# Intramolecular Cyclopropane Formation by Insertion of an Iron–Carbene Species into a C–H Bond

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The bimetallic carbene complex [Cp*Fe(CO)$_2$($\mu$-$\eta^1$,$\eta^6$-CHCMe$_2$C$_6$H$_5$)FeCp][PF$_6$]$_2$ **2**, spectroscopically observed by $^1$H NMR at −80 °C, undergoes intramolecular C–H insertion to give [CpFe($\eta^6$-1-phenyl-1-methylcyclopropane)][PF$_6$] **3**.

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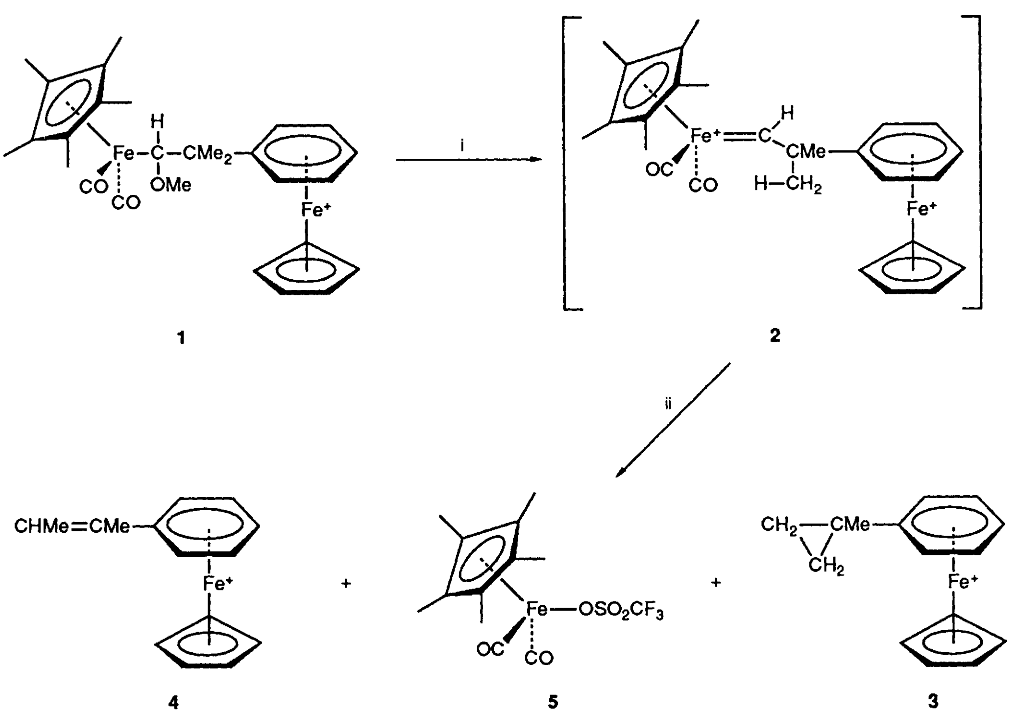
Insertion of a carbene fragment into a carbon–hydrogen bond is one among the carbene-transfer reactions that play a pivotal role in organic synthesis.[1] However, examples of metal–carbene complexes are still very rare,[2,3] since Fp(carbene)$^+$ [Fp=(C$_5$H$_5$)Fe(CO)$_2$] complexes are known to rearrange rapidly by $\beta$-to-$\alpha$ hydrogen or carbon shift affording the corresponding Fp($\eta^2$-alkene)$^+$ complexes.[4,5] We are developing[6] the study of new dinuclear iron$_2$ ($\eta^1$-carbene) complexes in which one of the carbene substituents, *i.e.* a phenyl group, is $\pi$-coordinated to a different iron centre. Such a complexation



**Scheme 1** *Reagents and conditions*: i, $CH_2Cl_2$, −80 °C, $CF_3SO_3SiMe_3$; ii, $CH_2Cl_2$, −40 °C. Spectroscopic ratio **3**:**4** = 75:25.

of the arene should inhibit the facile 1,2-phenyl migration and, therefore, lead to new rearrangement processes. We report here an intramolecular carbene C–H bond insertion from such a species, leading to a complex containing cyclopropane.

The syntheses of the precursor di-iron complexes are easily achieved by an electrophilic ligand coupling reaction from two mononuclear species. Thus, the complex $[Cp^*Fe(CO)_2\{\mu\text{-}\eta^1,\eta^6\text{-}CH(OMe)CMe_2C_6H_5\}FeCp][PF_6]$ **1**† $[Cp^*=(\eta^5\text{-}C_5Me_5)]$ is obtained in 50% yield by electrophilic addition of $[Cp^*Fe(CO)_2(CHOMe)][PF_6]$[7] on $[CpFe(\eta^5\text{-}C_6H_5CMe_2)]$.[8]‡ The dicationic carbene complex $[Cp^*Fe(CO)_2(\mu\text{-}\eta^1,\eta^6\text{-}CHCMe_2C_6H_5)FeCp]^{2+}$ **2**† is then generated by treatment of the α-methoxy compound **1** with $Me_3SiOSO_2CF_3$ at −80 °C in $CH_2Cl_2$. The dication **2** is stable in $CD_2Cl_2$ solution up to −40 °C, as indicated by the slow disappearance of the low-field resonance due to the carbene proton at δ 16.12 ppm in the $^1H$ NMR spectrum. When the reaction is performed on a 1 mmol scale under similar conditions, the rearrangement products of **2** are obtained, namely $[CpFe(\eta^6\text{-}C_6H_5\overline{CMeCH_2CH_2})][PF_6]$ **3**,† $[CpFe(\eta^6\text{-}C_6H_5CMe{=}CHMe)][PF_6]$ **4**,† and $[Cp^*Fe(CO)_2(OSO_2CF_3)]$ **5**.[7] The cationic compounds **3** and **4**, cleanly separated from the red soluble compound **5** by addition of diethyl ether, are thus isolated in a quantitative yield. $^1H$ NMR analysis of the crude reaction product shows that **3** and **4** are respectively formed in a ratio of 75:25 as in the $^1H$ NMR experiment (based on the integration of the methyl resonances). Pure compound **3** is then isolated as a yellow powder (42%) by crystallisation in $CH_2Cl_2$. In the proton coupled $^{13}C$ NMR spectrum of **3**, the equivalent methylene carbons of the cyclopropyl ring give rise to an upfield triplet at δ 20.1 ppm ($^1J_{C\text{-}H}$ 161 Hz). The formation of the cyclization product **3** arises from an intramolecular insertion of the carbene fragment into the γ-C–H bond (with respect to the two iron centres); the $Cp^*Fe(CO)_2^+$ fragment, thus released, is recovered as the triflate adduct **5** (Scheme 1). Side 1,2-methyl migration reaction affords the alkenylbenzene complex **4** in a minor amount. We did not observe any $Fe_2(\eta^2,\eta^6\text{-alkenylbenzene})$ intermediate, the labile alkene ligand probably being displaced by the coordinating $CF_3OSO_2^-$ anion.

Coordination of the aromatic ring by the $CpFe^+$ moiety induces a dramatic change in the reactivity of the carbene species. The related mononuclear carbene complex $[Fp({=}CHCMe_2Ph)]^+$ has been reported to undergo 1,2-phenyl migration to give $[Fp(\eta^2\text{-}CHPh{=}CMe_2)]^+$.[5] In the present case, the phenyl shift is inhibited by its complexation, an unprecedented feature. This bimetallic system, in which the carbene fragment is still highly reactive owing to its $\eta^1$-coordination mode, allows a facile C–H insertion reaction leading to the formation of a $C_3$ ring. Moreover, the $CpFe^+$ unit can be regarded as a trap for the reaction products resulting from the carbene transfer reaction; this allows a better handling and characterisation of the species especially in the case of volatile organic compounds.

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† *Selected spectroscopic data*: for **1**: $^1H$ NMR ($CD_2Cl_2$) δ 6.17 (m, Ph), 4.93 (s, 5H, $C_5H_5$), 3.55 (s, 1H, CH), 2.63 (s, 3H, OMe), 1.71 (s, 15H, $C_5Me_5$), 1.51 (s, 3H, Me), 1.41 (s, 3H, Me). $^{13}C\{^1H\}$ NMR ($CD_3CN$) δ: 223.2 (CO), 218.0 (CO), 101.2 (*C*HOMe), 97.5 (*C*$_5$Me$_5$), 76.7 ($C_5H_5$), 59.1 (OMe), 48.5 (*C*Me$_2$), 27.6 (Me), 23.8 (Me), 10.1 ($C_5$*Me*$_5$). For **2**: $^1H$ NMR ($CD_2Cl_2$, −80 °C) δ: 16.12 (s, 1H, =CH), 643 (m, Ph), 5.14 (s, 5H, Cp), 1.90 (s, 15H, $C_5Me_5$), Me obscured by $C_5Me_5$. For **3**: $^1H$ NMR ($CD_3CN$) δ: 6.14 (m, 3H, Ph), 6.03 (m, 2H, Ph), 4.96 (s, 5H, $C_5H_5$), 1.52 (s, 3H, Me), 1.14 (m, 2H, cyclopropyl CHCH), 1.08 (m, 2H, cyclopropyl CHCH). $^{13}C\{^1H\}$ NMR ($CD_3CN$) δ: 115.2 ($C_6$ *ipso*), 88.0 ($C_6$ ring), 87.1 ($C_6$ *para*), 84.9 ($C_6$ ring), 77.3 ($C_5H_5$), 22.7 (Me), 20.1 ($CH_2$), 18.3 (quaternary cyclopropyl C). For **4**: $^1H$ NMR ($CD_3CN$) δ: 6.31 (qq, $^3J_{H\text{-}H}$ 7, $^4J_{H\text{-}H}$ 1 Hz, 1H, =CH), 6.16–6.04 (2 × m, Ph), 4.92 (s, 5H, $C_5H_5$), 2.11 (m, 3H, =CPh*Me*), 1.84 (dq, $^3J_{H\text{-}H}$ 7, $^5J_{H\text{-}H}$ 1 Hz, 3H, =CH*Me*). Satisfactory elemental analyses were obtained for **1** and **3**.

‡ The precursor complex $[CpFe(Pr^iC_6H_5)][PF_6]$ was kindly provided by Dr J.-R. Hamon.

We are continuing to examine the mechanism of the above reaction and the synthetic utility of these new bimetallic carbene complexes.

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