Organometallics **1988**, *7*, 604–612

Secondary Methoxycarbene Complexes $[(\eta^5\text{-}C_5Me_5)M(CO)_2(CHOMe)]^+$ (M = Fe, Ru): Dynamic NMR Studies and Electrophilic Properties

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Received March 20, 1987

The anionic complex $[(\eta^5\text{-}C_5Me_5)Ru(CO)_2]^-K^+$ (3), a precursor of $(\eta^5\text{-}C_5Me_5)Ru(CO)_2(CH_2OMe)$ (2), is conveniently obtained by reduction of $[(\eta^5\text{-}C_5Me_5)Ru(CO)_2]_2$ by using a dispersion of potassium in boiling THF overnight. The methoxymethyl complexes $(\eta^5\text{-}C_5Me_5)M(CO)_2(CH_2OMe)$ (1, M = Fe; 2, M = Ru) undergo an α-hydride abstraction with $Ph_3C^+PF_6^-$ giving specifically the corresponding secondary methoxycarbene complexes $[(\eta^5\text{-}C_5Me_5)M(CO)_2(CHOMe)]^+PF_6^-$ (4, M = Fe; 5, M = Ru). Monitoring the above reaction by variable-temperature ^1H and ^{13}C NMR experiments shows that the carbene complexes 4 and 5 are formed at −80 °C as a mixture of cis and trans isomers in a 90:10 and 95:5 kinetic ratio, respectively; upon warming, the cis form irreversibly isomerizes into the more sterically favored trans isomer. NOE studies on 5 indicate that isomerism in these systems arises from restricted carbene carbon–oxygen bond rotation. Complex **4a** $(4^+CF_3SO_3^-)$ is also formed in the reaction of 1 with $Me_3SiOSO_2CF_3$ that proceeds by an intermolecular hydride transfer from the unreacted methoxymethyl complex 1 to the methylene cation intermediate $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2({=}CH_2)]^+$. Reaction of 4 (−80 °C) with PPh_3 gives the unstable α-methoxyphosphonium salt $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2(CHOMePPh_3)]^+PF_6^-$ (8) which was characterized at −20 °C by ^1H, ^{31}P, and ^{13}C NMR spectroscopy. The preferred conformation of 8 is discussed. The [:CHOMe] ligand of 4 or 5 inserts into the Si–H bond of Et_3SiH and Me_2PhSiH, giving the methoxymethylsilanes **10** and **11**, whereas 4 converts Ph_3SiH into Ph_3SiMe and Ph_3SiOMe via a hydride/methoxide exchange. The new alkene complexes $[(\eta^5\text{-}C_5Me_5)M(CO)_2(CH_2{=}CHR)]^+PF_6^-$ (**12**, M = Fe, R = H; **13**, M = Fe; R = Ph; **14**, M = Ru, R = H; **15**, M = Ru, R = Ph) are synthesized when the insertion reaction is carried out in the presence of $CH_2{=}CHR$. Complex **15a** $(15^+CF_3SO_3^-)$ can be also obtained from 2 upon treatment with $Me_3SiOSO_2CF_3$ in the presence of styrene. The X-ray crystal structure of **15a** shows that it crystallizes in the monoclinic space group $P2_1/c$ with unit cell parameters a = 8.533 (4) Å, b = 23.663 (7) Å, c = 11.480 (6) Å, β = 100.77 (7)°, and Z = 4. The structure was solved and refined (4333 reflections) to the final values for the residual R = 0.053 and R_w = 0.061.

Introduction

Since 1964, the year of the first synthesis and characterization of a stable transition-metal carbene complex by Fischer and Maasböl,[1] many carbene complexes have been obtained and have attracted intense interest, especially when heterocarbenes are coordinated to group 6 transition metals.[2,3] For group 7 and 8 transition metals some information is now available on the reactivity of related compounds,[4] mainly in connection with the Fischer–Tropsch synthesis and analogous processes.[5] Group 6 transition-metal carbene complexes have become increasingly important as reagents for organic synthesis or as precursors for new organometallic complexes.[2,5,6] In contrast, the scope of such applications for hetero-substituted carbene complexes of Fe or Ru has not yet been explored. This led us to investigate the synthesis, stability, and reactivity of a series of pentamethylcyclopentadienyl–iron and –ruthenium secondary alkoxycarbene complexes. Although homologous compounds are already known for cyclopentadienyl[5a] and related hydride transfer chemistry is well-documented,[5] we have used the now well-known $\eta^5\text{-}C_5Me_5$ ligand in order to protect the labile carbene ligand against competitive decomposition reactions and also to explore the role of bulky C_5Me_5 in determining the conformation adopted by the methoxycarbene fragment.

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Table I. NMR Spectral Characterization of Secondary Methoxycarbene Complexes $[(\eta^5\text{-}C_5Me_5)M(CO)_2\ (CHOMe)]^+\ PF_6^-$[a]

M	T, °C	NMR	CH	OMe	C_5Me_5	CO
Fe	26	^1H	12.27 (s)	4.67 (s)	1.94 (s)	
		^{13}C	325.3 (d, $^1J_{C\text{-}H}$ = 150 Hz)	78.5 (dq, $^1J_{C\text{-}H}$ = 152 Hz, $^3J_{C\text{-}H}$ = 8 Hz)	103.4 9.6 (q, $^1J_{C\text{-}H}$ = 129 Hz)	209.6
Ru[b]	26	^1H	12.25 (br. q, $^4J_{H\text{-}H}$ = 0.5 Hz)	4.76 (d, $^4J_{H\text{-}H}$ = 0.5 Hz)	2.09 (s)	
		^{13}C	308.8 (d, $^1J_{C\text{-}H}$ = 152 Hz)	78.8 (dq, $^1J_{C\text{-}H}$ = 152 Hz, $^3J_{C\text{-}H}$ = 8 Hz)	105.7 10.2 (q, $^1J_{C\text{-}H}$ = 129 Hz)	195.9
Ru[c]	−80	^1H	12.51 (q, $^4J_{H\text{-}H}$ = 1 Hz)	4.67 (d, $^4J_{H\text{-}H}$ = 1 Hz)	2.04 (s)	
		^{13}C	310.8 (d, $^1J_{C\text{-}H}$ = 157 Hz)	71.3 (dq, $^1J_{C\text{-}H}$ = 151 Hz, $^3J_{C\text{-}H}$ = 12 Hz)	106.8 10.4 (q, $^1J_{C\text{-}H}$ = 130 Hz)	196.9

[a] Chemical shifts in δ; solvent $CD_2Cl_2/CHDCl_2$ internal reference; ^1H (300 MHz); ^{13}C (75 MHz). [b] Trans isomer. [c] Cis isomer.

We report here: (i) a convenient access to the anionic complex $[(\eta^5\text{-}C_5Me_5)Ru(CO)_2]^-K^+$ (**3**), a useful precursor of alkyl derivatives, (ii) the synthesis and spectral characterization of the new secondary methoxycarbene bound to $Fe(C_5Me_5)$ (**4**) and $Ru(C_5Me_5)$ (**5**), (iii) dynamic NMR studies of the kinetic (cis) and thermodynamic (trans) isomers of **5** and cis to trans transformation, (iv) the reactivity of these carbene species toward nucleophilic reagents, especially carbene insertion into Si–H bonds allowing the synthesis of new organosilylated compounds, and (v) a new access to the unknown alkene complexes of the $C_5Me_5M(CO)_2$ series.

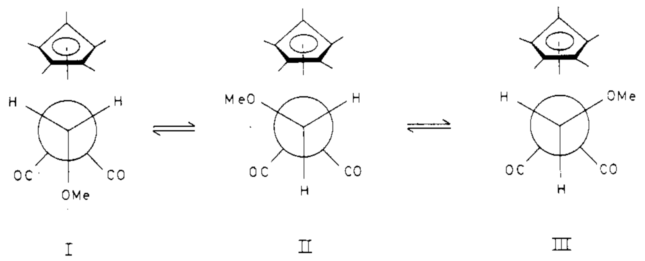
Results and Discussion

Synthesis of $(\eta^5\text{-}C_5Me_5)M(CO)_2(CH_2OMe)$ (1, M = Fe; 2, M = Ru) Complexes. The preparation of the methoxymethyl complexes $(\eta^5\text{-}C_5Me_5)M(CO)_2(CH_2OMe)$ (**1**, M = Fe;[7] **2**, M = Ru[8]) is identical with that of their $\eta^5\text{-}C_5H_5$ analogues,[9,10] i.e. alkylation with $ClCH_2OMe$ of the corresponding anion $[(\eta^5\text{-}C_5R_5)M(CO)_2]^-X^+$ ($X^+ = Na^+$ or K^+). However, access to the Ru anionic complex $[(\eta^5\text{-}C_5Me_5)Ru(CO)_2]^-K^+$ (**3**) has proved to be difficult; indeed, its formation by reduction of the dimer $[(\eta^5\text{-}C_5Me_5)Ru(CO)_2]_2$ in THF with Na/K alloy requires 3 days.[8] We have found that this synthesis is improved by using a dispersion of potassium metal in refluxing THF. The reaction is complete overnight on 2-mmol scale; the methoxymethyl derivative $(\eta^5\text{-}C_5Me_5)Ru(CO)_2(CH_2OMe)$ (**2**) is then obtained directly, without isolating **3**, in 89% yield (eq 1).

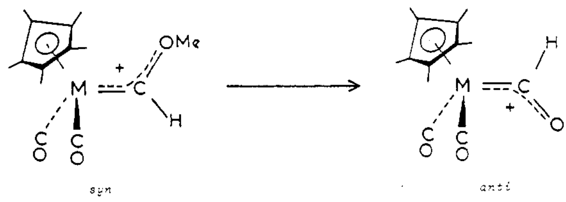
$$[(\eta^5\text{-}C_5Me_5)Ru(CO)_2]_2 \xrightarrow[\text{THF, reflux}]{\text{K}} \underset{\mathbf{3}}{2[(\eta^5\text{-}C_5Me_5)Ru(CO)_2]^-K^+} \xrightarrow{2ClCH_2OMe} \underset{\mathbf{2}}{2(\eta^5\text{-}C_5Me_5)Ru(CO)_2(CH_2OMe)} \quad (1)$$

The IR spectrum (pentane) of **2** is similar to that of **1**[7b] in displaying four carbonyl stretching bands, at 2010, 2000, 1950, and 1940 cm^{-1}. This phenomenon has been reported for other primary alkyl complexes and is a consequence of a rotational isomerism[9b,11] detectable on the IR time scale. Indeed, complex **2**, like **1**, can adopt three staggered conformations (Scheme I); the conformers II and III, being enantiomorphs, are spectroscopically equivalent. However, rotation is fast on the 75-MHz ^{13}C NMR time scale, making the carbonyl ligands of **2** magnetically equivalent so that they appear as a singlet at δ 204.6.

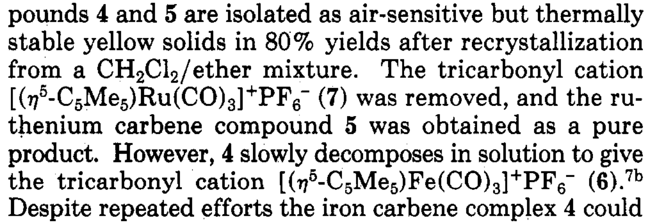
Scheme I



Scheme II



Synthesis of $[(\eta^5\text{-}C_5Me_5)M(CO)_2(CHOMe)]^+PF_6^-$ (4, M = Fe; 5, M = Ru). The secondary methoxycarbene complexes $[(\eta^5\text{-}C_5Me_5)M(CO)_2(CHOMe)]^+PF_6^-$ (**4**, M = Fe; **5**, M = Ru), as for the corresponding $(\eta^5\text{-}C_5H_5)Fe$ derivatives,[5a] are readily synthesized by hydride abstraction from the methoxymethyl precursor **1** or **2** with 1 equiv of $Ph_3C^+PF_6^-$ at −80 °C in CH_2Cl_2 (eq 2). Methoxide abstraction does not occur since quantitative formation of triphenylmethane has been established by GC. Compounds **4** and **5** are isolated as air-sensitive but thermally stable yellow solids in 80% yields after recrystallization from a CH_2Cl_2/ether mixture. The tricarbonyl cation $[(\eta^5\text{-}C_5Me_5)Ru(CO)_3]^+PF_6^-$ (**7**) was removed, and the ruthenium carbene compound **5** was obtained as a pure product. However, **4** slowly decomposes in solution to give the tricarbonyl cation $[(\eta^5\text{-}C_5Me_5)Fe(CO)_3]^+PF_6^-$ (**6**).[7b] Despite repeated efforts the iron carbene complex **4** could not be obtained in analytically pure form, but about 90–95% purity was achieved.



Both the iron and ruthenium carbene complexes **4** and **5** are characterized by IR, ^1H, and ^{13}C NMR spectroscopy. For example, the ^1H NMR spectrum (CD_2Cl_2, 26 °C) of **4** exhibits a low-field signal at δ 12.27 due to the carbene proton; the other signals corresponding to the methoxy group and the C_5Me_5 ligand are located at δ 4.67 and 1.94,

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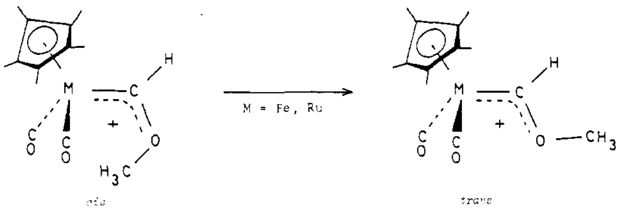
(9) (a) Jolly, P. W.; Pettit, R. *J. Am. Chem. Soc.* **1966**, *88*, 5044. (b) Moss, J. R.; Pelling, S. *J. Organomet. Chem.* **1982**, *236*, 221.

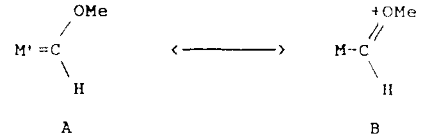
(10) Methoxymethyl complexes $(\eta^5\text{-}C_5R_5)M(CO)_2(CH_2OMe)$ are also accessible by $NaBH_3CN$ reduction of the tricarbonyl cation $[(\eta^5\text{-}C_5R_5)M(CO)_3]^+$ in methanol, see: (a) Bodnar, T.; Coman, E.; Menard, K.; Cutler, A. *Inorg. Chem.* **1982**, *21*, 1275. (b) Lin, C. Y.; Milstein, D.; Wreford, S. S. *Organometallics* **1983**, *2*, 1461. (c) Nelson, G. O. *Organometallics* **1983**, *2*, 1474.

(11) Stanley, K.; Baird, M. C. *J. Am. Chem. Soc.* **1975**, *97*, 4292.

Scheme III



Scheme IV



respectively. These ^{1}H chemical shifts compare well with those reported by Cutler[5a] for the related complex [(η^5-C_5H_5)Fe(CO)$_2$(CHOMe)]$^+PF_6^-$. Moreover, the ^{13}C resonance of the carbene carbon atom at δ 325.3 (d, $^1J_{C-H}$ = 150 Hz) confirms the proposed structure. Note that the CO ligands are magnetically equivalent and resonate as a singlet at δ 209.6 (see Table I); this indicates that either the carbene ligand rapidly rotates around the M=C bond or adopts the favored vertical orientation[12] (i.e. a syn or anti conformation, Scheme II). This aspect is discussed later.

Dynamic ^{1}H and ^{13}C NMR Studies. The hydride abstraction reaction has been monitored by variable-temperature ^{1}H and ^{13}C NMR experiments. The reaction, spectroscopically quantitative, is instantaneous at −80 °C and leads to the formation of the methoxycarbene complex [(η^5-C_5Me_5)M(CO)$_2$(CHOMe)]$^+PF_6^-$ (M = Fe, Ru) as a mixture of two geometric isomers (ratio of **4**, 90:10, and of **5**, 95:5). Upon warming, the major isomer isomerizes to the thermodynamically more stable form, i.e. the isolated compound. We propose that isomerism in this system arises from restricted rotation about the carbene carbon–oxygen bond: i.e., cis and trans isomers[13] arise from different orientations of the *O*-methyl substituent relative to the C=O bond (Scheme III), which has a partial double-bond character as a consequence of the contribution of the mesomeric form B (Scheme IV). Although this phenomenon has not been observed for the related (η^5-C_5H_5)Fe series,[5a] such isomerism is well-known in alkoxycarbene complexes of various metals.[2,4k,14] In the case described here, the conversion of the cis isomer into the trans is irreversible, and this proposal can therefore be corroborated by a full spectral study of the two isomers of **5**, the Ru compound being more appropriate for this purpose.[15]

As illustrated in Figure 1, the optimally resolved ^{1}H NMR spectrum (CD_2Cl_2) at −60 °C of *cis*-**5** displays a broad quartet (δ 12.51 ($^4J_{H-H}$ = 1 Hz)) for the carbene proton and a doublet (δ 4.67 ($^4J_{H-H}$ = 1 Hz)) for the methoxy group. Selective irradiations of these proton resonances give rise to respective singlets; therefore, the multiplicity results from an unprecedented ^4J(H–C–O–C–H) coupling for such a carbene. As the temperature rises, isomerization takes place; the signals due to *trans*-**5** increase while those of *cis*-**5** decrease. At −20 °C the resonances of *trans*-**5** appear at δ 12.15 (CH, br, q, $^4J_{H-H}$ = 0.5 Hz) and 4.73 (OMe, d, $^4J_{H-H}$ = 0.5 Hz). As for the cis isomer, the multiplicity of these signals is a consequence of a coupling between the protons of the carbene carbon substituents. The isomerization is irreversible; upon cooling to −80 °C NMR spectroscopy shows that the trans isomer does not transform back to the cis form.

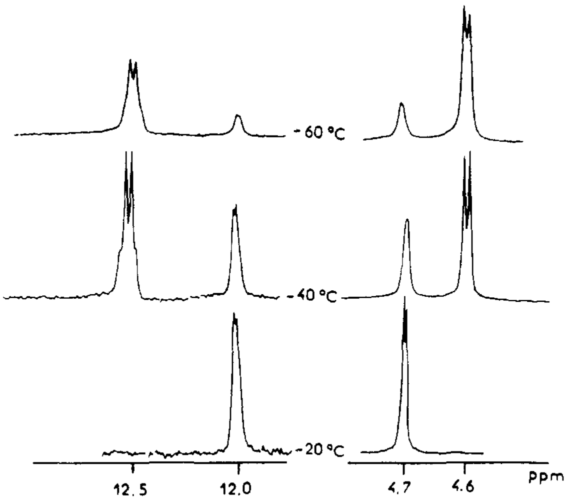


Figure 1. Variable-temperature 300-MHz ^{1}H NMR spectra of [(η^5-C_5Me_5)Ru(CO)$_2$(CHOMe)]$^+PF_6^-$ (**5**) in CD_2Cl_2.

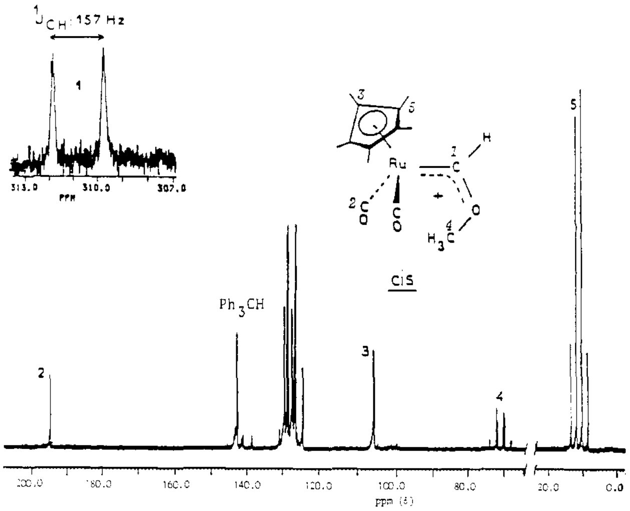


Figure 2. Proton-coupled 75-MHz ^{13}C NMR spectrum of *cis*-[(η^5-C_5Me_5)Ru(CO)$_2$(CHOMe)]$^+PF_6^-$ (**5**) in CD_2Cl_2 at −80 °C.

Carbon-13 NMR studies confirm the existence of two isomers. In the 75-MHz proton-coupled ^{13}C NMR spectrum (CD_2Cl_2) of *cis*-**5** (Figure 2), recorded at −80 °C, the carbene carbon atom appears as a characteristic downfield doublet at δ 310.8 ($^1J_{C-H}$ = 157 Hz) and the methoxy group resonates as a slightly split quartet at δ 71.3 ($^1J_{C-H}$ = 151 Hz, $^3J_{C-H}$ = 12 Hz). The ^{13}C NMR (CD_2Cl_2, 26 °C) chemical shifts of *trans*-**5** are rather different; for example, the methoxy group shift (δ 78.8 ($^1J_{C-H}$ = 152 Hz, $^3J_{C-H}$ = 8 Hz)) is at significantly lower field than that of the cis and the resonance of the carbene carbon atom is located at δ 308.8 (d, $^1J_{C-H}$ = 152 Hz). The spectroscopic data are compiled in Table I.

The observed phenomenon could be, a priori, explained in terms of isomerism about either the M=C or C=O bond. Indeed, the existence of geometric isomers due to restricted rotation about the metal–carbene carbon bond is well-established in rhenium–carbene (hetero-substituted or

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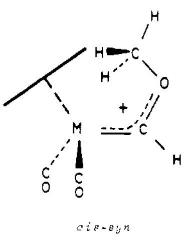
[12] Schilling, B. E. R.; Hoffman, R.; Lichtenberger, D. L. *J. Am. Chem. Soc.* **1979**, *101*, 585 .

[13] The cis isomer is defined as that in which the *O*-methyl group and the organometallic moiety are cis with respect to the C=O bond.

[14] Kreiter, C. G.; Fischer, E. O. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 761.

[15] It was at first believed that the existence of geometric isomers in the iron series was due to a restricted rotation about the Fe=C bond. Guerchais, V.; Lapinte, C. *J. Chem. Soc., Chem. Commun.* **1986**, 894.

Chart I

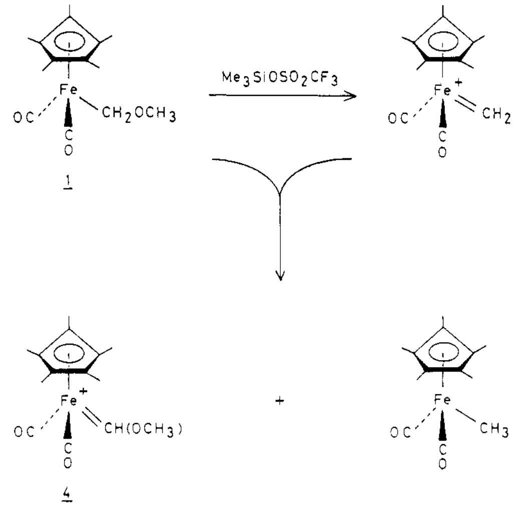


otherwise) complexes.[4k,5f,16] However, rotational barriers around the M═C bond in alkylidene complexes are substantially higher for Re than for Fe and Ru systems (ΔG^*[(Fe═CH$_2$)[7a,17a,18] or (Ru═CH$_2$)[17b]] ≈ 10 kcal·mol^{-1}; ΔG^*(Re═CH$_2$)[5f,19]] >15 kcal·mol^{-1}). Moreover, the electron-donating methoxy group in **5** will lower the metal–carbene carbon bond order (Scheme IV). The different dynamic NMR data are better rationalized as a consequence of a C$\overline{\cdot\cdot}$O isomerism. The following NOE experiments provide very strong evidence for this: irradiation of the respective C$_5$Me$_5$ resonance results in a large enhancement of the carbene proton resonance for both the cis and trans isomers (NOE; *cis*-**5** (−80 °C), 24%, *trans*-**5** (26 °C), 14%). These results provide additional evidence that the two isomers are not isomeric due to restricted rotation about the M$\overline{\cdot\cdot}$C bond (Scheme II). In such an event, only the anti form is expected to induce a NOE upon irradiation of the C$_5$Me$_5$ resonance. Moreover, as expected for a cis–trans isomerism about the C$\overline{\cdot\cdot}$O bond, irradiation of the OMe resonance for each of the isomers produces an enhancement of the CH resonance solely in the case of the thermodynamic product (NOE; *cis*-**5**, 0%, *trans*-**5**, 8%).

The different coupling constants $^4J_{H-H}$ and $^3J_{C-H}$ for the kinetic ($^4J_{H-H}$ = 1 Hz, $^3J_{C-H}$ = 12 Hz) and thermodynamic ($^4J_{H-H}$ = 0.5 Hz, $^3J_{C-H}$ = 8 Hz) products also suggest a different orientation of the *O*-methyl group relative to the carbene proton, i.e. C$\overline{\cdot\cdot}$O isomerism. In the cis isomer the orientation of the carbene H and Me groups (see Scheme III) would be expected to produce larger values of $^4J_{H-H}$ and $^3J_{C-H}$ than the orientation in the trans isomer; these respective atoms adopt a W conformation in the cis geometry.[20] Therefore the kinetic isomer is concluded to have the cis conformation. On the basis of steric considerations, the trans isomer appears to be the more thermodynamically stable.[21]

It has been suggested, on the basis of molecular models, that the cis conformation, in which the *O*-alkyl substituent is oriented toward the Cp ring (as depicted in Chart I), is not sterically allowed in the alkoxycarbene complexes of general type $(\eta^5\text{-}C_5H_5)M(CO)_2(M'Ph_3)[C(OR)R']$.[22] The presence of the very bulky C$_5$Me$_5$ ligand in our system makes the cis-syn form very unfavorable (Chart I). Lesser steric crowding in the trans isomer corresponds to greater thermodynamic stability of the latter and might explain the irreversible character of the isomerization.

Intermolecular Hydride Transfer. The methoxycarbene complex **4a** ($4^+CF_3SO_3^-$) is also produced (albeit indirectly) from the reaction of **1** with Me$_3$SiOSO$_2$CF$_3$ as indicated by ^{1}H NMR experiments; the cis and trans isomers of **4a** are generated at −80 °C in a 50:50 ratio. The electrophilic methylene complex $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2(CH_2)]^+CF_3SO_3^-$, transiently formed,[7a] is capable of abstracting a hydride from the methoxymethyl precursor **1**, giving **4a** and the methyl derivative $(\eta^5\text{-}C_5Me_5)Fe(CO)_2(CH_3)$ (eq 3). Such a bimolecular hydride transfer reaction is now well-established for various methylene cations.[5e–f,23] This reaction inhibits the bimolecular disproportionation of the methylene complex to the ethylene complex $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2(C_2H_4)]^+CF_3SO_3^-$ which is only produced under inverse equimolar addition conditions.[24]



(3)

In conclusion, the hydride abstraction reactions described here generate C$\overline{\cdot\cdot}$O geometric isomers; M$\overline{\cdot\cdot}$C geometric isomers in such a system, which might result from a stereospecific hydride abstraction,[25] would probably not be observed due to rapid isomerization.[26] The cis selectivity probably results from a better steric approach of the bulky trityl cation toward the methoxymethyl precursor. The cis–trans kinetic ratio depends on the hydride abstracting reagent. The highly reactive transient methylene complex is presumably a much less specific electrophilic agent.

Reaction with PPh$_3$. The electrophilic nature of complex **4** is illustrated by its reaction with triphenylphosphine to give the α-methoxyphosphonium adduct $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2(CHOMePPh_3)]^+PF_6^-$ (**8**); the reaction occurs at −80 °C, and **8** is formed in quantitative spectroscopic yield (eq 4). However, attempts to isolate **8** were

$$\underset{\mathbf{4}}{[(\eta^5\text{-}C_5Me_5)Fe(CO)_2(CHOMe)]^+PF_6^-} \xrightarrow[-80\ ^\circ C]{PPh_3} \underset{\mathbf{8}}{[(\eta^5\text{-}C_5Me_5)Fe(CO)_2(CHOMePPh_3)]^+PF_6^-} \quad (4)$$

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[16] 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. Kiel, W. A.; Lin, G.-Y.; Bodner, G. S.; Gladysz, J. A. *Ibid.* **1983**, *105*, 4958. Kiel, W. A.; Burho, W. E.; Gladysz, J. A. *Organometallics* **1984**, *3*, 879.

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[21] For X-ray crystal structures of alkoxyalkylcarbene bound to Ru-(η^5-C$_5$H$_5$), see, for example: Bruce, M. I.; Humphrey, M. G.; Snow, M. R.; Tiekink, E. R. T. *J. Organomet. Chem.* **1986**, *314*, 213. Consiglio, G.; Morandini, F.; Ciani, G. F.; Sironi, A. *Organometallics* **1986**, *5*, 1976.

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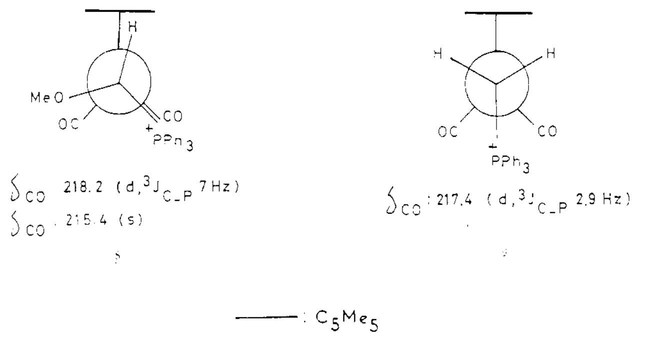
[23] Markhan, J.; Tolman, W.; Menard, K.; Cutler, A. *J. Organomet. Chem.* **1985**, *294*, 45. Davies, S. G.; Maberly, T. R. *Ibid.* **1985**, *296*, C37. Kegley, S. E.; Brookhart, M.; Husk, G. R. *Organometallics* **1982**, *1*, 760.

[24] Guerchais, V., unpublished results.

[25] Seeman, J. I.; Davies, S. G. *J. Am. Chem. Soc.* **1985**, *107*, 6522.

[26] Although several alkylidene complexes in the (η^5-C$_5$H$_5$)Fe series have been generated from diastereoisomeric complexes, no evidence of restricted rotation about the Fe═C bond have been found: (a) Casey, C. P.; Miles, W. H.; Tukada, H. *J. Am. Chem. Soc.* **1985**, *107*, 2924. (b) Brookhart, M.; Tucker, J. R. *Ibid.* **1981**, *103*, 979. (c) Reference 4e.

Chart II



unsuccessful; these afforded a mixture of the corresponding α-methylenephosphonium salt $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2(CH_2PPh_3)]^+PF_6^-$ (**9**) and cation **6**. Proton NMR analysis of the decomposition products also indicates the formation of MeOH, but further mechanistic studies have not been explored.

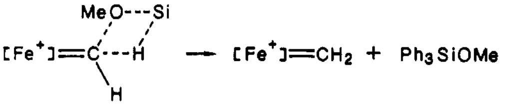
The structure of **8** has been assigned on the basis of its ^1H, ^{13}C, and ^{31}P NMR spectra (Experimental Section), its synthesis being performed in an NMR tube. It is noteworthy that in the ^{13}C NMR spectrum (CD_2Cl_2, -20 °C) of **8** the diastereotopic carbonyl ligands give rise to a doublet (δ 218.2 ($^3J_{C-P}$ = 7 Hz)) and a singlet (δ 215.4). In contrast, the CO signal (δ 217.4) of the methylene adduct **9** exhibits a smaller $^3J_{C-P}$ value of 2.9 Hz.[7a] Differences in the ^{31}P–CO coupling constants between **9** and **8** are to be expected since a bulky OMe group in **8** has replaced a hydrogen atom in **9** destroying the plane of symmetry (Chart II). A tentative explanation for the lack of ^{31}P–CO coupling for one of the CO resonances in **8** is the adoption of a preferred conformation such as that illustrated by the Newman projection in Chart II where the iron center has octahedral stereochemistry.[25] The Karplus equation would suggest one small or zero $^3J_{P-CO}$ value for such a conformation.

Insertion of the Methoxymethylene Ligand into the Si–H Bond. Cation **4** converts Me_2PhSiH and Et_3SiH into the respective methoxymethylsilanes $Me_2PhSiCH_2OMe$, (**10**) and Et_3SiCH_2OMe (**11**) in 59 and 60% yields (GC), respectively. Similarly, the reaction of Et_3SiH with the ruthenium analogue **5** affords **11**, in 50% yield (GC). Compounds **10** and **11** result from the insertion of the [:CHOMe] fragment into the Si–H bond of the silanes[27] (eq 5).

$$>\!Si\text{-}H \xrightarrow[\textbf{4 or 5}]{[M^+\!=\!CHOMe]} >\!Si\text{-}CH_2OMe \qquad (5)$$

Compound **10** is isolated from the reaction mixture by extraction with ether; the insoluble organoiron products precipitate. Chromatographic workup gives **10** as a spectroscopically pure colorless liquid. The more volatile triethyl derivative **11** is isolated by using a trap to trap distillation procedure. Compounds **10** and **11** were characterized on the basis of their spectral data. Thus, the ^1H NMR spectrum (C_6D_6) of **10** exhibits two singlets at δ 3.17 and 3.15 assigned to the methoxy and methylene protons, respectively. The synthesis of **10** was reported by Eaborn and Jeffrey,[28] through the reaction of $Me_2PhSiCH_2Cl$ with sodium methoxide over 10 days.

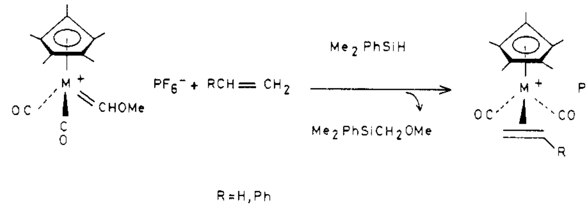
The reaction of **4** with Ph_3SiH (2 equiv) does not yield the insertion product Ph_3SiCH_2OMe but affords the derivatives Ph_3SiOMe[29] and Ph_3SiMe[30] in a 1:1 ratio with 88% overall yield based on **4** (GC). According to the data published by Connor et al.,[31] the formation of Ph_3SiOMe can be explained by a four-center transition state involving a Si–O interaction enhanced here by the electron-withdrawing phenyl groups (eq 6). Then Ph_3SiMe would come from the insertion of a methylene fragment[32]—produced in the first step—into the Si-H bond of a second molecule of Ph_3SiH, proceeding via a three-center mechanism.[31]



(6)

The foregoing data illustrate the behavior of the d^6 secondary methoxycarbene cations **4** and **5** toward hydrosilanes. As for free carbenes,[33] the metal-coordinated [:CHOMe] fragment is capable of inserting into the Si–H bond; such reactions are useful in trapping carbene intermediates and could be also of synthetic interest. On the other hand, with use of the more hydridic silane Ph_3SiH,[34] the reaction proceeds by a competitive pathway involving a hydride transfer to the electrophilic carbene carbon center in concert with a methoxide abstraction.

Synthesis of η^2-Alkene Complexes. Treatment of **4** or **5** with either Me_2PhSiH or Et_3SiH in the presence of an alkene (ethylene or styrene) gives, besides **10** and **11**, the new η^2-alkene complexes $[(\eta^5\text{-}C_5Me_5)M(CO)_2(CH_2{=}CHR)]^+PF_6^-$ (**12**, M = Fe, R = H; **13**, M = Fe, R = Ph; **14**, M = Ru, R = H; **15**, M = Ru, R = Ph) (eq 7). The insertion reaction, described above, frees a coordination site on the metal; this permits the introduction under mild conditions of a two-electron alkene ligand into the molecule. The methoxycarbene complexes **4** and **5** do not cyclopropanate the alkenes used.



(7)

The alkene complexes are isolated as stable yellow solids in 80% crude yield, and ruthenium alkene complexes are obtained as pure sample, but the iron ones are contaminated by about 5–10% of the tricarbonyl cation **6** which results from the decomposition of the initial carbene complex **4**. Each of these complexes shows characteristic olefinic ^1H and ^{13}C resonances shifted upfield upon coordination. The CO ligands of the styrene complexes **13** and **15** are diastereotopic since the molecule is chiral.

Complexes **12** and **6** can be converted back into the precursor complex **1** (70% yield) by reacting a THF slurry of **12** and **6** with Na/Hg, followed by alkylation with chloromethyl methyl ether of $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]^-Na^+$ thus produced (Scheme V). Such a reaction permits the recovery of the organometallic moiety that has proven to be a useful carbene-stabilizing group.

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(28) Eaborn, C.; Jeffrey, J. C. *J. Chem. Soc.* **1957**, 137.

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(31) Connor, J. A.; Rose, P. D.; Turner, R. M. *J. Chem. Soc., Dalton Trans.* **1976**, 108.

(32) The transient methylene complex $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2({=}CH_2)]^+$, generated at -80 °C from 1 + $Me_3SiOSO_2CF_3$, quantitatively converts in situ Ph_3SiH into the methylene insertion product Ph_3SiMe. Guerchais, V., unpublished observations.

(33) Kirmse, W. *Carbene Chemistry*, 2nd ed.; Academic: New York, 1971; Vol. 1.

(34) Weber, W. P. *Silicon Reagents for Organic Synthesis*; Springer-Verlag: Berlin, 1983, 275.

Scheme V

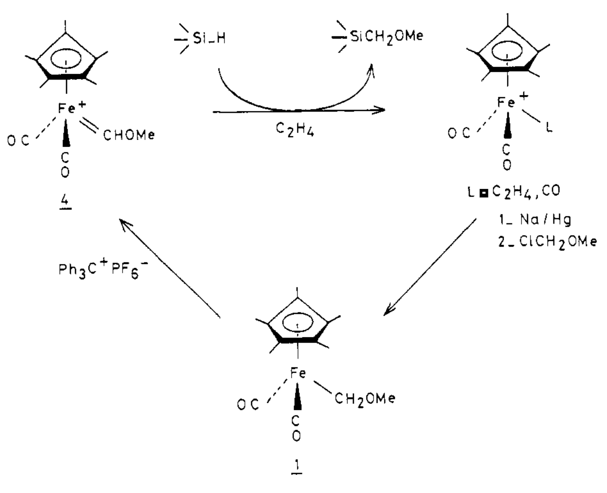

Table II. Selected Bond Distances and Angles for [(η^5-C_5Me_5)Ru(CO)$_2$(CH_2=CHPh)]$^+$$CF_3SO_3^-$ (15a)

Bond Distances (Å)			
Ru–C(11)	1.904 (8)	Ru–C(21)	2.272 (6)
Ru–C(12)	1.898 (6)	C(20)–C(21)	1.348 (8)
Ru–C(20)	2.331 (5)	Ru–C_5Me_5 (centroid)	1.881
Bond Angles (deg)			
C(11)–Ru–C(12)	92.0 (3)	C(20)–Ru–C(21)	34.0 (2)
C(11)–Ru–C(20)	110.3 (3)	Ru–C(11)–O(1)	173.1 (7)
C(11)–Ru–C(21)	79.9 (3)	Ru–C(12)–O(2)	173.7 (7)
C(12)–Ru–C(20)	86.8 (3)	H(21A)–C(21)–H(21B)	113 (5)
C(12)–Ru–C(21)	103.1 (3)	C(14)–C(20)–H(20)	111 (3)

The attempted synthesis of the ethylene complex **12** by THF displacement from [(η^5-C_5Me_5)Fe(CO)$_2$(THF)]$^+$$PF_6^-$ has been reported to fail.[7b] We have also tried to prepare the iron cation **12** by treatment of the halogeno compounds (η^5-C_5Me_5)Fe(CO)$_2$X (X = Br, Cl, I) in CH_2Cl_2 with 1 equiv of $AgBF_4$ or $AgPF_6$ in the presence of ethylene, but the reaction affords an as yet unidentified organometallic product; no traces of **12** were detected.[35]

Although the cationic alkene iron complexes are not obtained in pure form, our procedure is useful since the classical routes to them are ineffective. Moreover, we have found that the styrene complex [(η^5-C_5Me_5)Ru(CO)$_2$(CH_2=CHPh)]$^+$$CF_3SO_3^-$ (**15a**, $CF_3SO_3^-$ salt of **15**) is also formed upon reaction of **2** with $Me_3SiOSO_2CF_3$ in the presence of an excess of styrene.[24] Quantitative formation of phenylcyclopropane—together with **15a**—suggests the intermediacy of the methylene cation [(η^5-C_5Me_5)Ru(CO)$_2$(=CH_2)]$^+$$CF_3SO_3^-$. As in eq 7, the styrene (rather than the couteranion[36] $CF_3SO_3^-$) occupies the vacant site resulting from the carbene transfer. The structure of **15a** has been determined by X-ray crystallography.

Crystal and Molecular Structure of [(η^5-C_5Me_5)Ru(CO)$_2$(CH_2=CHPh)]$^+$$CF_3SO_3^-$ (15a). An ORTEP representation of complex **15a** is shown in Figure 3. Selected bond distances and angles are listed in Table II. The molecule adopts the pseudooctahedral geometry invariably observed for piano-stool complexes:[25] the C_5Me_5 ring is assumed to occupy three ligand sites and the carbonyl and styrene ligands are positioned in the other three sites (the Ru–styrene link is considered as a single vector to the centroid of the C=C bond).

Interest focuses on the structural features of the alkene ligand. The structural parameters imply a relatively weak interaction between metal and olefin: the Ru–C(20) and Ru–C(21) distances (2.331 (5) and 2.272 (6) Å, respectively) are somewhat greater than those observed in other η^2-C=C Ru systems,[37] and the C=C bond length (1.348 (8) Å) is particularly short, corresponding to a normal uncomplexed double bond. Steric repulsion between the alkene ligand and one of the methyls on the Cp ring is unlikely to be a factor here since the shortest nonbonding contact is H(9A)···H(20) of 2.48 Å. Electronic factors, however, militate for a not very strong bond: d^6 ML_5 units, such (η^5-C_5Me_5)Ru(CO)$_2$, are weak bases: i.e., the energy of the occupied π-type metallic frontier orbital is rather low, too far from the energy of the vacant π^*-accepting level of the ethylenic moiety to provide a strong Ru to C=C π-back-bonding interaction[38] However, the closely related (η^5-C_5Me_5)Re(CO)$_2$(η^2-Me_2C=CHCOMe) complex[39] exhibits a longer C=C bond (1.42 (2) Å), but the differences in the nature of the metal and the ethylenic ligand together with a rather low accuracy of this structure determination do not permit a detailed comparison.

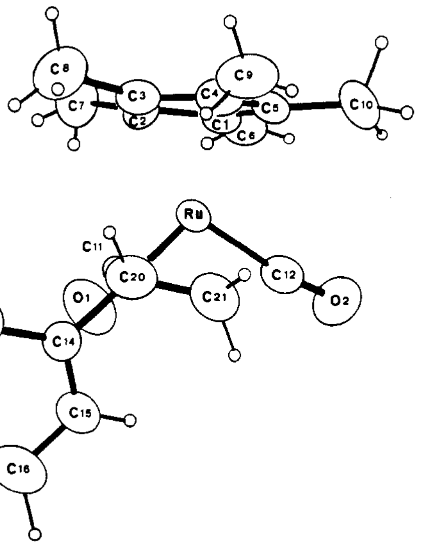

Figure 3. An ORTEP representation of [(η^5-C_5Me_5)Ru(CO)$_2$(CH_2=CHPh)]$^+$$CF_3SO_3^-$ (**15a**).

It has been shown, on the basis of NMR studies, that in [(η^5-C_5H_5)Fe(CO)$_2$(η^2-alkene)]$^+$ complexes, the alkene rapidly rotates about the metal–alkene axis against a rotational barrier of ca. 8 kcal·mol^{-1}.[12,38,40] The thermodynamically preferred conformation is that in which the C=C bond is parallel to the plane of the C_5H_5 ligand. The crystal structure of compound 15a reveals that the styrene adopts this particular orientation; the axis of the C(20)–C(21) olefinic bond is nearly parallel to the plane of the C_5Me_5 ring (deviation of 6.69°). Moreover, the substituted carbon atom C(20) is further from the Ru atom than unsubstituted C(21), a feature already observed for unsymmetrical olefin complexes.[38-40]

Experimental Section

General Data. All manipulations were performed under an argon atmosphere by using standard Schlenk techniques. Solvents were dried, distilled, and deaerated prior to use. Reagent grade tetrahydrofuran (THF), diethyl ether, and pentane were distilled

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(35) Thépot, J.-Y.; Guerchais, V., work in progress.

(36) In contrast, the iron analogue **13** is not obtained from **1** under similar reaction conditions, but the triflate adduct (η^5-C_5Me_5)Fe(CO)$_2$(OSO_2CF_3) is isolated: see ref 7a.

(37) (a) Smart, E. L. *J. Chem. Soc., Dalton. Trans.* **1976**, 390. (b) De C. T. Carrondo, M. A. A. F.; Chaudret, B. N.; Cole-Hamilton, D. J.; Skapski, A.; Wilkinson, G. *J. Chem. Soc., Chem. Commun.* **1978**, 463.

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(40) (a) Faller, J. W.; Johnson, B. U. *J. Organomet. Chem.* **1975**, *88*, 101. (b Laycock, D. E.; Baird, M. C. *Inorg. Chim. Acta* **1980**, *42*, 263.

from sodium benzophenone ketyl; methylene chloride was distilled from P_2O_5. The precursor complexes $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]_2$,[7b] $[(\eta^5\text{-}C_5Me_5)Ru(CO)_2]_2$,[10c,41] and $(\eta^5\text{-}C_5Me_5)Fe(CO)_2(CH_2OMe)$[7] were prepared according to published procedures. $Ph_3C^+PF_6^-$ was synthesized by a literature method.[42] All other chemicals were used as received. Caution: chloromethyl methyl ether should be used with care due to its toxicity. Infrared solution spectra were recorded on a Pye Unicam SP 1100 spectrophotometer using 0.1-mm cells with KBr windows and were calibrated with polystyrene film. Proton, ^{31}P, and ^{13}C NMR spectra were recorded on a Bruker WP 80 FT or AM 300 WB instrument. All chemical shifts are in parts per million (δ) with reference to residual $CHDCl_2$ (δ 5.30), C_6HD_5 (δ 7.15), CHD_2CN (δ 1.96), or Me_4Si for ^1H NMR data, CD_2Cl_2 (δ 53.8), C_6D_6 (δ 128.0), or CD_3CN (δ 1.26) for ^{13}C resonances, and 85% H_3PO_4 for ^{31}P resonances. Mass spectra were obtained on a Varian MAT 311 (70 eV) instrument at the Centre Régional de Mesures Physiques de l'Ouest (Université de Rennes I). GLC analyses were performed on a Delsi GC 121 chromatograph equipped with a Hewlett-Packard 3390 A integrator, by using a glass column (length, 1.4 m; i.d., 3 mm) packed with Apiezon L (15%) on Chromosorb WAW. Elemental analyses were performed by the Service Central de Microanalyse du CNRS at Lyon. NMR data for compounds **4** and **5** are summarized in Table I.

Preparation of $(\eta^5\text{-}C_5Me_5)Ru(CO)_2(CH_2OMe)$ (2). A Schlenk tube was charged with 390 mg (10 mmol) of potassium, 1.17 g (2 mmol) of $[(\eta^5\text{-}C_5Me_5)Ru(CO)_2]_2$, and 20 mL of degassed THF. The reaction mixture was refluxed overnight; the resulting yellow-brown solution was filtered at room temperature through glass-wool, then cooled to −60 °C, treated with 0.3 mL (4 mmol) of $ClCH_2OMe$, and evaporated to dryness in vacuo. The residue was extracted with pentane (2 × 10 mL). Evaporation of the solvent gave 1.2 g (89%) of **2** as a brown oil: IR (pentane) 2010, 2000, 1950, 1940 (s, ν(CO)), 1070 (s, ν(C–O)) cm^{-1} (lit.[8] 1998, 1938 cm^{-1}); ^1H NMR (C_6D_6) δ 4.59 (s, 2 H, CH_2), 3.26 (s, 3 H, OMe), 1.60 (s, 15 H, C_5Me_5) (lit.[8] δ 4.67, 3.34, 1.70); $[^1H]^{13}C$ NMR (C_6D_6) δ 204.6 (CO), 99.8 (C_5Me_5), 64.8 (CH_2), 60.9 (OMe), 9.6 (C_5*Me*$_5$).

Preparation of $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2(CHOMe)]^+PF_6^-$ (*trans*-4). To a Schlenk tube were introducted 1.33 g (4.55 mmol) of $(\eta^5\text{-}C_5Me_5)Fe\ (CO)_2(CH_2OMe)$ (**1**) and 10 mL of CH_2Cl_2, the mixture was cooled to −80 °C, and then 1.75 g (4.51 mmol) of $Ph_3C^+PF_6^-$ was added under argon to the yellow solution. After being stirred for 1 h at −80 °C, the reaction mixture was slowly warmed to −30 °C. The solvent was evaporated to dryness and the residue washed with ether to remove Ph_3CH. **4** (1.42 g, 71%) was obtained as a pale yellow microcrystalline solid after recrystallization from CH_2Cl_2–ether. Spectroscopic data indicated that the solid contained a small amount (5–10%) of $[(\eta^5\text{-}C_5Me_5)Fe(CO)_3]^+PF_6^-$ (**6**), the product of decomposition of **4**, which was impossible to eliminate. **4**: IR (CH_2Cl_2) 2060 (s, ν(CO)), 2010 (s, ν(CO)) cm^{-1}. Anal. Calcd for $C_{14}H_{19}FeF_6O_3P$ + $C_{13}H_{15}FeF_6O_3P$ (90:10): C, 38.42; H, 4.31. Found: C, 38.10; H, 4.39.

Preparation of $[(\eta^5\text{-}C_5Me_5)Ru(CO)_2(CHOMe)]^+PF_6^-$ (*trans*-5). According to the procedure described above, 337 mg (1 mmol) of $(\eta^5\text{-}C_5Me_5)Ru(CO)_2(CH_2OMe)$ (**2**) was treated with 388 mg (1 mmol) of $Ph_3C^+PF_6^-$ to give 385 mg (80%) of the ruthenium compound **5** as a yellow-brown solid: IR (CH_2Cl_2) 2085 (s, ν(CO)), 2035 (s, ν(CO)) cm^{-1}. Anal. Calcd for $C_{14}H_{19}F_6O_3PRu$: C, 34.93; H, 3.98. Found: C, 35.16; H, 3.80.

Generation and Spectral Characterization of $[(\eta^5\text{-}C_5Me_5)M(CO)_2(CHOMe)]^+PF_6^-$ (M = Ru, *cis*- and *trans*-5; M = Fe, *cis*- and trans-4). **A.** $(\eta^5\text{-}C_5Me_5)Ru(CO)_2(CH_2OMe)$ (**2**, 10 mg, 0.029 mmol), was dissolved in 0.4 mL of CD_2Cl_2 in a ^1H NMR tube. To the solution, cooled to −80 °C and degassed with argon, was added 12 mg (0.031 mmol) of $Ph_3C^+PF_6^-$ in 0.2 mL of CD_2Cl_2. The tube was shaken and transferred to a −80 °C NMR probe. The ^1H NMR spectrum recorded at −80 °C reveals the quantitative formation of **5** (ratio *cis*-**5**:*trans*-**5** = 95:5). Upon warming, *cis*-**5** converted into *trans*-**5**. Carbon-13 spectra were obtained from a sample prepared from 169 mg (0.50 mmol) of **2** and 198 mg (0.51 mmol) of $Ph_3C^+PF_6^-$ in 4 mL of CD_2Cl_2 at −80 °C in a standard 10-mm NMR tube. NMR data are summarized in Table I.

B. As described in A, the ^1H NMR spectrum of **4** (cis:trans = 90:10) was recorded at −80 °C starting from a CD_2Cl_2 solution of 10 mg (0.034 mmol) of **1** and 15 mg (0.038 mmol) of $Ph_3C^+PF_6^-$; ^1H NMR (CD_2Cl_2) δ 12.68 and 12.23 (br s, $=CH_{cis}$ and br s, $=CH_{trans}$, total 1 H), 4.70 (br s, 3 H, OMe), 1.97 (br s, 15 H, C_5Me_5).

NMR Characterization of $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2(CHOMe)]^+CF_3SO_3^-$ (4a). In a ^1H NMR tube was dissolved 15 mg (0.051 mmol) of **1** in 0.4 mL of CD_2Cl_2. After the solution was cooled to −80 °C, 9 μL (0.047 mmol) of $Me_3SiOSO_2CF_3$ was added via syringe. The 80-MHz ^1H NMR spectrum taken immediately (−80 °C) showed formation of **4a** (cis:trans = 50:50): ^1H NMR (CD_2Cl_2) δ 12.61 and 12.20 (br s, $=CH_{cis}$, and br s, $=CH_{trans}$, total 1 H, ratio 1:1), 4.62 (br s, 3 H, OMe), 1.87 (br s, 15 H, C_5Me_5).

Generation and Spectral Characterization of $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2(CHOMePPh_3)]^+PF_6^-$ (8). A solution of 218 mg (0.5 mmol) of **4** in 2 mL of CD_2Cl_2 was transferred via a canula to a standard 10-mm NMR tube. The solution was degassed and cooled to −80 °C, and a solution of 131 mg (0.5 mmol) of PPh_3 in 1 mL of CD_2Cl_2 was added via syringe. The reaction mixture immediately turned bright yellow. NMR spectra were recorded at −20 °C and indicated the quantitative formation of **8**: ^1H NMR (CD_2Cl_2) δ 7.74–7.65 (2 × m, 15 H, PPh_3), 5.13 (d, 1 H, $^2J_{P-H}$ = ca. 1.5 Hz, CH), 3.22 (s, 3 H, OMe), 1.58 (s, 15 H, C_5Me_5); $[^1H]^{13}C$ NMR (CD_2Cl_2) δ 218.2 (CO, d, $^3J_{P-C}$ = 7 Hz), 215.4 (CO, s), 134.5, 134.4, 130.3, 121.6 (Ph), 98.1 (C_5Me_5), 74.8 (CH, d, $^1J_{P-C}$ = 28 Hz), 62.5 (OMe, d, $^3J_{P-C}$ = 8 Hz), 9.7 (C_5*Me*$_5$); $[^1H]^{31}P$ NMR (CD_2Cl_2) δ 27.1 (PPh_3), −144.8 (PF_6^-, septet).

Attempted Isolation of 8. PPh_3 (262 mg, 1 mmol) was added to a stirred solution of 436 mg (1 mmol) of **4** in 20 mL of CH_2Cl_2 at −80 °C. The reaction mixture was then allowed to warm to room temperature. The solution was concentrated under vacuum, and addition of 20 mL of ether precipitated a yellow solid (415 mg). This contained **6** (66%) and **9** (33%), as shown by ^1H and $[^1H]^{13}C$ NMR spectroscopy. The structure of **9** was assigned on the basis of the similarity of its chemical shifts to those of the BF_4^- analogue, prepared independently.[7a]

Preparation of $Me_2PhSiCH_2OMe$ (10). In a Schlenk tube, 700 mg (1.6 mmol) of freshly prepared $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2(CHOMe)]^+PF_6^-$ (**4**) and 245 μL (1.6 mmol) of Me_2PhSiH were dissolved in 30 mL of CH_2Cl_2 at −60 °C. The reaction mixture was stirred for 1 h and warmed to room temperature. Gas chromatography (120 °C) of the resulting solution (the integrated nonsaturated solvent peak is used as internal standard) indicated a 59% yield of **10**. The solvent was evaporated to dryness and $Me_2PhSiCH_2OMe$ extracted with ether; the insoluble organoiron products are insoluble in this medium. (Chromatography on silica plates (0.2 mm, eluant petroleum ether) gave spectroscopically pure **10** as a colorless liquid: mass spectrum, *m/e* 165.0749 (M^+ − Me), calcd for $C_9H_{13}OSi$ *m/e* 165.0735; ^1H NMR (C_6D_6) δ 7.55–7.21 (2 × m, 5 H, Ph), 3.17 (s, 3 H, OMe), 3.15 (s, 2 H, CH_2), 0.31 (s, 6 H, Me); $[^1H]^{13}C$ NMR (C_6D_6) δ 137.9, 134.2, 129.5, 128.1 (Ph), 66.6 (CH_2), 63.2 (OMe), −4.3 (Me).

Characterization of Et_3SiCH_2OMe (11). A freshly prepared sample of 422 mg (0.97 mmol) of **1** was dissolved in 10 mL of CH_2Cl_2 at −60 °C, and 155 μL (0.97 mmol) of Et_3SiH was added via syringe. The reaction mixture was then slowly warmed to ambient temperature. GC analysis (80 °C) of the solution, by using the nonsaturated integrated solvent peak as internal standard, established a 60% yield of **11**. A trap to trap distillation was used to extract Et_3SiCH_2OMe (**11**) as a colorless liquid: mass spectrum, *m/e* 160.1274, calcd for $C_8H_{20}OSi$ *m/e* 160.1283; ^1H NMR (C_6D_6) δ 3.18 (s, 3 H, OMe), 3.07 (s, 2 H, CH_2), 0.96 (q, 6 H, CH_2), 0.55 (t, 9 H, CH_3).

Reaction of $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2(CHOMe)]^+PF_6^-$ (4) with Ph_3SiH. A solution of 436 mg (1 mmol) of **4** and 520 mg (2 mmol) of Ph_3SiH in 10 mL of CH_2Cl_2 was stirred at −60 °C for 2 h and then warmed to room temperature. The solution was analyzed by GC (180 °C) and found to contain Ph_3SiOMe (88% yield vs **4**) and Ph_3SiMe (88% yield vs **4**). After removal of the solvent in vacuo, the silanes were extracted with ether and chromatographed on silica plates (0.2 mm, eluant petroleum ether). Ph_3SiOMe:[29] ^1H NMR (CD_3CN) δ 7.59–7.41 (2 × m, 15 H, Ph), 3.58 (s, 3 H, OMe); mass spectrum, *m/e* 290.1132, calcd for

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Table III. Positional Parameters and Isotropic Thermal Parameters for $[(\eta^5\text{-}C_5Me_5)Ru(CO)_2(CH_2{=}CHPh)]^+CF_3SO_3^-$ (15a)[a]

atom	*x*	*y*	*z*	*B*, Å^2
Ru	0.37697 (6)	0.10467 (2)	0.63655 (4)	2.862 (9)
S	0.2634 (3)	0.3707 (1)	0.6549 (2)	5.69 (5)
F(1)	−0.0039 (9)	0.1268 (4)	1.0037 (7)	11.5 (2)
F(2)	−0.026 (1)	0.1195 (5)	1.1746 (8)	16.4 (3)
F(3)	0.0541 (9)	0.0515 (3)	1.102 (1)	15.7 (3)
O(1)	0.1227 (7)	0.0574 (3)	0.4413 (5)	6.5 (2)
O(2)	0.6454 (7)	0.0475 (3)	0.5454 (5)	6.7 (1)
O(3)	0.251 (1)	0.3164 (4)	0.652 (1)	17.9 (5)
O(4)	0.341 (1)	0.3928 (5)	0.5627 (7)	13.6 (3)
O(5)	0.3191 (9)	0.0978 (3)	1.2596 (6)	8.4 (2)
C(1)	0.2059 (8)	0.0879 (3)	0.7589 (6)	3.9 (2)
C(2)	0.3241 (8)	0.0441 (3)	0.7695 (6)	3.4 (1)
C(3)	0.4747 (8)	0.0699 (3)	0.8173 (6)	3.6 (2)
C(4)	0.4505 (9)	0.1280 (3)	0.8303 (6)	3.8 (2)
C(5)	0.2850 (9)	0.1399 (3)	0.7938 (6)	3.7 (2)
C(6)	0.0284 (9)	0.0793 (5)	0.7224 (8)	6.1 (2)
C(7)	0.296 (1)	−0.0178 (3)	0.7519 (7)	5.2 (2)
C(8)	0.625 (1)	0.0371 (4)	0.8589 (8)	6.1 (2)
C(9)	0.574 (1)	0.1673 (4)	0.8921 (7)	6.3 (2)
C(10)	0.210 (1)	0.1955 (4)	0.8066 (7)	6.2 (2)
C(11)	0.2226 (9)	0.0759 (3)	0.5088 (6)	4.1 (2)
C(12)	0.5473 (9)	0.0713 (3)	0.5756 (6)	4.3 (2)
C(13)	0.067 (1)	0.1017 (4)	1.1029 (9)	7.0 (3)
C(14)	0.6179 (8)	0.3068 (3)	1.0295 (6)	3.5 (1)
C(15)	0.7525 (9)	0.2789 (3)	1.0861 (7)	4.7 (2)
C(16)	0.8837 (9)	0.2726 (4)	1.0286 (9)	6.0 (2)
C(17)	0.881 (1)	0.2948 (4)	0.9206 (8)	5.7 (2)
C(18)	0.748 (1)	0.3218 (4)	0.8684 (7)	6.0 (2)
C(19)	0.6189 (9)	0.3284 (3)	0.9198 (7)	4.4 (2)
C(20)	0.4730 (9)	0.1917 (3)	0.5854 (6)	4.2 (2)
C(21)	0.3228 (8)	0.1842 (3)	0.5255 (7)	4.7 (2)
H(6A)	−0.067 (8)	0.114 (3)	0.689 (6)	4*
H(6B)	−0.028 (7)	0.084 (3)	0.799 (5)	4*
H(6C)	−0.002 (7)	0.038 (3)	0.668 (5)	4*
H(7A)	0.269 (7)	−0.043 (3)	0.808 (5)	4*
H(7B)	0.206 (7)	−0.023 (3)	0.704 (5)	4*
H(7C)	0.392 (7)	−0.043 (3)	0.736 (5)	4*
H(8A)	0.637 (7)	0.024 (3)	0.937 (5)	4*
H(8B)	0.703 (7)	0.058 (3)	0.852 (5)	4*
H(8C)	0.649 (7)	0.027 (3)	0.799 (5)	4*
H(9A)	0.568 (7)	0.194 (3)	0.871 (5)	4*
H(9B)	0.674 (7)	0.165 (3)	0.872 (5)	4*
H(9C)	0.573 (7)	0.178 (3)	0.976 (5)	4*
H(10A)	0.276 (7)	0.234 (3)	0.774 (5)	4*
H(10B)	0.224 (7)	0.208 (3)	0.882 (5)	4*
H(10C)	0.131 (7)	0.196 (3)	0.769 (5)	4*
H(15)	0.775 (7)	0.224 (3)	0.673 (5)	4*
H(16)	0.977 (7)	0.253 (3)	1.084 (5)	4*
H(17)	0.964 (7)	0.203 (3)	0.360 (5)	4*
H(18)	0.747 (7)	0.331 (3)	0.817 (5)	4*
H(19)	0.526 (7)	0.154 (3)	0.382 (5)	4*
H(20)	0.490 (7)	0.212 (3)	0.655 (5)	4*
H(21A)	0.300 (7)	0.174 (3)	0.434 (5)	4*
H(21B)	0.256 (7)	0.196 (3)	0.545 (5)	4*

[a] Estimated standard deviations in parentheses. Parameters with an asterisk were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(^4/_3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

Table IV. Experimental Crystallographic Data for 15a

formula	$C_{21}H_{23}F_3O_5SRu$
fw	545.5
cryst system	monoclinic
space group	$P2_1/c$
a, Å	8.533 (4)
b, Å	23.663 (7)
c, Å	11.480 (6)
β, deg	100.77 (7)
V, Å^3	2277 (1)
Z	4
d_{calcd}, Mg m^{-3}	1.72
cryst size, mm	0.25 × 0.2 × 0.15
θ limits, deg (*h*, 0.10; *k*, 0.28; *l*, 13.13)	1° < *θ* < 25°
octants collected	$+h,+k,\pm l$
diffractometer	CAD-4 Enraf-Nonius
radiatn Mo K_α (λ), Å	0.710 69
monochromator	graphite crystal
abs coeff (*μ*), cm^{-1}	9.33
scan type	$\omega/2\theta$
t_{max}, s	60
data collected	4333
obsd data	2277
R, R_w	0.053, 0.061

$C_{19}H_{18}OSi$ *m/e* 290.1127. Ph_3SiMe:[30] ^1H NMR (CD_3CN) δ 7.58–7.46 (2 × m, 15 H, Ph), 0.93 (s, 3 H, Me); mass spectrum, *m/e* 274.1185, calcd for $C_{19}H_{18}Si$ *m/e* 274.1178.

Preparation of $[(\eta^5\text{-}C_5Me_5)M(CO)_2(CH_2{=}CHR)]^+PF_6^-$ (12, M = Fe, R = H; 13, M = Fe, R = Ph; 14, M = Ru, R = H; 15, M = Ru, R = Ph). General Procedure. A CH_2Cl_2 solution of the methoxycarbene complex (1 mmol) and Et_3SiH or Me_2PhSiH (1 mmol) was stirred for 2 h in the presence of the appropriate alkene (atmospheric pressure of C_2H_4 or 1 equiv of styrene). The solvent was then removed under vacuum and the yellow solid washed with ether. Recrystallization from CH_2Cl_2/ether gave the (η^2-alkene)ruthenium complexes 14 and 15 in analytically pure form but did not allow further purification for the iron complexes. Proton NMR analysis of the compounds 12 and 13 (80%) showed the presence of about 5–10% of the corresponding cation $[(\eta^5\text{-}C_5Me_5)Fe(CO)_3]^+PF_6^-$.

$[(\eta^5\text{-}C_5Me_5)Fe(CO)_2(CH_2{=}CH_2)]^+PF_6^-$ (12): ^1H NMR (CD_2Cl_2) δ 3.14 (s, 4 H, C_2H_4), 1.94 (s, 15 H, C_5Me_5); $[^1H]^{13}C$ NMR (CD_2Cl_2) δ 211.8 (CO), 102.6 (C_5Me$_5$), 59.5 (C_2H_4), 9.5 (C$_5$*Me*$_5$); IR (CH_2Cl_2) 2050 (s, ν(CO)), 2020 (s, ν(CO)) cm^{-1}. Anal. Calcd for $C_{14}H_{19}FeF_6O_2P$ + $C_{13}H_{15}FeF_6O_3P$ (90:10): C, 39.75; H, 4.47. Found: C, 39.54; H, 4.39.

$[(\eta^5\text{-}C_5Me_5)Fe(CO)_2(CH_2{=}CHPh)]^+PF_6^-$ (13): ^1H NMR (CD_2Cl_2) δ 7.35–7.26 (2 × m, 5 H, Ph), 4.89 (dd, 1 H, $^3J_{H-H}$(trans) = 14.6 Hz, $^3J_{H-H}$(cis) = 8.8 Hz, C*H*Ph), 3.97 (dd, 1 H, $^2J_{H-H}$(gem) = 1.8 Hz, H_Z), 3.03 (dd, 1 H, H_E), 1.94 (s, 15 H, C_5Me_5); $[^1H]^{13}C$ NMR (CD_2Cl_2) δ 212.3 (CO), 211.0 (CO), 136.0, 131.0, 130.2, 126.9 (Ph), 102.4 (C_5Me$_5$), 86.4 (*C*HPh), 52.4 (CH_2), 9.6 (C$_5$*Me*$_5$); IR (CH_2Cl_2) 2060 (s, ν(CO)), 2020 (s, ν(CO)) cm^{-1}. Anal. Calcd for $C_{20}H_{23}FeF_6O_2P$ + $C_{13}H_{15}FeF_6O_3P$ (90:10): C, 47.29; H, 4.56. Found: C, 47.58; H, 4.31.

$[(\eta^5\text{-}C_5Me_5)Ru(CO)_2(CH_2{=}CH_2)]^+PF_6^-$ (14): ^1H NMR (CD_2Cl_2) δ 3.36 (s, 4 H, C_2H_4), 2.04 (s, 15 H, C_5Me_5); $[^1H]^{13}C$ NMR (CD_2Cl_2) δ 197.5 (CO), 105.1 (C_5Me$_5$), 58.0 (C_2H_4), 10.1 (C$_5$*Me*$_5$); IR (CH_2Cl_2) 2080 (s, ν(CO)), 2040 (s, ν(CO)) cm^{-1}. Anal. Calcd for $C_{14}H_{19}F_6O_2PRu$: C, 36.14; H, 4.12. Found: C, 36.21; H, 4.19.

$[(\eta^5\text{-}C_5Me_5)Ru(CO)_2(CH_2{=}CHPh)]^+PF_6^-$ (15): ^1H NMR (CD_2Cl_2) δ 7.36 (m, 5 H, Ph), 5.14 (dd, 1 H, $^3J_{H-H}$(trans) = 14.3 Hz, $^3J_{H-H}$(cis) = 8.8 Hz, C*H*Ph), 4.31 (dd, 1 H, $^3J_{H-H}$(trans) = 14.3 Hz, $^2J_{H-H}$(gem) = 1.4 Hz, H_Z), 3.13 (dd, 1 H, $^3J_{H-H}$(cis) = 8.8 Hz, $^2J_{H-H}$(gem) = 1.4 Hz, H_E), 2.03 (s, 15 H, C_5Me_5); $[^1H]$ ^{13}C NMR (CD_2Cl_2) δ 197.8 (CO), 196.8 (CO), 136.1, 130.7, 130.1, 126.6 (Ph), 104.9 (C_5Me$_5$), 86.3 (*C*HPh), 51.6 (CH_2), 10.0 (C$_5$*Me*$_5$); IR (CH_2Cl_2) 2080 (s, ν(CO)), 2040 (s, ν(CO)) cm^{-1}. Anal. Calcd for $C_{20}H_{23}F_6O_2PRu$: C, 44.37; H, 4.28; Ru, 18.67. Found: C, 44.07; H, 4.33; Ru, 18.69.

Preparation of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2(CH_2OMe)$ (1) from $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2(C_2H_4)]^+PF_6^-$ (12) and 6. A THF suspension of 150 mg (0.35 mmol) of a mixture of 12 and 6 in a 80:20 ratio was stirred on 3.22 g (1.4 mmol of Na) of Na/Hg overnight. The solution was transferred via a canula and treated with 27 μL (0.35 mmol) of $ClCH_2OMe$. After the solution was stirred for 1 h, the solvent was removed in vacuo and the residue extracted with pentane (2 × 15 mL). Chromatography on silica plates (1 mm, pentane–ether, 95:5) gave 70 mg (70%) of 1 as an amber oil. 1 was to be found pure by ^1H NMR and IR by comparison with an authentic sample.[7]

X-ray Structure Determination. Complex 15a was prepared by treatment at −80 °C of a CH_2Cl_2 solution of 2 and 1 equiv of $Me_3SiOSO_2CF_3$ in the presence of twofold excess of styrene. After evaporation of the solvent at room temperature, the residue was washed with ether. Crystals suitable for single X-ray diffraction studies were obtained from dichloromethane–ether at −20 °C. The data were measured on a CAD-4 Enraf Nonius automated diffractometer. Table IV gives the crystallographic data, data collection parameters, and refined details. The unit cell parameters were determined by least-squares fit of a set of 25 reflections. An absorption correction was not needed given the small value of μ (Mo Kα).

The structure was solved by the conventional Patterson method and Fourier differences. After isotropic and anisotropic refinements, hydrogen atoms were located from difference-Fourier syntheses. Full-matrix least-squares refinement of the structure (x, y, z, $\beta(i, j)$ for non-hydrogen atoms and x, y, z for hydrogen atoms) gave $R = 0.053$ and $R_W = 0.061$. Selected interatomic distances and angles are given in Table II. Final positional parameters and equivalent thermal parameters are listed in Table III. F_o and F_c values are available as supplementary material.

Acknowledgment. We are grateful to Dr. S. A. R. Knox (Bristol, U.K.) and Drs. J.-R. Hamon, J.-Y. Saillard, and S. Sinbhandit(Rennes) for helpful discussions. A gift of iron pentacarbonyl was generously provided by BASF (Ludwigshafen, West Germany).

Registry No. **1**, 89875-17-2; **2**, 86853-57-8; **3**, 92468-51-4; *trans*-**4**, 105669-94-1; *cis*-**4**, 105814-32-2; *trans*-**4a**, 112339-96-5; *cis*-**4a**, 112318-77-1; *trans*-**5**, 112173-26-9; *cis*-**5**, 112318-76-0; **6**, 82025-16-9; **8**, 105698-25-7; **9**, 100197-92-0; **10**, 17876-91-4; **11**, 112173-17-8; **12**, 105669-96-3; **13**, 112173-19-0; **14**, 112173-21-4; **15**, 112173-23-6; **15a**, 112173-24-7; $[(\eta\text{-}C_5Me_5)Ru(CO)_2]_2$, 70669-56-6; Me_2PhSiH, 766-77-8; Et_3SiH, 617-86-7; Ph_3SiH, 789-25-3; C_2H_4, 74-85-1; Ph_3SiOMe, 1829-41-0; Ph_3SiMe, 791-29-7; styrene, 100-42-5.

Supplementary Material Available: Complete tables of bond lengths and angles for **15a** and a table of general temperature factor expressions (3 pages); a listing of observed and calculated structure factors (9 pages). Ordering information is given on any current masthead page.

Alkylation of Cyclic and High Polymeric Phosphazenes via Reactions between Aluminum Alkyls and Aminophosphazenes[1,2]

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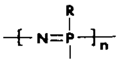
Received March 24, 1987

(Dimethylamino)chlorophosphazenes react with $(CH_3)_3Al$, $(C_2H_5)_2AlCl$, or $(C_2H_5)_3Al$ to replace chlorine atoms geminal to the amino groups by alkyl units. Subsequent treatment of these products with hydrogen chloride brings about replacement of the dimethylamino groups by chlorine. These reactions have been investigated for cyclic phosphazene trimers that bear one, two, or three dimethylamino units, for cyclic phosphazene tetramers that bear two or four dimethylamino units, and for a mixed-substituent high polymeric phosphazene substrate. Chlorine replacement by aluminum alkyls is promoted by the electron-supplying character of the amino side groups, and three plausible mechanisms are presented. Alkylation is accompanied by phosphorus–nitrogen bond cleavage during reactions that involve the high polymer. The new cyclophosphazenes were characterized by elemental analysis, mass spectrometry, and ^{31}P and ^1H NMR analysis. The high polymeric derivatives were also examined by gel permeation chromatography and differential scanning calorimetry.

A growing interest exists in the synthesis of long-chain poly(organophosphazenes) of structure 1 that contain alkyl or aryl groups attached to the skeleton through phosphorus–carbon bonds.[3,4] Interest in such species is connected with their structural similarity to the well-known poly(organosiloxanes), together with the prospect that they may have special photolytic or thermal properties, or may be useful as biomedical materials.[5]



$$\left[\!-N{=}\overset{R}{\underset{R}{\overset{|}{\underset{|}{P}}}}-\right]_n$$

1

Three main synthetic pathways exist that could yield polymers of type 1. First, such species might be accessible via the reactions of high polymeric halogenophosphazenes, such as $(NPCl_2)_n$ or $(NPF_2)_n$, with organometallic reagents in a manner analogous to that already developed for the synthesis of alkoxy-, aryloxy-, or aminophosphazene high polymers.[5,6] However, the reactions of $(NPCl_2)_n$ with Grignard or organolithium reagents are often complicated by skeletal cleavage or cross-linking reactions.[2,3,7,8]

A second approach involves the ring-opening polymerization of alkyl- or arylcyclophosphazenes. Such compounds can be prepared by the reactions of main-group organometallic reagents with cyclic halogenophosphazenes.[2,9] However, so far, only cyclophosphazenes that bear *both* organic and halogeno side groups have been polymerized to the corresponding linear or macrocyclic high polymers.[10]

The third method for the synthesis of polymers of type 1 was developed by Neilson and Wisian-Neilson.[4] It involves the thermal decomposition of *P*-(trifluoroethoxy)-*N*-silylphosphinimines and has yielded a number of medium molecular weight alkyl- and arylphosphazene polymers.

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(1) This paper is part of a series on phosphorus–nitrogen ring systems and high polymers. For a previous paper in this series see: Allcock, H. R.; Brennan, D. J.; Graaskamp. J. M. *Macromolecules* **1988**, *21*, 1.

(2) For a comprehensive review of the organometallic chemistry of phosphazenes see: Allcock, H. R.; Desorcie, J. L.; Riding, G. H. *Polyhedron* **1987**, *6*(2), 119.

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