

Hemilabile Properties of Chelate Iron Complexes: Synthesis and Structure of Oxametallacycles

Géraldine Poignant, Sourisak Sinbandhit, Loïc Toupet, and Véronique Guerschais*

UMR 6509 CNRS – Université de Rennes 1, “Organométalliques et Catalyse”, Université de Rennes 1, Beaulieu, F-35042 Rennes Cedex, France
Fax: (internat.) + 33-2/99281646
E-mail: guerschais@univ-rennes1.fr

Received April 22, 1998

Keywords: Carbene complexes / Aromatic substitution / Chelate iron complexes / Bond activation

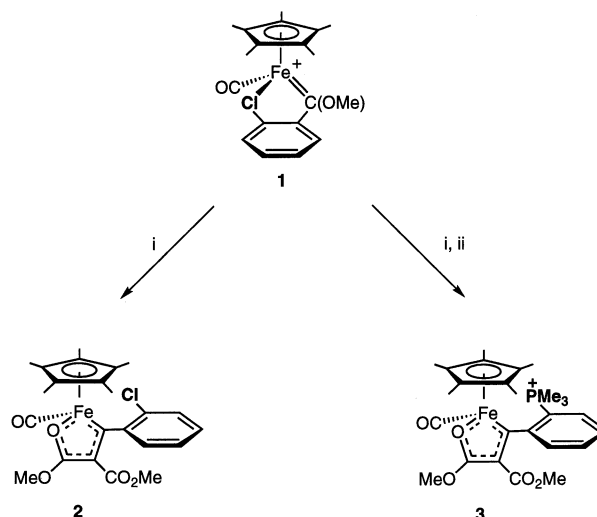
Oxametallacycles $[\text{Fe}(\text{C}_5\text{Me}_5)(\text{CO})\{\text{C}_3(\text{C}_6\text{H}_4\text{-}o\text{-Cl})(\text{CO}_2\text{Me})\text{-}(\text{R})\text{O}^a\}(\text{Fe-O}^a)]$ (**2**, R = OMe; **4**, R = Me) are accessible from the chelate (chloroaryl)carbene complex $[\text{Fe}(\text{C}_5\text{Me}_5)(\text{CO})\{\text{C}(\text{OMe})\text{C}_6\text{H}_4\text{-}o\text{-Cl}^a\}(\text{Fe-C}^a)]\text{[OTf]}$ (**1**) upon treatment with the appropriate carbanions. Their formation arises from the lability of the chlorine atom. The related phosphonium salt

$[\text{Fe}(\text{C}_5\text{Me}_5)(\text{CO})\{\text{C}_3(\text{C}_6\text{H}_4\text{-}o\text{-PMe}_3)(\text{CO}_2\text{Me})(\text{OMe})\text{O}^a\}(\text{Fe-O}^a)]\text{[OTf]}$ (**3**) is formed only for the bis(ester) derivative, via Ar-Cl bond activation. No reaction occurs for **4**, for which the coordination of the acetyl group has been supported by an X-ray analysis.

Aryl halides coordinating to metal centers are the focus of general interest especially for the functionalization of aromatic rings.^[1] Halogenoarenes can be activated towards nucleophilic displacement by η^6 complexation to electron-deficient transition-metal centers.^[2] We have previously reported that Ar-Cl bond cleavage can be achieved by complexation of the halide group.^[3] Moreover, alkyl halide complexes $\text{M}(\eta^1\text{-XR})$ have been shown to undergo nucleophilic attack at the α -carbon atom in the presence of Lewis bases.^{[4][5][6]} This led us to investigate the reactivity of the electrophilic chelate (chloroaryl)carbene complex^[7] $[\text{Fe}(\text{C}_5\text{Me}_5)(\text{CO})\{\text{C}(\text{OMe})\text{C}_6\text{H}_4\text{-}o\text{-Cl}^a\}(\text{Fe-C}^a)]\text{[OTf]}$ (**1**) towards stabilized carbanions possessing coordinating carbonyl groups. Here, we report the access to new oxametallacycles, the lability of the chelated group, Cl versus C=O, involved in the formation of these species allows to induce nucleophilic aromatic substitution.

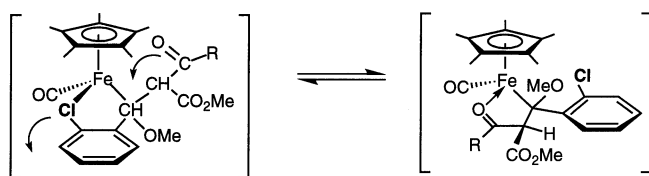
Complex **1** reacts at -80°C (1 h) with a THF solution of $\text{NaCH}(\text{CO}_2\text{Me})_2$ affording the oxametallacycle $[\text{Fe}(\text{C}_5\text{Me}_5)(\text{CO})\{\text{C}_3(\text{C}_6\text{H}_4\text{-}o\text{-Cl})(\text{CO}_2\text{Me})(\text{OMe})\text{O}^a\}(\text{Fe-O}^a)]$ (**2**) which is isolated after chromatography as a green powder (Scheme 1). The complexation of the carbonyl group is evidenced by the ^{13}C -NMR spectrum (CDCl_3); the most characteristic features are the signals at $\delta = 262.4$ (Fe-C_a), 124.9 [$\text{C}(\text{CO}_2\text{Me})$], and 177.3 (C-O) for the carbon atoms of the metallacycle. The low-field ^{13}C shift of the C_a resonance is intermediate between that of a carbene carbon atom and that of an alkenyl group, in agreement with two possible mesomeric forms. We assume that the formation of **2** results from an α attack by the nucleophile to give the C-C intermediate adduct, subsequent dissociation of the chlorine atom by the coordinating carbonyl group leads to the formation of a new five-membered ring (Scheme 2). Eventually, a spontaneous elimination of MeOH produces a more stable conjugated ring, i.e. the final product. Subsequent

Scheme 1. Reagents and conditions: i) $\text{NaCH}(\text{CO}_2\text{Me})_2$, THF, -80°C ; ii) PMe_3



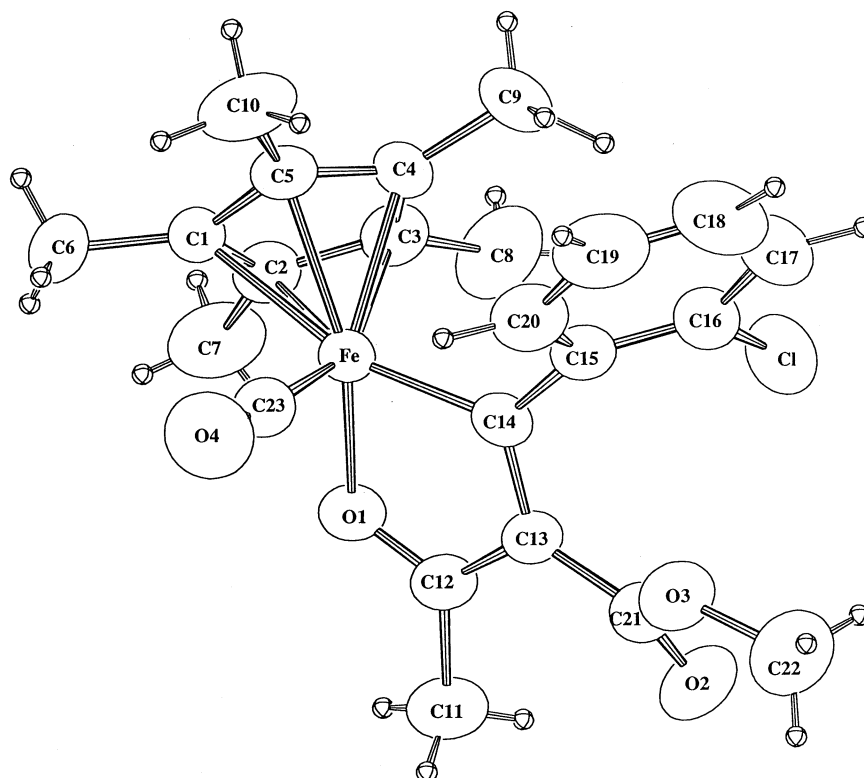
addition of PMe_3 to the reaction mixture affords the corresponding phosphonium salt $[\text{Fe}(\text{C}_5\text{Me}_5)(\text{CO})\{\text{C}_3(\text{C}_6\text{H}_4\text{-}o\text{-PMe}_3)(\text{CO}_2\text{Me})(\text{OMe})\text{O}^a\}(\text{Fe-O}^a)]\text{[OTf]}$ (**3**). The presence of the PMe_3 group is clearly established by NMR spectroscopy; its resonance is located at $\delta = 24.1$ in the $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum (CDCl_3). The $^3\text{J}(\text{P-H}_{\text{Ar}})$ and $^1\text{J}(\text{P-C}_{\text{Ar}})$ coupling constants of 15.6 Hz and 89 Hz, respectively, support the presence of the phosphorus atom on the aromatic ring. We assume that the formation of such species requires the activation of the Ar-Cl bond by the organo-iron fragment, the C=O group would be labile enough to be in equilibrium with the corresponding chloro-chelated species.

Scheme 2



not dissociate in such conditions, the phosphorus-substituted derivative is only formed for the bis(ester)-containing complex.

In summary, oxametallacycles – depending on the labile character of the chelated group – allow Ar–Cl bond activation under mild conditions, a process which is mediated by the organo–iron fragment acting as a Lewis acid.^[10] Studies on carbanions possessing other functional groups with different labile properties are under progress.

Figure 1. Molecular structure (ORTEP drawing) of **4**^[a]

^[a] Selected bond lengths [Å] and angles [°]: Fe–O1 1.951(3), O1–C12 1.254(6), C12–C13 1.429(6), C13–C14 1.387(6), Fe–C14 1.920(5); O1–Fe–C14 81.4(2), C14–Fe–C23 90.7(2), O1–Fe–C23 98.1(2), Fe–O1–C12 115.6(3), O1–C12–C13 116.9(4), C12–C13–C14 112.2(4), C13–C14–Fe 113.8(3).

Treatment of **1** with NaCH(CO₂Me)(COMe), in which two different coordinating functions are present, gives [Fe(C₅Me₅)(CO){C₃(C₆H₄-*o*-Cl)(CO₂Me)(Me)O^a}(Fe–O^a)] (**4**) in which the acetyl group is complexed to the iron center. Green crystals are obtained in 50% yield after purification by chromatography. The ¹³C resonances of the metallacycle [δ = 277.4 (Fe–C_o), 126.0 C(CO₂Me), 207.6 (C–O)] are similar to those of **2**, the acetyl group giving rise to a lower field signal. The molecular structure^[8] of **4** (Figure 1) confirms the proposed structure. The acetyl fragment coordinated to the iron center displays bond lengths which are closely similar to those of the chelate complex [Fe(C₅H₅)(*t*BuNC)[C₆F₄-*o*-C(O)Me](Fe–O^a)].^[9] The bond lengths of the five-membered ring are in agreement with a delocalized system.

By contrast, no reaction with PMe₃ is observed in the case of complex **4**. This suggests that the acetyl group does

We thank the *Région Bretagne* for a grant to G. P., the *CNRS* and the *Université de Rennes 1* for financial support.

Experimental Section

A THF solution of **1** (520 mg, 1 mmol) was treated at –80°C with a freshly prepared THF solution of 2 equiv. of NaCH(CO₂Me)(COR) (R = OMe, Me). After stirring for 3 h, the solution was concentrated to dryness. Compounds **2** and **4** were extracted with CH₂Cl₂ and chromatographed on alumina (eluent: pentane/Et₂O). Complex **2** (25%): ¹H NMR (200 MHz, CDCl₃): δ = 7.48 (dd, ³J_{HH} = 7.8 Hz, ⁴J_{HH} = 1.7 Hz, 1 H, Ar), 7.34 (dd, ³J_{HH} = 8.8 Hz, ⁴J_{HH} = 1.3 Hz, 1 H, Ar), 7.29 (td, ³J_{HH} = 7.6 Hz, ⁴J_{HH} = 1.3 Hz, 1 H, Ar), 7.11 (td, ³J_{HH} = 7.5 Hz, ⁴J_{HH} = 1.7 Hz, 1 H, Ar), 3.89 (s, 3 H, OMe), 3.49 (s, 3 H, OMe), 1.45 (s, 15 H, C₅Me₅). – ¹³C{¹H} NMR (50.3 MHz, CDCl₃): δ = 262.4 (Fe–C_o), 218.2 (CO), 177.3 (C–O), 161.9 (C=O), 150.9 (Ar_{ipso}), 128.7 (Ar), 127.1 (Ar), 126.9 (Ar), 126.5 (Ar), 126.3 (Ar_{Ci}), 124.9 (CCO₂Me), 92.6

(C₅Me₅), 54.1 (OMe), 51.4 (OMe), 9.3 (C₅Me₅). – IR (pentane, cm⁻¹): $\tilde{\nu}$ = 1934 (s, ν_{CO}), 1724.8 (m, $\nu_{\text{C=O}}$). – HRMS for C₂₃H₂₅ClFeO₅; m/z calcd. 472.0740 [M⁺]; found 472.0738. – It is noteworthy that the disubstituted complex [Fe(C₅Me₅)(CO){C₃(C₆H₄-*o*-CH(CO₂Me)₂)(CO₂Me)(OMe)O^a}(Fe-*O*^a)], in which the chloride has been replaced by the dimethylmalonate anion, is detected from the crude reaction mixture by HRMS (FAB) for C₂₉H₃₆FeNaO₁₀; m/z calcd. 623.1556; found 623.1543 [M⁺ + Na].

Complex **3** is obtained by addition of 3 ml of PMe₃ (1 M in toluene) at -80°C to the reaction mixture prepared as described above. Extraction with CH₂Cl₂ and crystallisation in CH₂Cl₂/Et₂O gave green microcrystals (17%). – ¹H NMR (300 MHz, CDCl₃): δ = 7.86 (dd, ³J_{PH} = 15.6 Hz, ³J_{HH} = 7.9 Hz, 1 H, Ar), 7.55 (m, 1 H, Ar), 7.45 (m, 2 H, Ar), 3.84 (s, 3 H, OMe), 3.49 (s, 3 H, OMe), 2.28 (d, ²J_{PH} = 13.8 Hz, 9 H, PMe₃), 1.42 (s, 15 H, C₅Me₅). – ¹³C{¹H} NMR (75.47 MHz, CDCl₃): δ = 261.5 (Fe-C_a), 218.3 (CO), 176.1 (C-O), 162.1 (C=O), 155.1 (d, ²J_{PC} = 8.7 Hz, Ar_{ipso}), 132.5 (d, ⁴J_{PC} = 3 Hz, Ar), 131.2 (d, ²J_{PC} = 12 Hz, Ar), 127.1 (d, ³J_{PC} = 13 Hz, Ar), 126.5 (CCO₂Me), 126.4 (d, ³J_{PC} = 11 Hz, Ar), 115.6 (d, ¹J_{PC} = 89 Hz, Ar), 92.0 (C₅Me₅), 54.1 (OMe), 51.5 (OMe), 13.1 (d, ¹J_{PC} = 56.7 Hz, PMe₃), 9.4 (C₅Me₅). – ³¹P{¹H} NMR (121.5 MHz, CDCl₃): δ = 24.11 (s, PMe₃). – IR (CH₂Cl₂, cm⁻¹): $\tilde{\nu}$ = 1938 (s, ν_{CO}), 1752 (m, $\nu_{\text{C=O}}$). – C₂₇H₃₄FeF₃O₈PS: calcd. C 48.96, H 5.17; found C 48.95, H 5.27.

Complex **4** (50%). – ¹H NMR (200 MHz, CDCl₃): δ = 7.43 (dd, ³J_{HH} = 7.7 Hz, ⁴J_{HH} = 1.8 Hz, 1 H, Ar), 7.36 (dd, ³J_{HH} = 8 Hz, ⁴J_{HH} = 1.3 Hz, 1 H, Ar), 7.29 (td, ³J_{HH} = 7.8 Hz, ⁴J_{HH} = 1.4 Hz, 1 H, Ar), 7.12 (td, ³J_{HH} = 7.5 Hz, ⁴J_{HH} = 1.7 Hz, 1 H, Ar), 3.50 (s, 3 H, OMe), 2.55 (s, 3 H, Me), 1.48 (s, 15 H, C₅Me₅). – ¹³C{¹H} NMR (50.3 MHz, CDCl₃): δ = 277.4 (Fe-C_a), 217.3 (CO), 207.6 (C-O), 163.7 (C=O), 151.9 (Ar_{ipso}), 128.7 (Ar), 127.2 (Ar), 126.9 (Ar), 126.6 (Ar), 126.5 (Ar_{C1}), 126.0 (CCO₂Me), 94.3 (C₅Me₅), 51.3 (OMe), 27.8 (Me), 9.3 (C₅Me₅). – IR (CH₂Cl₂,

cm⁻¹): $\tilde{\nu}$ = 1930 (s, ν_{CO}), 1694 (m, $\nu_{\text{C=O}}$). – C₂₃H₂₅ClFeO₄: calcd. C 60.48, H 5.52; found C 60.43, H 5.47.

- [1] V. V. Grushin, H. Alper, *Chem. Rev.* **1994**, *94*, 1047–1062 and references therein.
 [2] For a review, see: L. Balas, D. Jurrhy, L. Latxague, S. Grelier, Y. Morel, M. Hamdani, N. Ardoin, D. Astruc, *Bull. Soc. Chim. Fr.* **1990**, *127*, 401–426.
 [3] G. Poignant, S. Sinbandhit, L. Toupet, V. Guerschais, *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 963–965.
 [4] R. J. Kulawiec, R. H. Crabtree, *Coord. Chem. Rev.* **1990**, *99*, 89–115.
 [5] M. D. Butts, B. L. Scott, G. J. Kubas, *J. Am. Chem. Soc.* **1996**, *118*, 11831–11843.
 [6] T.-S. Peng, C. H. Winter, J. A. Gladysz, *Inorg. Chem.* **1994**, *33*, 2534–2542.
 [7] G. Poignant, S. Nlate, V. Guerschais, A. J. Edwards, P. R. Raithby, *Organometallics* **1997**, *16*, 124–132.
 [8] Crystal structure of **4**: Enraf-Nonius CAD4 diffractometer, Mo-*K*_α radiation, μ = 8.16 cm⁻¹, $F(000)$ = 1904, T = 294 K. Monoclinic *P2*/₁/*a*, a = 16.071(8), b = 14.745(6), c = 19.558(9) Å, β = 104.81(6)°, V = 4481(6) Å³, Z = 8, ρ = 1.354 g cm⁻³. 4227 reflections, 2179 with $I > 2\sigma(I)$ observed, $\omega/2\theta$ = 1, hkl : -26.26, 0.17, 0.23. Lorentz and polarisation corrections (DEFLT 1990), R = 0.041, R_w = 0.043, $w = 1/\sigma(F_o)^2 = [\sigma^2(I) + (0.04F_o)^2]^{-1/2}$, S_w = 2.92 (residual $\Delta\rho < 0.48$ e Å⁻³). Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no CCDC-101876. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int. code + 44(1223)366-033; E-mail: deposit@ccdc.cam.ac.uk].
 [9] M. L. H. Green, J. Haggitt, C. P. Mehnert, *J. Chem. Soc. Chem. Commun.* **1995**, 1853–1854. A. N. Chernega, A. J. Graham, M. L. H. Green, J. Haggitt, J. Lloyd, C. P. Mehnert, N. Metzler, J. Souter, *J. Chem. Soc., Dalton Trans* **1997**, 2293–2303.
 [10] The parent C₅H₅ complex was expected to be a better Lewis acid, however, attempts to synthesize the chelate complex [Fe(C₅H₅)(CO){C(OMe)C₆H₄-*o*-Cl^a}(Fe-C^a)] [OTf] was unsuccessful: C. Schulz, V. Guerschais, unpublished results.

[98122]