

Cycloaddition Reactions between Vinylidene Iron(II) Complexes and Alkynes: The First Stable Cyclobutenylidene Complexes

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$[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})\text{LFe}=\text{C}=\text{CH}_2]^+\text{CF}_3\text{SO}_3^-$ complexes react with phenylpropyne with formation of [2 + 2] cycloadducts $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})\text{LFe}=\text{C}(\text{Me})=\text{C}(\text{Ph})\text{-CH}_2]^+\text{CF}_3\text{SO}_3^-$ (structurally characterized by X-ray crystallography); addition of phenyllithium leads to a stable cyclobutenyl complex in good yield.

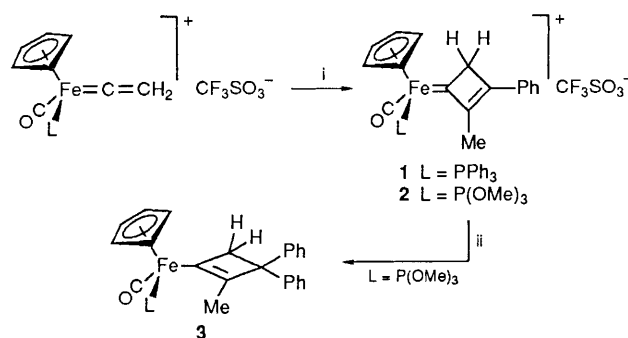
In a few recent investigations vinylidene complexes have been treated with alkynes to form vinylvinylidene complexes.¹ The mechanism of these reactions is not well understood, but it is believed, that it proceeds through initial dipolar cycloadditions *via* unstable cyclobutenylidene intermediates. Here we report on the synthesis, structure and reactivity of the first stable examples of this class of compounds.

Phenylpropyne reacts with $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})\text{LFe}=\text{C}=\text{CH}_2]^+\text{X}^-$ in tetrahydrofuran (thf) solution at low temperatures to give the cyclobutenylidene complexes **1** (L = PPh₃) and **2** [L = P(OMe)₃] in good yields (45–60%) (Scheme 1). The red compounds can be isolated by precipitation with diethyl ether and subsequent chromatographic work-up with dichloromethane on silica gel. The ¹H NMR spectra exhibit a set of doublets for the methylene group of the cyclobutenylidene ring [δ 3.61 and 3.52; ²J(H,H) = 14.64 Hz for **1**. δ 3.78 and 3.70; ²J(H,H) = 11.2 Hz for **2**]. The signal of the methyl substituent appears at δ 1.93 for **1** and δ 2.38 for **2**, respectively. The carbenic character of the ring ligand is clearly demonstrated by the ¹³C NMR spectrum where the signals for the carbene carbons are located at low field [δ 328.1, d, ²J(C,P) = 18.1 Hz for **1**. δ 322.1, d, ²J(C,P) = 16.5 Hz for **2**]. The structure of compound **2** was additionally determined by X-ray crystallography.[†]

The ORTEP plot of the structure of **2** (Fig. 1) shows the presence of the cyclobutenylidene structure deduced from the spectroscopic data. As expected from theory,³ the cyclic carbene ligand is coordinated to the Fe moiety such that the four-membered ring is tilted towards the phosphine ligand

[†] Crystal data for **2**: C₂₁H₂₄F₃FePSO₇, *M* = 564.3, monoclinic, space group *P*2₁/*n* (No. 14), *a* = 869.4(1), *b* = 1179.7(2), *c* = 2424.3(3) pm, β = 93.30°, *U* = 2482 × 10⁶ pm³, *D*_c = 1.510 g cm⁻³, *Z* = 4, *F*(000) = 1160, λ (Mo-K α) radiation, = 71.07 pm, μ = 8.09 cm⁻¹, CAD4 (Enraf-Nonius) diffractometer, 4882 measured reflections, 2 θ range 2–50°, 3744 unique with *F* > *I* > 0.06 (*I*). Structure solved by direct methods and refined by full-matrix least-squares to *R* = 6.2% and *R*_w = 4.7%. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

(19.8°), its plane being almost parallel to the Fe–CO axis.^{4,5} The Fe–C(1) distance (184.6 pm) is comparable to distances found in carbene complexes of type $[(\text{C}_5\text{H}_5)(\text{CO})\text{LFe}=\text{CX}_2]^+$ (X = Cl,F).⁵ The phenyl substituent of the cyclobutenylidene



Scheme 1 Reagents and conditions: i, MeC≡CPh, –78°C to room temp., 12 h; ii, PhLi, –60°C, Et₂O

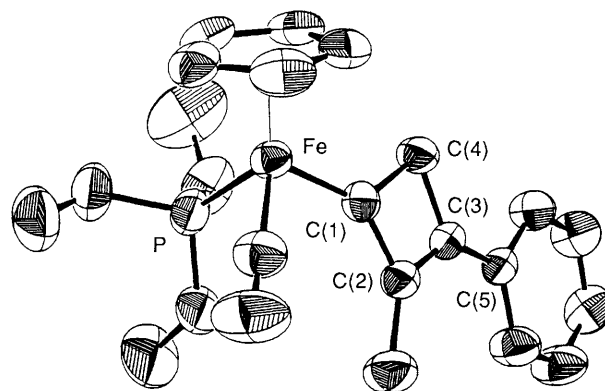


Fig. 1 ORTEP drawing of **2**: selected distances (pm) and angles (°): Fe–C(1) 185(3), C(1)–C(2) 144(3), C(2)–C(3) 137(3), C(3)–C(4) 152(3), C(4)–C(1) 155(3), C(3)–C(5) 145(3); C₅H₅–cyclobutenylidene 70.2°, cyclobutenylidene–phenyl ring 7.5°

ligand is approximately coplanar with the ring, which allows optimal π -donation to the carbene ligand. Preliminary reactivity studies of complexes **1** and **2** show that nucleophiles can be added at C-3 of the carbene ligand. Thus, reaction of phenyllithium with **2** gives the cyclobutenyl complex **3** in ca. 60% yield. Its structure was confirmed spectroscopically. ‡

Compound **3** is thermally stable and does not undergo ring opening. Similar behaviour has been found for perfluoro-cyclobutenyl complexes.⁶ Complexes **1** and **2** do not rearrange to the corresponding ring-opened vinylvinylidene complexes at ambient temperatures. At elevated temperatures they decompose within several hours to as yet unidentified products.

‡ Spectroscopic data for **3**: ¹H NMR (400 MHz, CD₂Cl₂, room temp.) δ 1.81 (s, CH₃), 2.82 (d, ²J_{H,H} 11.7 Hz, 1H, CH₂), 2.91 (d, ²J_{H,H} 11.7 Hz, 1H, CH₂), 3.50 [d, ³J_{P,H} 11.2 Hz, 9H, P(OMe)₃] 4.65 (s, 5H, C₅H₅), 7.16–7.25 (m, 10H, Ph); ¹³C{¹H} NMR (400 MHz, CD₂Cl₂, room temp.) δ 220.3 (d, ²J_{C,P} 46.4 Hz, CO), 161.8 (s, Fe–C=C), 152.1 (d, ²J_{C,P} 42.8 Hz, Fe–C=C), 148.1, 128.1, 128.0, 127.9, 127.6, 125.2 (Ph), ³¹P{¹H} NMR (CD₂Cl₂, 400 MHz, room temp.) δ 188.4.

We are grateful to the Stiftung Volkswagenwerk for financial support.

Received, 21st March 1991; Com. 1/01368H

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