$

4) CH_3OTf 5) $NaBH_4$, CH_3O^-, CH_3OH

Results

The required (1-methylcycloalkyl)methoxymethyl complexes **7–9** were prepared from the known carboxylic acids **1** via the acid chlorides **2** as outlined in Scheme I. The trimethyl phosphite ligated iron(II) acyls **4** were formed from the Fp acyls **3** by photolysis in the presence of excess trimethyl phosphite.[2d,f] Methylation of the Fp or Fp′ acyls

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[1] (a) Bly, R. S.; Silverman, G. S. *Organometallics* **1984**, *3*, 1765. (b) Bly, R. S.; Hossain, M. M.; Lebioda, L. *J. Am. Chem. Soc.* **1985**, *107*, 5549. (c) Bly, R. S.; Bly, R. K.; Hossain, M. M.; Lebioda, L.; Raja, M. *J. Am. Chem. Soc.* **1988**, *110*, 7723. (d) Bly, R. S.; Silverman, G. S.; Bly, R. K. *J. Am. Chem. Soc.* **1988**, *110*, 7730. (e) Bly, R. S.; Bly, R. K. *J. Chem. Soc., Chem. Commun.* **1986**, 1046.

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3 or 4, respectively, with methyl triflate produces the corresponding iron(II) Fischer carbenes **5** or **6**. The Fp carbenes **5** were not isolated but, in the manner of Brookhart et al.,[2a,b] reduced in situ to the desired Fp methoxyalkyls **7** with basic sodium borohydride. The Fp′ carbenes **6a–d** were isolated prior to reduction. They are thermally unstable but, with the exception of **6c**, can be characterized spectroscopically. We observe but a single conformer by ^1H NMR spectroscopy at ~25 °C or by $^{13}C\{^1H\}$ NMR spectroscopy at 10 °C. On the basis of the earlier investigations of Brookhart,[2] Gladysz,[3] Davies,[4] and Liebeskind,[5] we presume it to be the more stable synclinal[6a] rotomer in each case. As noted previously by Brookhart et al.,[2b] the phosphite-ligated acyls are considerably more reactive than their Fp analogues.

Reduction of racemic Fischer carbene **6a** with basic borohydride gives a 2.5:1 mixture of racemic diastereomers. On the basis of the observed splitting of the C α-hydrogen and the β-carbon by phosphorus ($^3J_{PH} = 13.6$ Hz, $^3J_{PC} = 3.3$ Hz) in the ^1H and $^{13}C\{^1H\}$ NMR spectra of the major component **8a**, we assign it the *RS,SR* configuration.[2e,4d,e,6d,7] The minor diastereomer **9a** ($^3J_{PH} = 7.8$ Hz, $^3J_{PC} \approx 0$ Hz) is thus *RR,SS*. Similar reductions of **6b–d** yield a single diastereomer in each case.

The reduced products **8** and/or **9** are unstable even at reduced temperatures—we do not know whether the diastereoselectivities are kinetic or thermodynamic. Both Ayscough and Davies[4g] and Brookhart and Buck[2f] have previously noted that borohydride reduction of a Cp(CO)(Ph_3P or Et_3P)Fe-type Fischer carbene proceeds stereoselectively, but it seems unlikely that trimethyl phosphite (cone angle 107°) could produce the high kinetic diastereoselectivity observed with either a triphenylphosphine (cone angle 184°) or triethylphosphine (cone angle 132°) ligated carbene.[2e,5a]

Scheme II

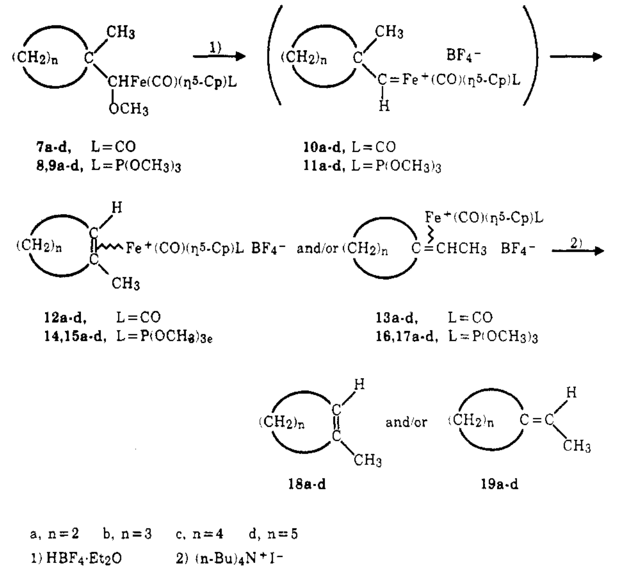

Table I. Fraction of Ring-Enlarged versus Methyl-Migrated Olefin in Decomplexed Product Mixtures from the Rearrangement of Fp- or Fp′-η^1-(1-methylcycloalkyl)methylidene Tetrafluoroborates (10 or 11)

Fp- or Fp′-(η^1-1-methylcycloalkyl)-methylidene	1-methyl-homocyclo-alkene (%)	ethylidene-cycloalkane (%)
10a	**18a**: >99.5	**19a**: <0.5
10b	**18b**: >99.5	**19b**: <0.5
10c	**18c**: >99.5	**19c**: <0.5
10d	**18d**: ~0.8	**19d**: ~99.2
11a	**18a**: >99.5	**19a**: <0.5
11b	**18b**: >99.5	**19b**: <0.5
11c	**18c**: >99.5	**19c**: <0.5
11d	**18d**: <0.5	**19d**: >99.5

We attribute the poor yields for the conversion of **3b–d** to **7b–d** (30%, 21%, and 38%, respectively) to the formation during each reduction of substantial amounts of Fp dimer and unknown organometallic byproducts presumably arising from further reduction of the methoxyalkyls.[2a,b,f] These byproducts are not formed when either **5a** or the phosphite-ligated carbenes **6** are reduced in a similar manner.

Protonation of the Fp and Fp′ methoxyalkyls **7–9** in dichlorodideuteriomethane at reduced temperature produces alkylidenes **10** or **11** whose rearrangements were followed by monitoring the vinyl, cyclopentadienyl, and/or methyl hydrogen and/or -carbon resonances or, in the case of **11a**, the ^{31}P resonance of the product π-complex(s), by NMR. In contrast to our earlier studies of polycyclic or acyclic Fp methylidenes,[1] we were not able to detect the putative Fp alkylidenes **10** spectroscopically; their rearrangement, even at −80 °C, is too rapid. As expected,[8] the Fp′ alkylidenes **11** are less reactive: at −80 °C the presence of **11a,c,d** is revealed by characteristic ^{13}C resonances of the methylidene and/or cyclopentadienyl carbons at δ

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[2] (a) Brookhart, M.; Tucker, J. R.; Husk, G. R. *J. Am. Chem. Soc.* **1981**, *103*, 979. (b) Brookhart, M.; Tucker, J. R.; Husk, G. R. *J. Am. Chem. Soc.* **1983**, *105*, 258. (c) Brookhart, M.; Timmers, D.; Tucker, J. R.; Williams, G. D.; Husk, G. R.; Brunner, H.; Hammer, B. *J. Am. Chem. Soc.* **1983**, *105*, 6721. (d) Buck, R. C.; Brookhart, M. *Abstracts of Papers*, 191st National Meeting of the American Chemical Society, New York, April 13–18, 1986; American Chemical Society: Washington, DC, 1986; INOR 422. (e) Brookhart, M.; Liu, Y.; Buck, R. C. *J. Am. Chem. Soc.* **1988**, *110*, 2337. (f) Brookhart, M.; Buck, R. C. *J. Am. Chem. Soc.* **1989**, *111*, 559.

[3] (a) Constable, A. G.; Gladysz, J. A. *J. Organomet. Chem.* **1980**, *202*, C21. (b) Kiel, W. A.; Lin, G.-Y.; Constable, A. G.; McCormick, F. B.; Strouse, C. E.; Eisenstein, O.; Gladysz, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 4865. (c) Buhro, W. E.; Wong, A.; Merrifield, J. H.; Lin, G.-Y.; Constable, A. C.; Gladysz, J. A. *Organometallics* **1983**, *2*, 1852. (d) Kiel, W. A.; Lin, G.-Y.; Bodner, G. S.; Gladysz, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 4958. (e) Merrifield, J. H.; Lin, G.-Y.; Kiel, W. A.; Gladysz, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 5811. (f) Hatton, W. G.; Gladysz, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 6157. (g) Crocco, G. L.; Gladysz, J. A. *J. Am. Chem. Soc.* **1985**, *107*, 4103. (h) Georgiou, S.; Gladysz, J. A. *Tetrahedron* **1986**, *42*, 1109. (i) O'Connor, E. J.; Kobayashi, M.; Floss, H. G.; Gladysz, J. A. *J. Am. Chem. Soc.* **1987**, *109*, 4837. (j) Bodner, G. S.; Smith, D. E.; Hatton, W. G.; Heah, P. C.; Georgiou, S.; Rheingold, A. L.; Geib, S. J.; Hutchinson, J. P.; Gladysz, J. A. *J. Am. Chem. Soc.* **1987**, *109*, 7688.

[4] (a) Baird, G. D.; Davies, S. G. *J. Organomet. Chem.* **1983**, *248*, C1. (b) Ambler, P. W.; Davies, S. G. *Tetrahedron Lett.* **1985**, *26*, 2129. (c) Baird, G. J.; Davies, S. G.; Maberly, T. R. *Organometallics* **1984**, *3*, 1764. (d) Davies, S. G.; Seeman, J. I. *Tetrahedron Lett.* **1984**, *25*, 1845. (e) Seeman, J. I.; Davies, S. G. *J. Chem. Soc., Chem. Commun.* **1984**, 1019. (f) Seeman, J. I.; Davies, S. G. *J. Am. Chem. Soc.* **1986**, *108*, 6328. (g) Ayscough, A. P.; Davies, S. G. *J. Chem. Soc., Chem. Commun.* **1986**, 1648. (h) Davies, S. G.; Dordor-Hedgecock, I. M.; Warner, P. *J. Organomet. Chem.* **1985**, *285*, 213. (i) Davies, S. G.; Dordor-Hedgecock, I. M.; Warner, P. *Tetrahedron Lett.* **1985**, *26*, 2125. (j) Brown, S. L.; Davies, S. G.; Warner, P.; Jones, R. H.; Prout, K. *J. Chem. Soc., Chem. Commun.* **1985**, 1446. (k) Davies, S. G.; Walker, J. C. *J. Chem. Soc., Chem. Commun.* **1986**, 609.

[5] (a) Liebeskind, L. S.; Welker, M. E.; Fengl, R. W. *J. Am. Chem. Soc.* **1986**, *108*, 6328. (b) Liebeskind, L. S.; Fengl, R. W.; Welker, M. E. *Tetrahedron Lett.* **1985**, *26*, 3075, 3079. (c) Liebeskind, L. S.; Welker, M. E.; Goedken, V. *J. Am. Chem. Soc.* **1984**, *106*, 441. (d) Liebeskind, L. S.; Welker, M. E. *Organometallics* **1983**, *2*, 194.

[6] (a) The synclinal rotamer is that in which the highest priority[6b] groups Fe (Cp) and C (OMe) define a 60 ± 30° torsion angle.[6c] In an anticlinal rotamer they define a 120 ± 30° angle. (b) Stanley, K.; Baird, M. C. *J. Am. Chem. Soc.* **1975**, *97*, 6598. (c) Cf.: *Pure Appl. Chem.* **1976**, *43*, 11. (d) Following the Baird convention,[6b] we specify the configuration of the metal center first.

[7] Wetzel, R. B.; Kenyon, G. L. *J. Chem. Soc., Chem. Commun.* **1973**, 287.

[8] (a) Bodnar, T.; Cutler, A. R. *J. Organomet. Chem.* **1981**, *231*, C31. (b) Brookhart, M.; Tucker, J. R.; Flood, T. C.; Jensen, J. *J. Am. Chem. Soc.* **1980**, *102*, 1203.

Table II. Diastereomeric Fp′-(η^2-olefin)$^+$ Product Ratios from the Rearrangement of Fp′-η^1-(1-methylcycloalkyl)methylidene Tetrafluoroborates (11)

Fp′-η^1-(1-methylcycloalkyl)methylidene	product mixture[a]	ratio
11a	14a/15a	~4.5/1[b] ~1.8/1[c]
11b	14b	*d*
11c	14c/15c	~1/1[b]
11d	16d	*d*

[a] The assignments are arbitrary; we do not know the relative configurations of these two diastereomers. [b] At −66 °C. [c] At −66 °C after 5 1-min warmings to approximately room temperature. [d] A single π-complex was observed at −78 °C.

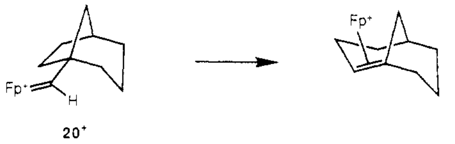
392–361 and/or 89.7–91.5, respectively and, in **11a**, by the ^{31}P resonance at δ 169. We have been unable to detect the Fp′ alkylidene **11b** in the reaction mixture from the protonation of **8b** and/or **9b**. As the cyclobutylalkylidenes **10b** and **11b** are predicted (vide infra) to be the most reactive of the iron(II) alkylidenes that we have examined,[1c] perhaps this is not unexpected.

The identity of the dominant or exclusive η^2-olefin rearrangement product of alkylidenes **10** and **11** (Scheme II) was inferred from the methyl hydrogen resonance at δ ~1.8 in the ^{1}H NMR spectra of the reaction mixtures of **10** and **11** and $HBF_4 \cdot Et_2O$ in CD_2Cl_2 at −20 °C (cf. Scheme II). It appears as a singlet in the product mixtures of **10a–c** and **11a–c** but is split into a doublet (J = 6 Hz) by a vicinal hydrogen in those of **10d** and **11d**. The η^2-olefin products **12a–c**, **13d**, **14a–c** and/or **15a–c**, and **16d** and/or **17d**, though reasonably stable in dichloromethane at −20 °C, being trisubstituted, are but marginally so at room temperature. The Fp′ π-complexes are appreciably less stable thermally than their Fp counterparts. No attempt was made to isolate the η^2-olefin complexes at room temperature, but rather they were decomposed in situ with excess tetrabutylammonium iodide.[9] The volatiles were vacuum-transferred, and the decomplexed olefins **18** and **19** were analyzed by $^{13}C\{^1H\}$ NMR and by capillary GLPC. The assignments, except for that of **18a**, were confirmed by admixture and comparison with known, pure (99+%) samples of the relevant 1-methylcycloalkene and/or ethylidenecycloalkane. The rearrangement products after decomplexation are summarized in Table I.

The chiral Fp′ alkylidenes **11** are expected a priori to produce diastereomeric Fp′(η^2-olefin) complexes **14** and **15** and/or **16** and **17**. As indicated in Table II the presence of diastereomeric π-complexes has been observed by NMR in the cyclopropyl and cyclopentyl cases **11a** and **11c**, respectively. In **11a** the initially formed ~4.5/1 mixture of **14a** and **15a** at −66 °C isomerizes to an ~1.8/1 mixture when warmed briefly but repeatedly to room temperature. When the latter mixture is recooled to −66 °C, it does *not* revert to the original mixture, implying that the isomerization is irreversible at this temperature. In the cases of **11b** and **11d**, a single diastereomer is apparent in the product mixture. Because of the lability of the trisubstituted Fp′[η^2-(olefin)]$^+BF_4^-$'s at or below room temperature, we have not attempted to utilize synthetically the diastereospecificity present in the ring enlargements or methyl migration.

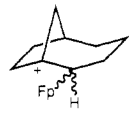
Discussion

The alkylidene-to-olefin rearrangements reported here as well as those discussed earlier[1] are surprisingly regioselective: but a single regioisomeric η^2-olefin complex can be observed by ^{13}C or ^{1}H NMR in each case. We have attributed similar regioselectivity in the rearrangement of Fp[η^1-(1-bicyclo[3.2.1]octyl)methylidene]$^+$ (**20$^+$**) (eq 3) to

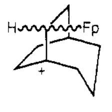


(3)

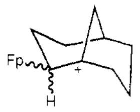
large differences in the stability of the bridgehead-cation-like transition states that are required: 1-bicyclo[4.2.1]nonyl-like (**21$^+$**) for propano bridge migration, 1-bicyclo[3.2.2]nonyl-like (**22$^+$**) for methano bridge migration, or 1-bicyclo[3.3.1]nonyl-like (**23$^+$**) for ethano bridge migration. Only ethano bridge migration is observed (eq 3) apparently because the 1-bicyclo[3.3.1]nonyl cation-like transition state ($|23^+|^\ddagger$) is about 4 kcal/mol more stable (less strained) than either of the other two.



21$^+$

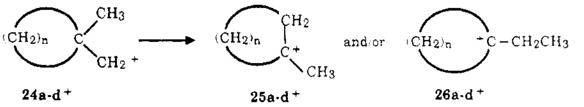


22$^+$



23$^+$

If this suggestion is correct, it should also apply to the putative (1-methylcycloalkyl)methylidene rearrangements reported here. We have tested its applicability by modeling the strain energies of the transition states SE^+_{ts} for ring enlargement and for methyl migration, respectively, using cations **25$^+$** and **26$^+$** (eq 4) (cf. Table III).



(4)

Whereas we employed a linear free energy relation based upon the ethanolysis rates of the corresponding bridgehead bromides[10,11] for our earlier estimates of bridgehead cation SE's, our present estimates were made utilizing the molecular mechanics software routine PCMODEL derived from C. Still's (Columbia) MODEL program (VAX version 1.1) modified by K. Steliou (Montreal), adapted to the IBM-PC by M. M. Midland (California, Riverside), worked on

Table III. Estimated Relative Strain-Energy Differences for the Alternate Methyl Migration or Ring Enlargement of Fp- or Fp′-[η-1-(1-cycloalkyl)methylidenes]$^+$ (10$^+$ or 11$^+$) Modeled as Ametallic Carbocations

SM^{+a}	SE^+_{sm}, kcal/mol	RC^{+b}	SE^+_{ts}, kcal/mol	δH,[c] kcal/mol	ΔH_{corr},[d] kcal/mol
24a$^+$	28.22	**25a$^+$**	27.95	−0.27	0.14
		26a$^+$	77.94	49.72	49.72
24b$^+$	28.23	**25b$^+$**	8.36	−19.87	−19.56
		26b$^+$	26.97	−1.26	−1.36
24c$^+$	10.49	**25c$^+$**	5.77	−4.72	−5.31
		26c$^+$	8.79	−1.70	−1.70
24d$^+$	5.55	**25d$^+$**	10.55	5.00	5.41
		26d$^+$	6.26	0.71	0.71
29$^+$	1.78	**30$^+$**	2.97	1.19	1.84

[a] Carbocation models for starting alkylidenes **10$^+$** and **11$^+$**. [b] Carbocation models for ring-enlarged, **25$^+$**, and methyl-migrated, **26$^+$**, products, i.e. **18$^+$** and **19$^+$**, respectively. [c] $\delta H \approx SE^+_{ts} - SE^+_{sm}$. [d] $(2T \ln X)/10^3$ added to δH to decrease the relative rate constant, k, by a factor of X times. T is assumed to be 298 K, the temperature at which PCMODEL estimates the heat of formation.

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(9) Giering, W. P.; Rosenblum, M.; Tancrede, J. *J. Am. Chem. Soc.* **1972**, *94*, 7170.

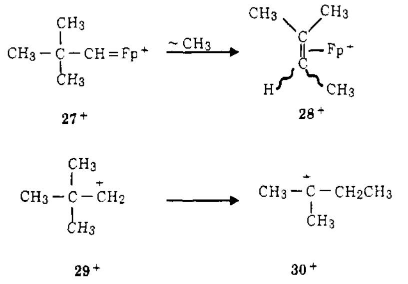
(10) Bingham, R. S.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1971**, *93*, 3189.

(11) Becker, K. R. *Helv. Chim. Acta* **1977**, *60*, 94.

further by J. J. Gajewski and K. E. Gilbert (Indiana) and marketed by Serena Software of Bloomington, IN. This program utilizes the MMP2 force field of Allinger[12] supplemented by the generalized parameters of Still and extended to other nuclei including carbocations by Gajewski, Steliou, and Gilbert themselves. We have made no attempt to supplement or alter the parameter set included with PCMODEL.[13] The SE's of cations **25**$^+$ and **26**$^+$, estimated in this manner, are listed in Table III.

Comparison of the estimated SE$^+$'s of the carbocation transition-state models **25**$^+$ and **26**$^+$ suggests that *ring enlargement* (RE) is strongly favored in methylidenes **10a** and **11a** and in **10b** and **11b** and modestly favored in **10c** and **11c** while *methyl migration* (MM) is modestly favored in **10d** and **11d**. Thus, the course of the rearrangement appears to be dictated by the relative stability of two rather "late", i.e. rearranged, transition states—one for ring enlargement and another for methyl migration—not yet significantly stabilized by d_π–p_π interaction with the vicinal iron moiety.[2a,b,14,15]

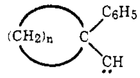
In an effort to predict the relative reactivities of the methylidenes **10** and **11**, we have extended our SE estimates using PCMODEL to include the starting methylidenes themselves which we model (SE$^+_{sm}$) with the neopentyl-like (1-methylcycloalkyl)carbinyl cations **24a–d**$^+$, respectively. These estimated SE$^+_{sm}$'s are included in Table III together with the estimated δH's of rearrangement approximated as $\delta H \approx \delta SE^+ = SE^+_{ts} - SE^+_{sm}$.[1c,d] Included, for comparison, is an estimate of δH for the rearrangement of [Fp(η^1-neopentylidene)]$^+$ (**27**$^+$) to [Fp(η^2-2-methyl-2-butene)]$^+$ (**28**$^+$) (eq 5), modeled similarly with **29**$^+$ and **30**$^+$,



(5)

respectively. It is the most reactive [Fp(η^1-methylidene)]$^+$ whose absolute rearrangement rate (at −95 °C) we have to date been able to measure.[1c] The predicted approximate relative reactivities of the [Fp(η^1-methylidenes)]$^+$ are as follows: **10b**$^+$ ≫ **10c**$^+$ > **10a**$^+$ > **10d**$^+$ ≥ **27**$^+$, in general accord with our original expectation. When these *relative* reactivities are corrected statistically[16] for the fact that methyl migration is three times as likely in **29**$^+$ as it is in **10**$^+$ and but half as likely as ring enlargement in **10**$^+$, the following relative rates of methyl migration (MM) and ring enlargement (RE) are suggested: **10b**$^+$(RE) ≫ **10c**$^+$(RE) > **10c**$^+$(MM) ≥ **10b**$^+$(MM) > **10a**$^+$(RE) ≥ **10d**$^+$(MM) > **29**$^+$(MM) > **10d**$^+$(RE) ≫ **10a**$^+$(MM).

Table IV. Ring Enlargement (RE) versus Phenyl Migration (PM) in the Rearrangement of Ametallic (1-Phenylcycloalkyl)carbenes ("Methylenes")[17]



	% RE	% PM
n = 2	100	
n = 3	92	8
n = 4	80	20
n = 5	59	41
n = 6	57	43

Our method of estimating the relative reactivities of iron(II) alkylidenes, modeled as it is upon ametallic cations,[13] i.e. Fp ≡ Fp′ ≡ H, does not distinguish between the carbonyl and the trimethyl phosphite ligated cases nor does it discriminate between possible diastereoisomeric transition states when the metal moiety is chiral.

It is interesting to compare the high regioselectivities of these stabilized Fp and Fp′ methylidene rearrangements (Table I) with the relative lack of regioselectivity observed in the rearrangements of related (1-phenylcycloalkyl)carbenes.[17] The unstabilized, ametallic carbenes or "methylenes" of similar ring size yield mixtures of ring-enlarged (RE) and phenyl-migrated (PM) cycloalkenes and cyclobenzylidenes (Table IV). The Fp-stabilized methylidenes ("carbenes"), being much less reactive, are considerably more selective. Carrying this analogy further, the even less reactive trimethyl phosphite ligated methylidenes rearrange even more regioselectively; cf. **10d** and **11d** (Table I).

At least one and perhaps all of the regioselective Fp′ alkylidene rearrangements are also diastereoselective. In **11a**, the case which we have examined most thoroughly, the ring enlargement at −66 °C produces at least 4.5 times as much as one diastereoisomeric η^2-1-methylcyclobutene complex as it does of the other, Table II. Though we feel that we could have detected both diastereomers had the minor product been present to the extent of ≥10%, we observe but a single diasteromer in the rearrangement of **11b** and **11d**.

The product ratios of Table II may not represent the true diastereoselectivities of these Fp′ alkylidene rearrangements because the trisubstituted Fp′ π-complexes are labile and rearrange to the other diastereomer and/or dissociate to free olefin at or below room temperature. In the case of **11a**, for example, the ring enlargement is accompanied by the *re–si* isomerization of one diastereomer to the other: at room temperature the ratio of **14a**-to-**15a** is 1.8 not 4.5.[18] Similarly, we do not know whether our observation of a single diastereomer in the rearrangements of **11b** and of **11d** indicates an unusually high kinetic diastereoselectivity or whether one of the initially formed diastereomers isomerizes to the other and/or decomplexes to free olefin under these experimental conditions.

Attack by an external nucleophile at the α-carbon of a $C_5H_5(NO)(PPh_3)Re$ or $C_5H_5(CO)(PPh_3)Fe$ η^1-alkylidene

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[12] QCPE No. 395, Quantum Chemistry Program Exchange, Department of Chemistry, Indiana University. Cf.: Midland, M. M. *J. Am. Chem. Soc.* **1986**, *108*, 5042.

[13] We were inhibited from modeling the cationic starting Fp alkylidenes and product Fp η^2-olefins more exactly by the fact that appropriate force constants for several of the bond types necessary to carry out such a calculation are not known and therefore not incorporated into the parameter set of PCMODEL. When the calculations are carried out by using >C=N$^+$Me$_2$ as a crude electronic (though not steric) model for >C=Fp$^+$ and either Me$_2$N$^+$ [η^2-(>C=C<)] or >C$^+$C(NMe$_2$)< as a model for Fp$^+$[η^2-(>C=C<)], the necessary force constants for which *are* included in PCMODEL, ring enlargement is predicted for **15a**$^+$ and **15b**$^+$ and methyl migration for **15d**$^+$; both appear equally probable in **15c**$^+$. A reviewer has suggested that the regioselectivities of these alkylidene rearrangements also correlate with the strain energy of the rearranged olefin. This is true in the present cases but is less so in the polycyclic cases reported previously.[1b,c]

[14] Cutler, A.; Fish, R. W.; Giering, W. P.; Rosenblum, M. *J. Am. Chem. Soc.* **1972**, *94*, 4354.

[15] Rosenblum, M. *Acc. Chem. Res.* **1974**, *7*, 122.

[16] Cf. Table III, footnote *d*.

[17] (a) Wilt, J. W.; Kosturik, J. M.; Orlowski, R. C. *J. Org. Chem.* **1965**, *30*, 1052. (b) Wilt, J. W.; Zawadzki, J. F.; Schultenover, D. G. *J. Org. Chem.* **1966**, *31*, 876.

[18] This *re–si* interconversion cannot be a simple case of kinetic vs thermodynamic control for it is apparently irreversible; **14a** isomerizes to **15a** by a path that does *not* involve a retro β-to-α carbon shift. Other cases of *re–si* isomerization in Fe(II) η^2-olefin complexes are known,[2a–d,f,3d,19] some of which clearly do not involve carbon or hydrogen shifts.

[19] Bly, R. S.; Silverman, G. S.; Bly, R. K. *Organometallics* **1985**, *4*, 374.

can be highly stereoselective.[2-5] Monoalkyl-substituted transition-metal methylidenes normally exist in solution as a mixture of synclinal and anticlinal conformers with the latter being favored.[2-5] When the barrier separating the two rotamers is high relative to the activation energy of nucleophilic attack, stereoselectivity results from preferential reaction of the more prevalent anticlinal rotamer from the *re* face of the *R* enantiomer and/or the *si* face of the *S* enantiomer.[3] However, when the rotational barrier is low relative to the activation energy of nucleophilic addition, Curtin–Hammett conditions obtain[20] and the observed diastereoselectivity arises from preferential reaction of the less stable, intrinsically more reactive,[2e] synclinal rotamer at the *si* face of the *R* enantiomer and/or the *re* face of the *S* enantiomer.[2-5] With triethylphosphine (cone angle 132°) rather than triphenylphosphine (cone angle 145°) and/or phenyl- rather than methyl-substituted methylidenes, Brookhart has shown that the observed stereoselectivity of nucleophilic addition to Fe(II) alkylidenes is best rationalized as an intermediate case dependent upon the relative rates of both rotational interconversion *and* nucleophilic attack.[2e]

We are interested in this question because the ring enlargements of Fp′ η^1-(1-methylcycloalkyl)methylidenes may be regarded as intramolecular nucleophilic substitutions at C(α) in which migrating carbon takes the place of an external nucleophile. The diastereoselectivities that we observe in the ring enlargements of **10a–c** are expected to be interpretable in a comparable manner.[4d,e] Unfortunately, in none of these cases do we know the rotational barrier of synclinal–anticlinal interconversion. The cone angle of trimethyl phosphite is 107°, smaller than that of either triphenylphosphine or triethylphosphine, but 1-methylcycloalkyl is more sterically demanding than either methyl or phenyl. Nor do we know the activation energy for ring enlargement or the configuration of the major diastereomer that is produced. We are still investigating these questions and expect our findings to be the subject of a subsequent publication.

Experimental Section

General Procedures. All operations were carried out under dry, oxygen-free nitrogen or helium atmospheres using standard Schlenk-line or drybox techniques. Proton NMR spectra were recorded at 90, 300, or 500 MHz on a Varian EM-390, Bruker AM-300.13, or Bruker AM-500.13 spectrometer, respectively, the ^{13}C NMR spectra at 20.13, 75, or 125 MHz on a IBM NR-80, Bruker AM-300.13, or Bruker AM-500.13 spectrometer, respectively, and ^{31}P NMR spectra at 121.4 or 202.4 MHz on a Bruker AM-300.13 or AM-500.13 spectrometer, respectively. Proton chemical shifts (δ) are reported in parts per million downfield from TMS; ^{13}C and ^{31}P resonances (at all temperatures) were recorded with use of the δ 53.8 (CD_2Cl_2) or 77.0 ppm ($CDCl_3$) resonance of the solvent as an internal reference and are reported in parts per million down field from TMS. Infrared (IR) spectra were recorded on a Beckman IR-4210. The accurate-mass mass spectra were run on a VG Analytical, Ltd., 70SQ high-resolution, double-focusing mass spectrometer equipped with a VG 11/250 data system and analyzed by comparison with isotopic ion distributions calculated by the ISO program of VG Analytical, Ltd. Microanalyses were performed by Atlantic Microlab, Inc. The capillary GLPC's were carried out by using a Hewlett-Packard Model 5790A gas chromatograph equipped with an electronic integrator.

Solvents and Reagents. Reagent grade diethyl ether and tetrahydrofuran (THF) were distilled under nitrogen from sodium benzophenone ketyl. Reagent grade dichloromethane was distilled under nitrogen from P_2O_5. Reagent grade pentane and hexane were stirred overnight with concentrated sulfuric acid, washed with water, distilled from P_2O_5, stored over sodium ribbon and distilled from sodium under nitrogen immediately prior to use. Solvents used for spectrochemical determinations were degassed by the freeze–pump–thaw technique and stored under vacuum.

Preparation of Dicarbonyl(η^5-cyclopentadienyl)[η^1-(1-methyl-1-cycloalkyl)carbonyl]iron (3a–d). The starting Fp acyl derivatives **3** were prepared from the corresponding acid chlorides **2a–d** and potassium dicarbonyl(η^5-cyclopentadienyl)ferrate as described previously.[1c] The products were separated from Fp_2 contaminant by chromatography on neutral alumina (activity III) using benzene as an eluent followed by sublimation (**3a** or **3b**) or by recrystallization from hexane (**3c** or **3d**).

Dicarbonyl(η^5-cyclopentadienyl)[η^1-(1-methyl-1-cyclopropyl)carbonyl]iron (3a), mp 57–59 °C, was obtained in 57% yield. It has the following spectral properties: IR (CH_2Cl_2) 2010, 1954 (C≡O), 1625 cm^{-1} (C═O); ^{1}H NMR ($CDCl_3$) δ 4.86 (s, Cp), 1.44 (s, CH_3), 1.04 (q, 2 H), 0.46 (q, 2 H); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 257.3, 215.2, 86.2 (Cp), 42.3, 22.8, 16.4 (2 C); MS *m/e* $[M]^{\bullet+}$, calcd for $C_{12}H_{12}O_3Fe$ 260.0136, found 260.0125, $[M - CO]^{\bullet+}$, calcd for $C_{11}H_{12}O_2Fe$ 232.0186, found 232.0161, $[M - 2CO]^{\bullet+}$, calcd for $C_{10}H_{12}OFe$ 204.0238, found 204.0207. Anal. Calcd for $C_{11}H_{12}O_2Fe$: C, 55.42; H, 4.65. Found: C, 55.70; H, 4.44.

Dicarbonyl(η^5-cyclopentadienyl)[η^1-(1-methyl-1-cyclobutyl)carbonyl]iron (3b), mp 60–61 °C, was obtained in 73% yield. It has the following spectral properties: IR (CH_2Cl_2) 2000, 1950 (C≡O), 1628 cm^{-1} (C═O); ^{1}H NMR ($CDCl_3$) δ 4.85 (s, Cp), 2.28 (q, 2 H), 1.9–1.7 (m, 3 H), 1.52 (m, 1 H), 1.26 (s, CH_3); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 261.7, 215.6, 86.8 (Cp), 64.3, 31.6 (2 C), 22.8, 13.3; MS *m/e* $[M]^{\bullet+}$, calcd for $C_{13}H_{14}O_3Fe$ 274.0292, found 274.0262, $[M - CO]^{\bullet+}$, calcd for $C_{12}H_{14}O_2Fe$ 246.0343, found 246.0330. Anal. Calcd for $C_{13}H_{14}O_3Fe$: C, 56.96; H, 5.15. Found: C, 56.60; H, 5.15.

Dicarbonyl(η^5-cyclopentadienyl)[η^1-(1-methyl-1-cyclopentyl)carbonyl]iron (3c), mp 40–42 °C, was obtained in 50% yield. It has the following spectral properties: IR (CH_2Cl_2) 2010, 1950 (C≡O), 1625 cm^{-1} (C═O); ^{1}H NMR ($CDCl_3$) δ 4.82 (s, Cp), 2.00 (m, 2 H), 1.55 (m, 4 H), 1.33 (m, 2 H), 1.15 (s, CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 262.1, 215.4, 86.4 (Cp), 70.2, 36.4 (2 C), 25.1, 24.8 (2 C); MS *m/e* $[M]^{\bullet+}$, calcd for $C_{14}H_{16}O_3Fe$ 288.0449, found 288.0444, $[M - CO]^{\bullet+}$, calcd for $C_{13}H_{16}O_2Fe$ 260.0500, found 260.0488. Anal. Calcd for $C_{14}H_{16}O_3Fe$: C, 58.36; H, 5.62. Found: C, 58.05; H, 5.61.

Dicarbonyl(η^5-cyclopentadienyl)[η^1-(1-methyl-1-cyclohexyl)carbonyl]iron (3d), mp 51–52 °C, was obtained in 69% yield. It has the following spectral properties: IR (CH_2Cl_2) 2000, 1945 (C≡O), 1623 cm^{-1} (C═O); ^{1}H NMR ($CDCl_3$) δ 4.83 (s, Cp), 1.71 (q, 2 H), 1.45–1.2 (m, 8 H), 1.00 (s, CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 262.5, 215.7, 86.5 (Cp), 61.2, 35.2 (2 C), 26.0, 22.9 (2 C), 22.3; MS *m/e* $[M]^{\bullet+}$, calcd for $C_{15}H_{18}O_3Fe$ 302.0605, found 302.0600, $[M - CO]^{\bullet+}$, calcd for $C_{14}H_{18}O_2Fe$ 274.0656, found 274.0642.

Preparation of Carbonyl(η^5-cyclopentadienyl)(trimethyl phosphite)[η^1-(1-methyl-1-cycloalkyl)carbonyl]iron (4a–d). These Fp′ acyls were prepared from the corresponding Fp acyls **3a–d** by the method of Buck and Brookhart.[2d-f]

Carbonyl(η^5-cyclopentadienyl)(trimethyl phosphite)[η^1-(1-methyl-1-cyclopropyl)carbonyl]iron (4a). In a typical preparation, a solution of 0.607 g (2.33 mmol) of **3a** and 0.579 g (4.66 mmol) of trimethyl phosphite in 30 mL of hexane was placed in a Pyrex side-arm flask under nitrogen and irradiated by using a GE 150W flood lamp. The progress of the reaction was monitored by IR, observing the decrease of the terminal CO stretches at 2010 and 1954 cm^{-1} and the concomitant increase of terminal and ketonic CO stretches at 1930 and 1590 cm^{-1}, respectively. Irradiation was stopped when the conversion was judged to be 80–90% complete (~20 h). The solvent and excess phosphite were removed under vacuum, and the residue was chromatographed on alumina (Alcoa F-20) eluting with ether/hexane. Separation of the yellow unreacted starting material could be observed as the ether content of the eluent was gradually increased from 1 to 10%. When elution of **3a** was complete, the

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[20] (a) Curtin, D. Y. *Rec. Chem. Prog.* **1954**, *15*, 111. (b) Cf.: Seeman, J. I. *Chem. Rev.* **1983**, *83*, 1983.

[21] Plotkin, J. S.; Shore, S. G. *Inorg. Chem.* **1981**, *20*, 285.

[22] These assignments are supported by a refocused INEPT determination [Morris, G. A.; Freeman, R. *J. Am. Chem. Soc.* **1979**, *101*, 760].

[23] Table II, footnote *a*.

[24] Organic Technology, Inc., Coshocton, OH.

ether content was increased to 20% to elute the dark yellow product. Evaporation of the solvent gave 0.682 g (82%) of crystalline **4a**: mp 54–55 °C, ^{1}H NMR ($CDCl_3$) δ 4.62 (d, J_{HP} = 0.91 Hz, Cp), 3.60 (d, J_{HP} = 11.2 Hz, $P(OCH_3)_3$), 1.49 (s, CH_3), ~1.17 (m, 1 H), 0.90 (m, 1 H), 0.36 (m, 2 H); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 270.6 (d, J_{CP} = 31.2 Hz, C=O), 220.0 (d, J_{CP} = 49.8 Hz, C≡O), 84.1 (d, J_{CP} = 1.4 Hz, Cp), 52.5 (d, J_{CP} = 5.1 Hz, $P(OCH_3)_3$), 41.8 (d, J_{CP} = 7.9 Hz, >C<), 23.7, 16.3, 15.7; MS *m/e* $[M]^{\bullet+}$ calcd for $C_{14}H_{21}O_5FeP$ 356.0476, found 356.0475, $[M - CO]^{\bullet+}$ calcd for $C_{13}H_{21}O_4FeP$ 328.0527, found 328.0537. Compounds **4b–d** were prepared in a similar manner.

Carbonyl(η^5-cyclopentadienyl)(trimethyl phosphite)[η^1-(1-methyl-1-cyclobutyl)carbonyl]iron (4b), mp 36–37 °C, was obtained in 60% yield. It has the following spectral properties: IR 1925 (C≡O), 1585 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 4.64 (d, J_{HP} = 0.91 Hz, Cp), 3.64 (d, J_{HP} = 11.3 Hz, $P(OCH_3)_3$), 2.41 (m, 1 H), 2.22 (m, 1 H), 1.70 (m, 3 H), 1.50 (m, 1 H), 1.22 (s, CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 278.0 (d, J_{CP} = 33.2 Hz, C=O), 219.3 (d, J_{CP} = 47.7 Hz, C≡O), 83.3 (d, J_{CP} = 1.3 Hz, Cp), 64.5 (d, J_{CP} = 6.7 Hz, >C<), 51.9 (d, J_{CP} = 5.1 Hz, $P(OCH_3)_3$) 32.3, 31.9, 20.9, 13.5; MS *m/e* $[M]^{\bullet+}$ calcd for $C_{15}H_{23}O_5FeP$ 370.0633, found 370.0625, $[M - CO]^{\bullet+}$ calcd for $C_{14}H_{23}O_4FeP$ 342.0675, found 342.0683.

Carbonyl(η^5-cyclopentadienyl)(trimethyl phosphite)[η^1-(1-methyl-1-cyclopentyl)carbonyl]iron (4c), a dark yellow oil, was obtained in 76% yield. It has the following spectral properties: IR (CH_2Cl_2) 1915 (C≡O), 1585 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 4.60 (s, Cp), 3.63 (d, J_{HP} = 11.2 Hz, $P(OCH_3)_3$), 2.08 (m, 1 H), 1.96 (m, 1 H), ~1.6–1.2 (m, 6 H), 1.09 (s, CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 276.5 (d, J_{CP} = 30.5 Hz, C=O), 220.1 (d, J_{CP} = 49.5 Hz, C≡O), 83.7 (d, J_{CP} = 1.3 Hz, Cp), 70.4 (d, J_{CP} = 6.2 Hz, >C<), 51.8 (d, J_{CP} = 5.2 Hz, $P(OCH_3)_3$), 36.6 (2 C), 25.6, 24.6, 24.5; MS *m/e* $[M]^{\bullet+}$ calcd for $C_{16}H_{25}O_5FeP$ 384.0789, found 384.0773, $[M - OCH_3]^{\bullet+}$ calcd for $C_{15}H_{22}O_4FeP$ 353.0605, found 353.0596.

Carbonyl(η^5-cyclopentadienyl)(trimethyl phosphite)[η^1-(1-methyl-1-cyclohexyl)carbonyl]iron (4d), mp 34–35 °C, was obtained in 66% yield. It has the following spectral properties: IR 1910 (C≡O), 1585 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 4.61 (d, J_{HP} = 0.81 Hz, Cp), 3.63 (d, J_{HP} = 11.1 Hz, $P(OCH_3)_3$), 1.7–1.1 (m, 10 H), 1.00 (s, CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 276.5 (d, J_{CP} = 30.1 Hz, C=O), 221.6 (d, J_{CP} = 50.9 Hz, C≡O), 84.3 (d, J_{CP} = 1.4 Hz, Cp), 61.2 (d, J_{CP} = 6.1 Hz, >C<), 52.2 (d, J_{CP} = 5.3 Hz, $P(OCH_3)_3$), 35.6, 35.4, 26.8, 23.4, 23.2, 22.0; MS *m/e* $[M - OCH_3]^{\bullet+}$ calcd for $C_{16}H_{24}O_4FeP$ 367.0761, found 367.0745, $[M - (OCH_3 \text{ and } CO)]^{\bullet+}$ calcd for $C_{15}H_{24}O_3FeP$ 339.0812, found 339.0807.

Preparation of Carbonyl(η^5-cyclopentadienyl)(trimethyl phosphite)[η^1-(1-methyl-1-cycloalkyl)methoxymethylidene]iron Trifluoromethanesulfonates (6a–d). The methoxycarbenes were prepared by reaction of the corresponding acyls **4a–d** with a large excess of methyl triflate in dichloromethane solution.[2a,d]

Carbonyl(η^5-cyclopentadienyl)(trimethyl phosphite)[η^1-(1-methyl-1-cyclopropyl)methoxymethylidene]iron Trifluoromethanesulfonate (6a). In a typical proceedure a solution of 0.324 g (0.910 mmol) of **4a** and 1 mL (~1.4 g, 8.8 mmol) of methyl triflate in 6 mL of dichloromethane was kept in the dark at room temperature for ~3 h or until the only carbonyl absorption detectable by IR was that of the product (1990 cm^{-1}). The solvent and excess reagent were removed under reduced pressure. The nonvolatile, yellow residue was washed with ether and dried at room temperature under vacuum to give 0.290 g (61%) of yellow crystals: ^{1}H NMR ($CDCl_3$) δ 5.03 (d, J_{HP} = 1.0 Hz, Cp), 4.61 (s, OCH_3), 3.74 (d, J_{HP} = 11.5 Hz, $P(OCH_3)_3$), 1.40 (s, CH_3) superimposed upon a multiplet at δ ~1.4–1.0 (4 H); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 10 °C) δ 343.2 (d, J_{CP} = 35.0 Hz, C(OMe)=Fe^+), 213.8 (d, J_{CP} = 43.3 Hz, C≡O), 86.1 (Cp), 85.2 (trace of a second Cp?), 68.0 (OCH_3), 54.2 (d, J_{CP} = 7.9 Hz, $P(OCH_3)_3$), 41.2 (d, J_{CP} = 3.0 Hz, >C<), 22.0, 19.3, 18.0; MS (FAB) *m/e* $[M - CF_3SO_3]^+$ calcd for $C_{15}H_{24}O_5FeP$ 371.0711, found 371.0789.

Carbonyl(η^5-cyclopentadienyl)(trimethyl phosphite)[η^1-(1-methyl-1-cyclobutyl)methoxymethylidene]iron trifluoromethanesulfonate (6b) was obtained as a yellow crystalline solid in 95% yield: ^{1}H NMR (CD_2Cl_2) δ 5.05 (s, Cp), 4.70 (s, OCH_3), 3.77 (d, J_{HP} = 12.1 Hz, $P(OCH_3)_3$), 2.54 (q, 1 H), 2.30 (q, 1 H), 2.2 (m, 1 H), ~2.1–1.8 (m, 2 H), 1.58 (m, 1 H), 1.33 (s, CH_3); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −50 °C) δ 349.0 (d, J_{CP} = 29.5 Hz, C(OMe)=Fe^+), 213.9 (d, J_{CP} = 43.8 Hz, C≡O), 85.1 (Cp), 83.2 (trace of a second Cp?), 68.7 (OCH_3), 67.0 (d, J_{CP} = 3.7 Hz, >C<), 54.4 (d, J_{CP} = 9.2 Hz, $P(OCH_3)_3$), 35.4, 33.6, and 13.0 (CH_2), 24.0 (CH_3); MS (FAB) *m/e* $[M - CF_3SO_3]^+$ calcd. for $C_{16}H_{26}O_5FeP$ 385.0923, found 385.0867.

Carbonyl(η^5-cyclopentadienyl)(trimethyl phosphite)[η^1-(1-methyl-1-cyclopentyl)methoxymethylidene]iron trifluoromethanesulfonate (6c) was isolated as a brown oil and could not be obtained in crystalline form. Because of its apparent instability, this compound was not thoroughly dried at room temperature or characterized spectroscopically. It was washed with ether at −78 °C, dissolved in dichloromethane, and immediately reduced with borohydride to the methoxyalkyl **8b** (**9b**).

Carbonyl(η^5-cyclopentadienyl)(trimethyl phosphite)[η^1-(1-methyl-1-cyclohexyl)methoxymethylidene]iron trifluoromethanesulfonate (6d) was prepared as described for **6a** and was purified by washing with a 1:5 mixture of benzene and hexane. After further washing with several portions of benzene and hexane and drying under reduced pressure, a yellow solid was isolated in 76% yield. It has the following spectral properties: IR 1980 cm^{-1} (C≡O); ^{1}H NMR ($CDCl_3$) δ 5.05 (s, Cp), 4.92 (s, OCH_3), 3.78 (d, J_{HP} = 11.2 Hz, $P(OCH_3)_3$), 2.05–1.1 (m, 10 H), 1.11 (s, CH_3); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −10 °C) δ 353.8 (d, J_{CP} = 27.7 Hz, C(OMe)=Fe^+), 216.5 (d, J_{CP} = 47.6 Hz, C≡O), 85.6 (Cp), 70.3 (OCH_3), 64.4 (d, J_{CP} = 3.4 Hz, >C<), 54.8 (d, J_{CP} = 9.7 Hz, $P(OCH_3)_3$), 37.9, 36.3, 25.6, 23.3, and 23.0 (CH_2), 23.6 (CH_3); MS (FAB) *m/e* $[M - CF_3SO_3]^+$ calcd for $C_{18}H_{30}O_5FeP$ 413.1180, found 413.1217, $[M - CF_3SO_3 - CO]^+$ calcd for $C_{17}H_{30}O_4FeP$ 385.1231, found 385.1245.

Preparation of Dicarbonyl(η^5-cyclopentadienyl)[η^1-(1-methyl-1-cycloalkyl)methoxymethyl]iron (7a–d). The cyclic methoxymethyls **7a–d** were prepared by the reaction of **3a–d** with methyl trifluoromethanesulfonate in dichloromethane solution followed by reduction with sodium borohydride as described previously[1c,d,2d,f] and chromatography on neutral alumina using pentane and 2–5% ether/pentane as eluents. In the cyclopropyl case the only materials formed were the desired **7a** and a small amount of Fp_2. Each of the other cycloalkyls, in addition to the desired methoxymethyl **7b–d**, returned an unidentified yellow oil which eluted with pentane (see text), a small amount of Fp_2, and some unreacted starting material.

Dicarbonyl(η^5-cyclopentadienyl)[η^1-(1-methyl-1-cyclopropyl)methoxymethyl]iron (7a) was obtained as a yellow oil in 66% yield. It has the following spectral properties: IR (CH_2Cl_2) 2005, 1946 cm^{-1} (C≡O); ^{1}H NMR (CD_2Cl_2) δ 4.83 (s, Cp), 4.40 (s, >CHOMe), 3.25 (s, OCH_3), 1.16 (s, CH_3), 0.70 (m, 2 H), 0.35 (m, 1 H), 0.25 (m, 1 H); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −20 °C) δ 218.3, 217.9, 89.6, 86.5 (Cp), 59.3, 26.7, 21.5, 21.3, 13.8; MS *m/e* $[M]^{\bullet+}$, calcd for $C_{13}H_{16}O_3Fe$ 276.0449, found 276.0445, $[M - OCH_3]^{\bullet+}$, calcd for $C_{12}H_{13}O_2Fe$ 245.0265, found 245.0243.

Dicarbonyl(η^5-cyclopentadienyl)[η^1-(1-methyl-1-cyclobutyl)methoxymethyl]iron (7b) was obtained as a yellow oil in 30% yield. It has the following spectral properties: IR (CH_2Cl_2) 2005, 1945 cm^{-1} (C≡O); ^{1}H NMR (CD_2Cl_2) δ 4.99 (s, >CHOMe), 4.87 (s, Cp), 3.29 (s, OCH_3), 2.1–1.5 (m, 6 H), 1.21 (s, CH_3); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −20 °C) δ 219.2, 217.0, 93.2, 86.1 (Cp), 59.0 (OCH_3), 50.6 (>C<), 35.3, 33.6, and 13.7 (CH_2), 24.6 (CH_3); MS *m/e* $[M]^{\bullet+}$, calcd for $C_{14}H_{18}O_3Fe$ 290.0604, found too weak to measure, $[M - CO]^{\bullet+}$, calcd for $C_{13}H_{18}O_2Fe$ 262.0656, found 262.0650.

Dicarbonyl(η^5-cyclopentadienyl)[η^1-(1-methyl-1-cyclopentyl)methoxymethyl]iron (7c) was obtained as a yellow oil in 21% yield. It has the following spectral properties: IR (CH_2Cl_2) 1990, 1933 cm^{-1} (C≡O); ^{1}H NMR (CD_2Cl_2) δ 4.95 (s, >CHOMe), 4.87 (s, Cp), 3.27 (s, OCH_3), 1.8–1.2 (m, 8 H), 1.04 (s, CH_3); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −20 °C) δ 219.8, 216.9, 93.5, 86.3 (Cp), 58.6, 54.9, 40.0, 39.6, 26.0, 25.7, 25.2; MS *m/e* $[M]^{\bullet+}$, calcd for $C_{15}H_{20}O_3Fe$ 304.0762, found 304.0729 (very weak), $[M - CO]^{\bullet+}$, calcd for $C_{14}H_{20}O_2Fe$ 276.0813, found 276.0786, $[M - 2CO]^{\bullet+}$, calcd for $C_{13}H_{20}OFe$ 248.0864, found 248.0857.

Dicarbonyl(η^5-cyclopentadienyl)[η^1-(1-methyl-1-cyclohexyl)methoxymethyl]iron (7d) was obtained as a yellow oil in 38% yield. It has the following spectral properties: IR (CH_2Cl_2) 1990, 1930 cm^{-1} (C≡O); ^{1}H NMR (CD_2Cl_2) δ 4.88 (s, 6 H, Cp and >CHOMe), 3.25 (s, OCH_3), 1.6–1.1 (m, 10 H), 0.94 (s, CH_3); $^{13}C\{^1H\}$

NMR[22] (CD_2Cl_2, −25 °C) δ 219.9, 216.9, 95.3 (>CHOMe), 86.1 (Cp), 58.6 (OCH_3), 44.6 (>C<), 37.1 (2 C), 26.6 and 22.8 (2 C, CH_2), 21.2 (CH_3); MS *m/e* $[M]^{\bullet+}$, calcd for $C_{16}H_{22}O_3Fe$ 318.0918, found 318.0909 (weak), $[M - 2CO]^{\bullet+}$, calcd for $C_{14}H_{22}OFe$ 262.1020, found 262.1007.

Preparation of Carbonyl(η^5-cyclopentadienyl)(trimethyl phosphite)[η^1-(1-methyl-1-cycloalkyl)methoxymethyl]iron (8a–d or 9a–d). Carbenes **6a–d** were reduced by a procedure similar to that described by Brookhart et al.[2a,b] As indicated below the presence of diastereomers could be detected unequivocally only in the case of the cyclopropyl derivative **6a**. Compounds **8b–d** and/or **9b–d**, prepared in a similar manner, are considerably less stable than **8a** or **9a**; but one diastereomer could be detected by low-temperature $^{13}C\{^1H\}$ NMR in each case, though the presence of a small amount of the other diastereomer cannot be excluded.

Carbonyl(η^5-cyclopentadienyl)(trimethyl phosphite)[η^1-(1-methyl-1-cyclopropyl)methoxymethyl]iron (8a or 9a). In a typical preparation, a solution of 0.091 g (0.175 mmol) of **6a** was added dropwise with stirring to a cooled solution (dry ice/isopropyl alcohol) of sodium methoxide (prepared from 0.6 g, 0.028 g-atom, of sodium) and 0.40 g (0.10 mmol) of sodium borohydride in 15 mL of methanol. When addition was complete, the cold bath was removed and, after being stirred for 10 min, the reaction mixture was extracted with 10 mL of degassed water. The layers were separated and the aqueous layer was extracted with three, 5-mL portions of dichloromethane. The dichloromethane solutions were combined, and the solvent was removed under reduced pressure to give 0.058 g (89%) of an unstable yellow oil ($C{\equiv}O$, 1990 cm^{-1}). The product is an ~2.5:1 mixture of diastereomers **8a** and **9a**.[23] These products exhibit the following NMR spectra. **The major component 8a**:[23] ^1H (CD_2Cl_2) δ 4.63 (s, Cp), 3.61 (d, J_{HP} = 11.1 Hz, $P(OCH_3)_3$), 3.55 (d, $^3J_{PH}$ = 13.6 Hz, CH(OMe)Fe), 3.22 (s, OCH_3), 1.17 (s, CH_3), 0.62–0.20 (m); $^{13}C\{^1H\}$[22] (CD_2Cl_2, −40 °C) δ 220.1 (d, J_{CP} = 50.1 Hz, $C{\equiv}O$), 87.9 (d, J_{CP} = 34 Hz, *C*H(OMe)Fe), 83.5 (d, J_{CP} = 1.3 Hz, Cp), 59.3 (OCH_3), 51.3 (d, J_{CP} = 3.9 Hz, $P(OCH_3)_3$), 26.9 (d, $^3J_{CP}$ = 3.3 Hz, >C<), 22.2 (CH_3), 20.5 and 12.3 (CH_2); $^{31}P\{^1H\}$ δ 191.0 ($P(OCH_3)_3$). **The minor component 9a**:[23] ^1H (CD_2Cl_2) δ 4.58 (s, Cp), 4.11 (d, $^3J_{PH}$ = 7.8 Hz, CH(OMe)Fe), 3.60 (d, J_{HP} = 10.9 Hz, $P(OCH_3)_3$), 3.19 (s, OCH_3), 1.19 (s, CH_3), ~0.6–0.2 (m); $^{13}C\{^1H\}$[22] (CD_2Cl_2, −40 °C) δ 90.7 (d, J_{CP} = 30 Hz, *C*H(OMe)Fe), 82.4 (d, J_{CP} = 0.9 Hz, Cp), 59.2 (OCH_3), 51.8 (d, J_{CP} = 5.4 Hz, $P(OCH_3)_3$), 25.7 ($^3J_{CP} \simeq 0$ Hz, >C<), 22.7 (CH_3), 18.2 and 11.9 (CH_2); $^{31}P\{^1H\}$ δ 184.8 ($P(OCH_3)_3$). A mass spectrum of the mixture showed: *m/e* $[M]^{\bullet+}$, calcd for $C_{15}H_{25}O_5FeP$ 372.0789, found 372.0792.

Carbonyl(η^5-cyclopentadienyl)(trimethyl phosphite)[η^1-(1-methyl-1-cyclobutyl)methoxymethyl]iron (8b and/or 9b), a brown oil, was obtained in 41% yield. It has the following spectral properties: $^{13}C\{^1H\}$ NMR[22] (CD_2Cl_2, −40 °C) δ 222.5 (d, J_{CP} = 54.9 Hz, $C{\equiv}O$), 89.8 (d, J_{CP} = 28.0 Hz, *C*H(OMe)Fe), 83.2 (d, J_{CP} = 1.1 Hz, Cp), 58.5 (OCH_3), 51.9 (d, J_{CP} = 7 Hz, $P(OCH_3)_3$), 51.4 (>C<), 33.6, 32.1, and 13.8 (CH_2), 24.8 (CH_3); MS *m/e* $[M]^{\bullet+}$, calcd for $C_{16}H_{27}O_5FeP$ 386.0946, found 386.0943.

Carbonyl(η^5-cyclopentadienyl)(trimethyl phosphite)[η^1-(1-methyl-1-cyclopentyl)methoxymethyl]iron (8c and/or 9c), a brown oil, was obtained in 60% yield. It has the following spectral properties: $^{13}C\{^1H\}$ NMR[22] (CD_2Cl_2, −40 °C) δ 223.4 (d, J_{CP} = 57.1 Hz, $C{\equiv}O$), 88.9 (d, J_{CP} = 28.6 Hz, *C*H(OMe)Fe), 83.7 (d, J_{CP} = 1.7 Hz, Cp), 83.9 (trace of a second Cp?), 58.1 (OCH_3), 54.7 (d, J_{CP} = 0.9 Hz, >C<), 52.1 (d, J_{CP} = 7.4 Hz, $P(OCH_3)_3$), 38.7, 38.2 (CH_2), 25.4 and 25.0 (CH_2), 25.6 (CH_3); MS *m/e* $[M]^{\bullet+}$, calcd for $C_{17}H_{29}O_5FeP$ 400.1102, found 400.1122.

Carbonyl(η^5-cyclopentadienyl)(trimethyl phosphite)[η^1-(1-methyl-1-cyclohexyl)methoxymethyl]iron (8d and/or 9d), a brown oil, was obtained in 71% yield. It has the following spectral properties: $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −40 °C) δ 224.1 (d, J_{CP} = 58.4 Hz, $C{\equiv}O$), 92.1 (d, J_{CP} = 28.0 Hz, *C*H(OMe)Fe), 83.6 (d, J_{CP} = 1.4 Hz, Cp), 58.1 (OCH_3), 52.0 (d, J_{CP} = 7.9 Hz, $P(OCH_3)_3$), 44.0 (>C<), 36.5, 36.4, and 27.7 (2 C) 19.5. This compound decomposed when attempts were made to determine its mass spectrum.

Rearranged Dicarbonyl(η^5-cyclopentadienyl)(η^2-olefin)iron Tetrafluoroborates (12 or 13) from the Reaction of Dicarbonyl(η^5-cyclopentadienyl)[η^1-(1-methyl-1-cycloalkyl)methoxymethyl]iron (7a–d) with Tetrafluoroboric Acid Etherate. Solutions of ~25 mg of each of the methoxymethyls *in* 0.5 mL of dideuteriodichloromethane were placed in 5-mm NMR tubes. The solvent was slowly removed under vacuum so as to coat the lower portion of the tube with a thin film of the residual yellow oil. Solutions containing 20–30 mg of the acid in 0.5 mL of dideuteriodichloromethane were added with cooling in a dry ice/isopropyl alcohol bath. After mixing, each sample was inserted in the precooled (−20 °C) probe of the NR-80. The *proton spectrum* was determined within 30 min of insertion, and the $^{13}C\{^1H\}$ NMR spectrum was acquired during the next 10–12 h. In none of the cases does either spectrum show any evidence of unreacted starting material or of any organometallic other than a single π-complex. The Fp(η^2-trisubstituted olefin) tetrafluoroborates **12** or **13** are too unstable to be isolated at ambient temperature.

Structure assignments in the individual cases are based on the following spectroscopic evidence. The individual proton resonances are not sufficiently well resolved for a complete structural analysis in each case but do clearly indicate that the products obtained from **7a–c** at −20 °C are the ring-expanded η^2-olefin tetrafluoroborates **12a**, **12b**, and **12c**, respectively. The η^2-[CH=C(C*H*$_3$)] resonances of the cationic π-complexes $\mathbf{12}^+$ appear *in the ^1H spectra as singlets at δ 2.13, 1.98, and 1.84, respectively.* The η^2-[C*H*=C(CH$_3$)] resonance of $\mathbf{12a}^+$ appears as a broad singlet at δ 5.65 while the Cp-H's are at δ 5.51. In the cases of $\mathbf{12b}^+$ and $\mathbf{12c}^+$ the vinylic proton resonances overlap those of the Cp-H's at δ 5.50 and 5.45, respectively. In the case of $\mathbf{13d}^+$ (the cationic π-complex from **7d**) the Cp-H's appear as a singlet at δ 5.45, the η^2-[>C=C(CH$_3$)*H*] as a quartet (*J* = 6 Hz) at δ 5.02 and the η^2-[>C=C(C*H*$_3$)H] as a doublet (*J* = 6 Hz) at δ 2.00. Clearly $\mathbf{13d}^+$ is the product of methyl migration rather than ring expansion.

As enumerated below, all carbon spectra (CD_2Cl_2, −40 °C) display the requisite number of resonances; $\mathbf{12a}^+$, δ 212.9 and 208.8 ($C{\equiv}O$'s), 119.7 [η^2-(CH=*C*Me)], 89.2 (Cp), 80.2 [η^2-(*C*H=CMe)], 37.2, 28.2, 25.2; $\mathbf{12b}^+$, δ 212.9 and 208.8 ($C{\equiv}O$'s), 120.0 [η^2-(CH=*C*Me)], 89.2 (Cp), 77.0 [η^2-(*C*H=CMe)], 40.2, 34.3, 25.1, 20.4; $\mathbf{12c}^+$, δ 214.0 and 209.5 ($C{\equiv}O$'s), 119.8 [η^2-(CH=*C*Me)], 89.1 (Cp), 76.1 [η^2-(*C*H=CMe)], 34.6, 31.5, 28.6, 21.3, 20.0; $\mathbf{13d}^+$, δ 213.5 and 205.8 ($C{\equiv}O$'s), 117.2 [η^2-(>*C*=CHMe)], 88.9 (Cp), 73.1 [η^2-(>C=*C*HMe)], 43.3, 34.3, 34.2, 30.3, 25.6, 19.2.

Carbonyl(η^5-cyclopentadienyl)(trimethyl phosphite)[η^1-(1-methyl-1-cycloalkyl)methylidene]iron Tetrafluoroborates (11) and/or Rearranged Carbonyl(η^5-cyclopentadienyl)(trimethyl phosphite)(η^2-olefin)iron Tetrafluoroborates (14 or 15 and/or 16 or 17) from the Reaction of Carbonyl(η^5-cyclopentadienyl)(trimethyl phosphite)[η^1-(1-methyl-1-cycloalkyl)methoxymethyl]iron (8 or 9) with Tetrafluoroboric Acid Etherate. A solution of ~50 mg of **8** and **9** in ~0.3 mL of dichloromethane was placed in a 5-mm NMR tube, and the solvent was slowly evaporated under reduced pressure so as *to coat the lower portion of the tube with* a film of the residual yellow oil. The tube was cooled in liquid nitrogen, and ~0.5 mL of a solution containing 50 mg of $HBF_4{\cdot}Et_2O$ in CD_2Cl_2 was added by syringe. The frozen mixture was partially thawed in a dry ice/isopropyl alcohol bath and immediately inserted in the NR-80 spectrometer probe, precooled to −80 °C. The $^{13}C\{^1H\}$ NMR spectrum was determined to ascertain the presence of the *initially formed carbene* **11**. The temperature was then adjusted so that the rearrangement of **11** (Cp, δ ~92–89) to π-complex(es) (Cp, δ ~87–86) could be conviently observed. After ~2 half-lives the temperature was again increased to complete the reaction and to determine the spectrum of the final product(s).

Carbonyl(η^5-cyclopentadienyl)(trimethyl phosphite)[η^1-(1-methyl-1-cyclopropyl)methylidene]iron Tetrafluoroborate (11a) and Carbonyl(η^5-cyclopentadienyl)(trimethyl phosphite)[η^2-(1-methylcyclobutene)]iron Tetrafluoroborate (14a and 15a). Acidification of **8a** or **9a** at −80 °C as described above produces a single alkylidene, **11a**: $^{13}C\{^1H\}$ NMR[22] δ 363.1 (d, J_{CP} = 32 Hz, $=CH^+Fp'$), 214.3 (d, J_{CP} = 42 Hz, $C{\equiv}O$), 89.7 (Cp), 60.5 (>C<), 52.8 (d, $J_{CP} \approx 5$ Hz, $P(OCH_3)_3$), 38.2 and 37.3 (CH_2), 22.4 (CH_3).

The probe temperature was raised to −68 °C, and the spectrum was determined at ~2-h intervals. The half-life of the rearrangement of cationic carbene-to-cationic π-complexes $\mathbf{14a}^+$ or

15a$^+$, calculated from the integrated area of the gradually decreasing Cp resonance at δ 89.7 (carbene) and the simultaneously increasing resonances at δ 87.8 and 86.4 (π-complexes), was found to be ~7 h. At ~90% completion the ratio of the Cp resonances of the two product π-complexes was ~4:1. The $^{13}C\{^1H\}$ spectrum[22] of the **major component** (here arbitrarily designated **14a**$^+$) has the following resonances: δ 209.6 (d, $J_{CP} \approx 41$ Hz, C≡O), 108.6 [η^2-(Me*C*=CH)], 87.8 (Cp), 77.7 [d, $J_{CP} = 13$ Hz, η^2-(MeC=*C*H)], 55.4 (d, $J_{CP} = 9$ Hz, $P(OCH_3)_3$), 37.5 and 29.1 (CH_2), 27.8 (CH_3).

The probe temperature was increased to −46 °C and the $^{13}C\{^1H\}$ NMR spectrum again determined. At this temperature the ratio of the two product π-complexes becomes ~2:1. Resonances attributable to the **minor component** (here arbitrarily designated **15a**$^+$) occur at δ ~108.5 (?) [η^2-(Me*C*=CH)], 86.4 (Cp), 71.9 [d, $J_{CP} = 7$ Hz, η^2-(MeC=*C*H)], 54.3 (d, $J_{CP} = 8$ Hz, $P(OCH_3)_3$), 35.8, 26.1, and 25.9 (d, $J_{CP} \approx 4$ Hz). The C≡O resonance was too weak to be detected.

The carbene-to-π-complex rearrangement was also followed by monitoring the $^{31}P\{^1H\}$ NMR resonances at 121.4 or 202.4 MHz. At −66 °C the phosphorous resonance of cationic carbene **11a**$^+$ at δ 169 is slowly replaced by two new resonances at δ 164 and 163 whose relative integrated intensity is 1:4.5. The sample was removed momentarily from the probe, allowed to warm briefly (~0.5 min), reinserted in the cold probe, and the spectrum was redetermined. The resonance of the carbene (δ 169) was no longer evident while the relative intensities of the δ 164 and 163 resonances had become 1:2.5. After a second brief removal and reinsertion in the cold probe the ratio of the δ 164 and 163 resonances was 1:1.8. Warming for three additional ~0.5–1-min periods did not appear to change the product ratio further. The product π-complexes **14a** and **15a** are not stable at ambient temperature. After 2–5 min the solution darkens considerably and several new resonances appear.

Carbonyl(η^5-cyclopentadienyl)(trimethyl phosphite)[η^2-(1-methylcyclopentene)]iron Tetrafluoroborate (14b or 15b). Protonation of **8b** and/or **9b** at −80 °C presumably produces **11b** which could not be detected (see above) but rearranges to π-complex **14b** or **15b**: $^{13}C\{^1H\}$ NMR (−40 °C) δ 214.2 (d, $J_{CP} = 48.6$ Hz, C≡O), 106.2 [d, $J_{CP} = 3.8$ Hz, η^2-(>*C*=CH)], 87.3 (Cp), 75.4 [d, $J_{CP} = 2.0$ Hz, η^2-(>C=*C*H)], 54.7 (d, $J_{CP} = 9.5$ Hz, $P(OMe)_3$), 40.8 (d, $J_{CP} = 2$ Hz), 33.7, 25.5, 20.0.

Attempts to observe the nonrearranged cationic carbene by ^{31}P NMR were also unsuccessful. Only one π-complex was observed: $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −78 °C) δ 162. Warming for brief periods at room temperature did not result in isomerization to another π-complex.

Carbonyl(η^5-cyclopentadienyl)(trimethyl phosphite)[η^1-(1-methyl-1-cyclopentyl)methylidene]iron Tetrafluoroborate (11c) and Carbonyl(η^5-cyclopentadienyl)(trimethyl phosphite)[η^2-(1-methylcyclohexene)]iron Tetrafluoroborate (14c and 15c). Protonation of **8c** and/or **9c** at −68 °C produces **11c**; $t_{1/2} \approx 1.8$ h. The methylidene and the rearranged π-complexes are very unstable; rearrangement and decomplexation occur simultaneously. The Cp resonance of the initially formed cationic methylidene **11c**$^+$ occurs at δ 91.3. The two π-complexes **14c** and **15c** appear to be formed in approximately equal amounts; their $^{13}C\{^1H\}$ Cp resonances appear at δ 86.4 and 86.0. Resonances at δ 110.2 and 108.1, probably due to the methyl-substituted, π-complexed, olefinic carbons of the rearranged products also occur in roughly the same ratio. The remainder of the $^{13}C\{^1H\}$ NMR spectrum (presumably a mixture of π-complexes, unreacted methylidene and free, rearranged olefin) is too complex for meaningful analysis.

Carbonyl(η^5-cyclopentadienyl)(trimethyl phosphite)[η^1-(1-methyl-1-cyclohexyl)methylidene]iron Tetrafluoroborate (11d) and Carbonyl(η^5-cyclopentadienyl)(trimethyl phosphite)[η^2-(ethylidenecyclohexane)]iron Tetrafluoroborate (16d or 17d). Protonation of **8d** and/or **9d** at −43 °C produces **11d**: $t_{1/2} \approx 3.2$ h; $^{13}C\{^1H\}$ NMR (−43 °C) δ 392.3 [d, $J_{CP} = 30.1$ Hz, $(CH{=}Fp')^+$], 212.8 (d, $J_{CP} = 44$ Hz, C≡O), 91.5 (Cp), 66.7 (>C<?), ~54.1 (overlaps with the solvent, $P(OCH_3)_3$), 32.9, 25.6, 22.8, 21.5, 21.2 (?), 19.0. The $^{13}C\{^1H\}$ NMR spectrum[22] of the rearranged, π-complexed ethylidenecyclohexane **16d** or **17d** exhibits resonances at δ 216.3 (d, $J_{CP} = 49$ Hz, C≡O), 107.2 [η^2-(>*C*=CHMe)], 86.9 (Cp), 86.3 (~15%, Cp?), 67.7 [d, $J_{CP} = 7.8$ Hz, η^2-(>C=*C*HMe)], 54.9 (d, $J_{CP} = 9.8$ Hz, $P(OCH_3)_3$), 43.1, 36.7, 34.1, 30.5, 26.0 (CH_2), 18.7 (CH_3).

Decomplexation of Fp- and Fp′(η^2-olefins) (12, 13, and 14–17). Isolation and Spectral Analysis of the Rearranged Olefin(s) 18 and/or 19. The decomplexed, ring-enlarged and/or methyl-migrated olefinic product(s) were obtained in each case by adding excess tetrabutylammonium iodide to the NMR sample, inverting the tube several times to mix the contents, and allowing the mixture to stand at room temperature until its $^{13}C\{^1H\}$ spectrum showed that the Cp resonance(s) of the π-complex(es) at δ 88–86 had been largely or completely replaced by the Cp resonance of dicarbonyl(η^5-cyclopentadienyl)iodoiron at δ 84 or carbonyl(η^5-cyclopentadienyl)iodo(trimethyl phosphite)iron at δ 82. The decomplexed olefin **18** or **19**, together with ether and deuteriodichloromethane, was separated from the nonvolatiles by vacuum transfer into a second 5-mm NMR tube, and NMR spectra were determined.

1-Methyl-1-cyclobutene (18a): ^1H NMR δ 5.64 (br s, >C=CH), 2.40 (m, 2 H), 2.31 (m, 2 H), 1.66 (br s, CH_3); $^{13}C\{^1H\}$ NMR (CD_2Cl_2)[22] δ 147.0 (>C=), 128.1 (=CHMe), 33.0 and 26.8 (CH_2), 17.0 (CH_3).

The ^1H and $^{13}C\{^1H\}$ NMR spectra of **18b**, **18c**, and **19d**, isolated as described from the rearrangements of **10b–d** and **11b–d**, respectively, were identical with those of the known compounds (vide infra).[24]

Capillary gas chromatographic analysis of the decomplexed olefins 18 and/or 19 was carried out on a 10 m × 250 μm capillary coated with a 0.25-μm film of cross-linked methyl silicone at temperatures ranging from 10 to 30 °C. The highly volatile product(s) obtained from the cyclopropylmethylidenes **10a** and **11a** could not be completely separated from the dichloromethane solvent, but complete peak separation was achieved in the other cases. The identity of the decomplexed olefins in each product mixture was supported by admixture with authentic, pure (99+%) samples[24] of the appropriate 1-methylcycloalkene, viz. 1-methylcyclopentene, 1-methylcyclohexene, or 1-methylcycloheptene, and ethylidenecycloalkane, viz. ethylidenecyclopentane or ethylidenecyclohexane. In only one case, that of **10d**, does the initially formed alkylidene produce discernible amounts of both ring-enlarged **18d**, *and* methyl-migrated product, **19d**, cf. Table I.

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Registry No. **2a**, 16480-05-0; **2b**, 21890-82-4; **2c**, 20023-50-1; **2d**, 2890-61-1; **3a**, 123835-43-8; **3b**, 123835-44-9; **3c**, 123835-45-0; **3d**, 71988-12-0; **4a**, 123835-46-1; **4b**, 123835-47-2; **4c**, 123835-48-3; **4d**, 123835-49-4; **5a**, 123835-83-6; **5b**, 123835-85-8; **5c**, 123835-87-0; **5d**, 123835-89-2; **6a**, 123857-43-2; **6b**, 123835-51-8; **6c**, 123835-53-0; **6d**, 123835-55-2; **7a**, 123835-56-3; **7b**, 123835-57-4; **7c**, 123835-58-5; **7d**, 123835-59-6; **8,9a** isomer I, 123835-60-9; **8,9b** isomer I, 123835-61-0; **8,9c** isomer I, 123835-62-1; **8,9d** isomer I, 123835-63-2; **8,9a** isomer II, 123929-91-9; **8,9b** isomer II, 123929-92-0; **8,9c** isomer II, 123929-93-1; **8,9d** isomer II, 123929-94-2; **11a**, 123835-72-3; **11c**, 123835-76-7; **11d**, 123835-79-0; **12a**, 123835-65-4; **12b**, 123835-67-6; **12c**, 95014-01-0; **13a**, 123835-69-8; **13b**, 123835-70-1; **13c**, 123835-71-2; **13d**, 123835-68-7; **14a**, 123835-73-4; **14b**, 123835-75-6; **14c**, 123835-78-9; **16,17d** isomer I, 123835-81-4; **16,17d** isomer II, 123929-96-4; **18a**, 1489-60-7; **18b**, 693-89-0; **18c**, 591-49-1; **18d**, 1453-25-4; **19d**, 1003-64-1; $KFe(CO)_2(\eta^5\text{-}Cp)$, 60039-75-0.