

Single and Double C–C Bond Formation *via* Iron–Carbene Species: Access to New π - and σ , π -Vinylarene Complexes

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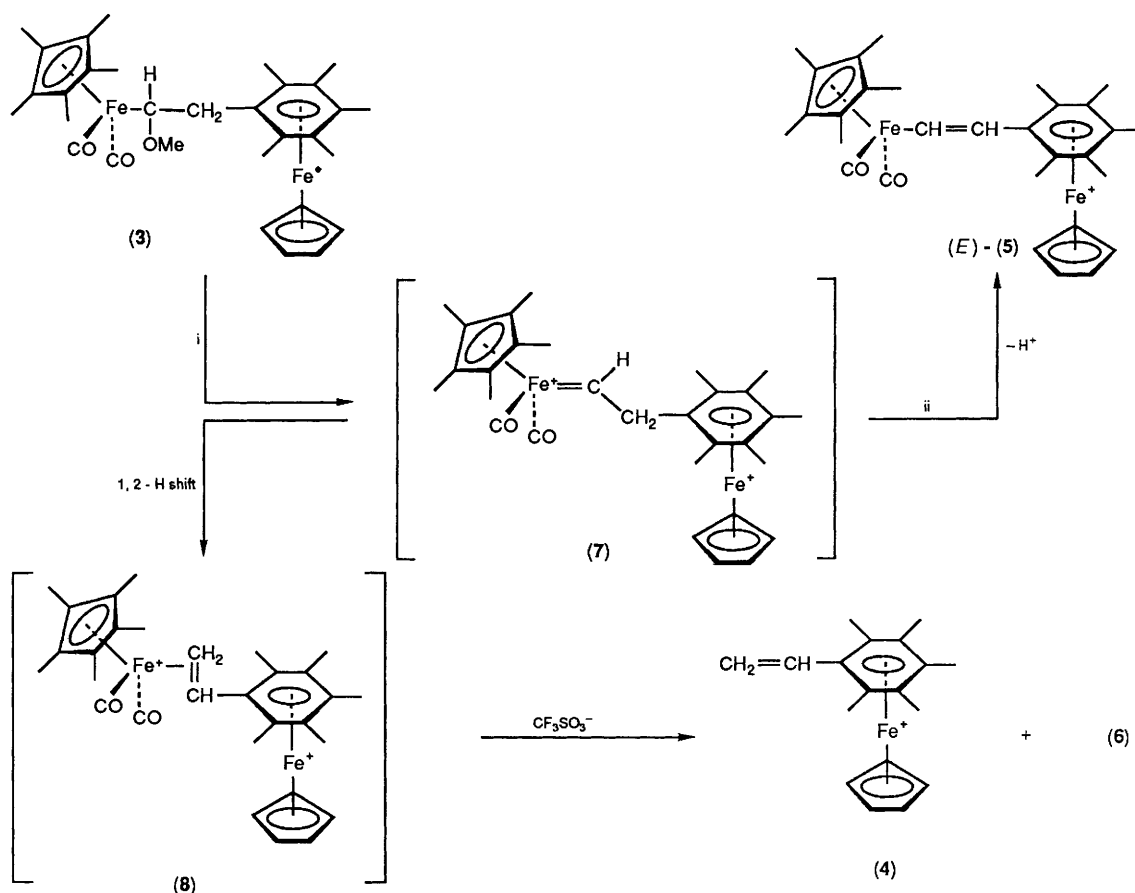
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The bimetallic complex $[(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2\{\mu\text{-}\eta^1, \eta^6\text{-CH}(\text{OMe})\text{CH}_2\text{C}_6\text{Me}_5\}\text{Fe}(\eta^5\text{-C}_5\text{H}_5)][\text{PF}_6]$ (**3**), which is readily prepared by electrophilic carbene–alkene coupling between (**1**) and (**2**), is specifically converted into either the η^6 -vinylpentamethylbenzene complex (**4**) or the related dinuclear ($\mu\text{-}\eta^1, \eta^6$ -vinylarene) complex (*E*)-(**5**).

Electrophilic carbene complexes $[\text{M}=\text{CHR}]^+$ are key intermediates in single and double carbon–carbon bond formation.^{1–3} In order to obtain more information on the mechanism of these processes and to explore further the utility of such complexes in organic and organometallic synthesis, we are investigating the chemistry of dinuclear complexes containing the $\text{M}_2(\mu\text{-}\eta^1, \eta^6\text{-CHCH}_2\text{Ar})$ unit, *i.e.*, in which the arylcarbene

ligand is an unusual σ, π -bridging ligand. We report here the generation of such a species and its role in the functionalisation of complexed hexamethylbenzene, namely the preparation of new vinylarene iron complexes.

The classical route to carbene complexes $[\text{M}=\text{CHR}]^+$ involves the ionization of α -alkoxyalkyl derivatives $\text{M}-\text{CH}(\text{OR}')\text{R}$, which are generally prepared from alkoxy-car-



Scheme 1. Reagents and conditions: i, CH₂Cl₂, CF₃SO₃SiMe₃ (1 equiv.), -80 °C; ii, CH₂Cl₂, PMe₃, HBF₄-OEt₂, -80 °C.

bene complexes by hydride reduction or using organolithium reagents.⁴⁻⁶ We have used a variant of the latter approach to generate the desired carbene species, employing as an organometallic alkylating agent the complex [(η⁵-C₅H₅)Fe(η⁵-C₆Me₅CH₂)] (2)⁷ with an exocyclic methylene group. Addition of (2) to the methoxycarbene complex [(η⁵-C₅Me₅)Fe(CO)₂(CHOMe)][PF₆] (1)⁸ in tetrahydrofuran (THF) at -80 °C effects electrophilic condensation⁹ to yield the bimetallic complex [(η⁵-C₅Me₅)Fe(CO)₂{μ-η¹,η⁶-CH(OMe)-CH₂C₆Me₅}Fe(η⁵-C₅H₅)][PF₆] (3).[†] Compound (3) is

[†] The new complexes (3), (4), and (5) were identified by elemental analysis, IR and NMR (¹H, ¹³C) spectroscopy. *Selected spectroscopic data* for (3): ¹H NMR (CD₃CN) δ 4.50 (s, 5H, C₅H₅), 4.45 (dd, 1H, ³J_{H-H} 11, ³J_{H-CH} 2 Hz, CH), 3.72 (dd, 1H, ²J_{H-H} 14, ³J_{H-H} 11 Hz, CH₂), 3.12 (dd, 1H, ²J_{H-H} 14, ³J_{H-H} 2 Hz, CH₂), 2.68 (s, 3H, OMe), 2.53 (s, 3H, *p*-Me), 2.45, 2.44, 2.43, 2.41 (s, diastereotopic Me), 1.88 (s, 15H, C₅Me₅); ¹³C{¹H} NMR (CD₂Cl₂) δ 220.1 (CO), 218.8 (CO), 104.1 (*ipso*-C₆), 99.9, 99.6, 99.5, 99.2, 98.0 (C₆ ring), 97.0 (C₅Me₅), 84.8 (CHOMe), 78.1 (C₅H₅), 59.7 (OMe), 46.6 (CH₂), 18.7, 18.1, 18.0, 17.9, 17.8 (C₆Me₅), 10.1 (C₅Me₅). For (4): ¹H NMR (CD₃CN) δ 6.83 [dd, 1H, ³J_{H-H} (*trans*) 18, ³J_{H-H} (*cis*) 11 Hz, CH], 5.87 [d, 1H, ³J_{H-H} (*cis*) 11 Hz, CH₂ (H_E)], 5.45 [d, 1H, ³J_{H-H} (*trans*) 18 Hz, CH₂ (H_Z)], 4.59 (s, 5H, C₅H₅), 2.46 (s, 3H, *p*-Me), 2.44, 2.40 (s, Me); ¹³C{¹H} NMR (CD₃CN) δ 133.9 (CH), 125.5 (CH₂), 102.6 (*ipso*-C₆), 100.8 (*p*-C₆), 100.1 (C₆ ring), 98.7 (C₆ ring), 79.4 (C₅H₅), 18.8 (C₆Me₅), 17.8 (*p*-Me), 17.5 (C₆Me₅). For (E)-(5): ¹H NMR (CD₃CN) δ 6.81 (d, 1H, ³J_{H-H} 17 Hz, CH_α), 6.44 (d, 1H, ³J_{H-H} 17 Hz, CH_β), 4.50 (s, 5H, C₅H₅), 2.43 (s, 3H, *p*-Me), 2.42 (s, 6H, Me), 2.41 (s, 6H, Me), 1.80 (s, 15H, C₅Me₅); ¹³C{¹H} NMR (CD₃CN) δ 218.4 (CO), 161.2 (Fe-CH), 135.6 (CH_β), 106.7 (*ipso*-C₆), 99.9 (C₆ ring), 99.6 (*p*-C₆), 98.3 (C₆ ring), 97.9 (C₅Me₅), 79.0 (C₅H₅), 19.2 (Me), 17.7 (*p*-Me), 17.6 (Me), 9.9 (C₅Me₅).

isolated as a thermally- and air-stable yellow powder in 90% yield. As expected for a chiral molecule, the methyl groups, the carbon atoms of the C₆ ring, and the carbonyl ligands are diastereotopic; their resonances are well differentiated in the ¹³C NMR spectrum.

The dinuclear complex (3), upon treatment with Me₃SiOSO₂CF₃ (1 equiv.) in CH₂Cl₂ at -80 °C, is converted to the new η⁶-vinylarene complex [(η⁵-C₅H₅)Fe(η⁶-C₆Me₅-CH=CH₂)][PF₆] (4)[†] and the dicarbonyl trifluoromethanesulphonate complex [(η⁵-C₅Me₅)Fe(CO)₂(OSO₂CF₃)] (6).⁸ These two compounds are easily separated; addition of ether precipitates ionic (4) while neutral (6) remains in solution, and compound (4) is thus obtained as yellow microcrystals in 60% yield after recrystallisation. We suggest that methoxide abstraction from (3) generates the transient dicationic carbene complex [(η⁵-C₅Me₅)Fe(CO)₂{μ-η¹,η⁶-CHCH₂C₆Me₅}Fe(η⁵-C₅H₅)]²⁺ (7), and that this species undergoes a 1,2β-hydrogen migration, paralleling the isomerisation of alkylidene complexes into η²-alkene complexes,¹⁻³ to give (8) and thence (4) and (6) (Scheme 1). Attempts to isolate (8) by treating (3) with the non-co-ordinating acid HBF₄ were unsuccessful.

The sequence (1) + (2) → (3) → (4) provides a useful route to η⁶-vinylarene complexes, since the complexation of functionalised arene substrates to the Fe(η⁵-C₅H₅) moiety cannot be achieved under the drastic conditions required for the ligand exchange reaction with ferrocene and AlCl₃.¹⁰

Monitoring the reaction of (3) with Me₃SiOSO₂CF₃ by variable temperature NMR spectroscopy did not allow the spectral observation of the intermediate dicationic carbene complex (7). Therefore, in an attempt to trap this transient species chemically as a phosphonium adduct, (3) was proto-

nated ($\text{HBF}_4\text{-OEt}_2$) in the presence of PMe_3 . However, the reaction afforded quantitatively the stable σ , π -vinylarene complex $[(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}\{\mu\text{-}\eta^1, \eta^6\text{-CH=CHC}_6\text{Me}_5\}\text{Fe}(\eta^5\text{-C}_5\text{H}_5)][\text{PF}_6]$, (*E*)-(5).[†] The stereospecificity of the reaction, *i.e.*, the formation of the *trans* geometric isomer (relative to the double bond), is established by the ^1H NMR spectrum of (5), which shows a large coupling constant $^3J_{\text{H-H}}$ of 17 Hz for the vinylic protons [doublets at δ 6.81 (H_α) and 6.44 (H_β)]. The formation of (*E*)-(5) clearly results from the loss of a β -vinylic proton from the dication (7), assisted by the basic phosphine PMe_3 . This pathway is favoured over electrophilic addition of PMe_3 to the α (carbene)-carbon because of the bimetallically enhanced acidity of the β -hydrogens. Although deprotonation of stable cyclopentadienyl-iron^{5,11} and -ruthenium¹² hetero-substituted carbene complexes with bases has been described previously, such a reaction is unprecedented for transient alkylidene complexes.¹³ Moreover, preliminary studies show that clean cleavage of the $\text{C}_5\text{H}_5\text{Fe}^+$ moiety can be achieved upon short photolysis of (*E*)-(5) giving the parent η^1 -vinyl complex.¹⁴

The reactions described here represent a convenient method for introducing unsaturation to iron-arene complexes; further investigations on other dinuclear systems are under way.

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