

Regioselective iron-mediated C–C coupling reactions: role of the iodide anion†

Karine Ferré,^a Philippe Le Mignot,^a Sourisak Sinbandhit,^b Loïc Toupet^c and Véronique Guerschais*^a^a UMR 6509 CNRS-Université de Rennes 1 'Organométalliques et Catalyse: Chimie et Electrochimie Moléculaires', Campus de Beaulieu, Université de Rennes 1, 35042 Rennes Cedex, France. E-mail: guerschai@univ-rennes1.fr^b Centre Régional de Mesures Physiques de l'Ouest (C.R.M.P.O.), Campus de Beaulieu, Université de Rennes 1, 35042 Rennes Cedex, France^c UMR CNRS 6626 Groupe Matière Condensée et Matériaux, Campus de Beaulieu, Université de Rennes 1, 35042 Rennes Cedex, France

Received (in Cambridge, UK) 12th April 2000, Accepted 16th June 2000

Published on the Web 6th July 2000

The chelate iron(allyloxy)carbene complexes $[\text{Fe}(\text{C}_5\text{H}_5)(\text{CO})\{\eta^3\text{-C}(\text{OCHR}^1\text{CH}=\text{CR}^2\text{R}^3)(\text{C}_6\text{H}_4\text{-}o\text{-Cl})\}][\text{BF}_4]$ (**2a–e**) yield in the presence of $[\text{nBu}_4\text{N}][\text{I}]$ the corresponding β,γ -unsaturated ketones $\text{R}^3\text{R}^2\text{C}=\text{CHCHR}^1\text{C}(\text{O})(\text{C}_6\text{H}_4\text{-}o\text{-Cl})$ (**3**); this reaction proceeds with high regioselectivity without rearrangement of the allyl fragment.

The design of transition metal complexes capable of selective C–C bond formation under mild conditions is highly desirable. Such a reaction can be achieved by carbene complexes which are good candidates to promote processes within the coordination sphere of the metal. For instance, chelate (allyloxy)carbene complexes have been postulated as key intermediates in the $[\text{Ru}(\text{Cp})(\text{PPh}_3)_2\text{Cl}]$ -catalysed coupling of allylic alcohol and terminal alkynes, affording β,γ -unsaturated ketones.^{1,2} Although $[\text{Ru}(\text{allyloxy})\text{carbene}]$ ($[\text{Ru}] = \text{Ru}(\text{Tp})(\text{Cl})$) complexes have been recently described,³ no direct evidence of such transformation from these species has been reported.⁴ The related chelate iron (allyloxy)carbene complexes⁵ can be useful models for providing an insight into the mechanism of this reaction, and this is likely to be important in the development and design of new catalysts. Iron (alkoxy)carbene complexes $[\text{Fe}(\text{C}_5\text{H}_5)(\text{CO})_2\{\text{C}(\text{OR})\text{R}'\}]$ are known to undergo facile *O*-dealkylation reactions in the presence of iodide anions,⁶ regenerating the starting acyl precursor $[\text{Fe}(\text{C}_5\text{H}_5)(\text{CO})_2\{\text{C}(\text{O})\text{R}'\}]$ along with RI. This prompted us to examine the deallylation reaction of *chelate* (allyloxy)carbene complexes under the same conditions, the coordinated allyl fragment thus generated is expected to be involved in a metal-mediated C–C coupling. We report herein the reactivity of the chelate (allyloxy)carbene complexes $[\text{Fe}(\text{C}_5\text{H}_5)(\text{CO})\{\eta^3\text{-C}(\text{OCHR}^1\text{CH}=\text{CR}^2\text{R}^3)(\text{C}_6\text{H}_4\text{-}o\text{-Cl})\}][\text{BF}_4]$ (**2**) towards iodide salts, and the formation of the corresponding β,γ -unsaturated ketones **3**. Since the iron moiety is not sterically encumbered, this facilitates the study of different substituted allyloxy derivatives, showing that this transformation is efficient and proceeds with excellent regioselectivity.

The *chelate* (allyloxy)carbene complexes ($\eta^3\text{-C,C,C}$) $[\text{Fe}(\text{C}_5\text{H}_5)(\text{CO})\{\eta^3\text{-C}(\text{OCHR}^1\text{CH}=\text{CR}^2\text{R}^3)(\text{C}_6\text{H}_4\text{-}o\text{-Cl})\}][\text{BF}_4]$ (**2a–e**), are readily accessible from the methoxycarbene complexes containing a labile CH_3CN ligand $[\text{Fe}(\text{C}_5\text{H}_5)(\text{CO})(\text{CH}_3\text{CN})\{\text{C}(\text{OMe})(\text{C}_6\text{H}_4\text{-}o\text{-Cl})\}][\text{BF}_4]$ (**1**).⁵ The structure of **2c**, containing a trisubstituted C=C fragment, has been confirmed by X-ray crystallography (Fig. 1).§ The reaction of **2** (**a**, $\text{R}^2 = \text{Ph}$, $\text{R}^1 = \text{R}^3 = \text{H}$; **b**, $\text{R}^2 = \text{Me}$, $\text{R}^1 = \text{R}^3 = \text{H}$; **c**, $\text{R}^2 = \text{R}^3 = \text{Me}$, $\text{R}^1 = \text{H}$; **d**, $\text{R}^1 = \text{Me}$, $\text{R}^2 = \text{R}^3 = \text{H}$; **e**, $\text{R}^1 = \text{R}^2 = \text{R}^3 = \text{H}$) with $[\text{nBu}_4\text{N}][\text{I}]$ in CH_2Cl_2 gives quantitatively the ketones $\text{R}^3\text{R}^2\text{C}=\text{CHCHR}^1\text{C}(\text{O})(\text{C}_6\text{H}_4\text{-}o\text{-Cl})$ (**3**) (Scheme 1). If the reaction is carried out in the presence of CO (1 atm), the organometallic fragment is recovered as $[\text{Fe}(\text{C}_5\text{H}_5)(\text{CO})_2(\text{I})]$.⁷ The *E*-configuration of **3a–b** is confirmed by the ¹H NMR data. The resonances of the olefinic protons of

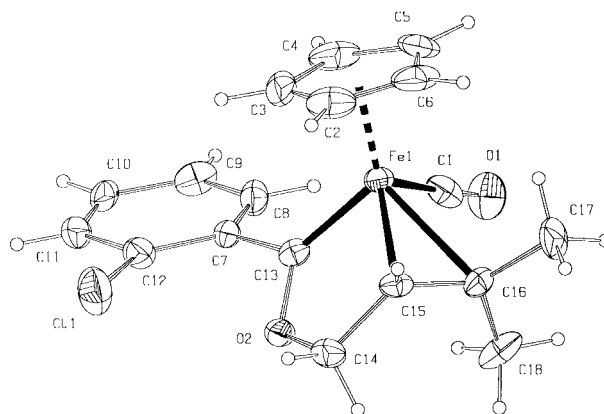
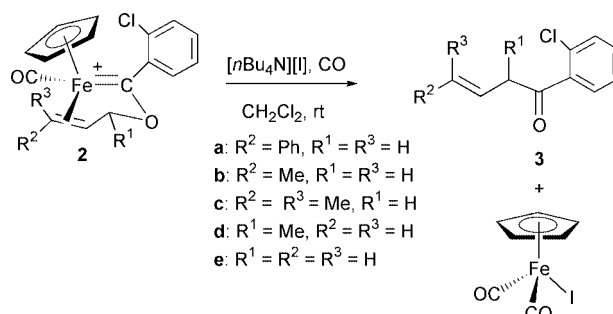


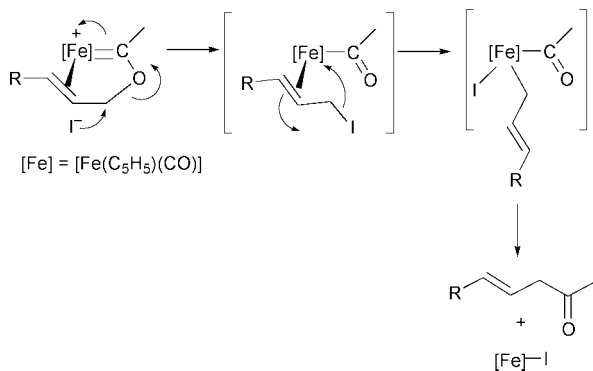
Fig. 1 ORTEP drawing of **2c**. Selected bond distances (Å) and angles (°): O2–C13 1.344(14), O2–C14 1.430(14), Fe–C13 1.828(11), C15–C16 1.41(2), C17–C16–C18 117.8(14), O2–C13–C7 108.9(9), C13–O2–C14 115.4(8).

3a are located at δ 6.54 (=CH) and 6.41 (=CHPh) with a typical coupling constant $^3J(\text{H,H}) = 16$ Hz, whereas those of **3b** appear at δ 5.66 (=CH, $^3J(\text{H,H}) = 15.3$ Hz) and 5.35 (=CHMe). Moreover, the formation of the conjugated isomer *i.e.* the α -enone, which would result from isomerisation of the C=C double bond, does not occur. Remarkably, no rearrangement of the initial allyl group is observed. Depending on the precursor used, the α - and γ -methyl substituted ketones **3d** and **3b** are formed, respectively. The above data indicate that the carbon atom of the allyl substituent, which is involved in the C–O bond cleavage, recombines to form the new C–C bond. The proposed mechanism showing the participation of the iodide is depicted in Scheme 2. Rupture of the C–O bond^{8,9} by nucleophilic attack of I[−] on the carbon atom yields a coordinated allyl iodide fragment, which then could oxidatively add to the iron center, inducing the decoordination of the olefinic unit. Then, the transient 18-electron Fe(IV) species reductively eliminates the acyl and the η^1 -allyl ligands to afford the observed ketone **3**, and the iron-containing compounds. The first step has been already



Scheme 1

† Electronic supplementary information (ESI) available: experimental data for compound **3**. See <http://www.rsc.org/suppdata/cc/b0/0029211/>



Scheme 2

observed for unchelated iron (alkoxy)carbene complexes,⁶ it can be explained by the substantial contribution of the resonance oxonium form, in which the C–O bond is weakened. Moreover, this shows that the C–C bond forming reaction occurs within the co-ordination sphere of the metal, and this requires pre-coordination of the allyloxy group, as previously suggested.^{1,10}

These results provide the direct evidence of the formation of β,γ -unsaturated ketones from *chelate* (allyloxy)carbene complexes. Moreover, the role of the iodide is crucial to initiate this process. Finally, the above data on the [Fe(Cp)(CO)]⁺ iron moiety, capable to coordinate tri- and disubstituted C=C bonds, show that the arrangement of the allyl group is maintained during this transformation, allowing regioselective reactions.

This work was supported by the CNRS. We thank the MENRT for a grant to K. F.

Notes and references

§ Crystal data for **2c**: C₁₈H₁₈O₂ClFeBF₄, $M = 444.43$ orthorhombic space group $P2_12_12_1$, $a = 7.462(7)$, $b = 11.991(3)$, $c = 21.169(7)$ Å, $V =$

1894(2) Å³, $Z = 4$, $\rho = 1.558$ g cm⁻³. CAD4 NONIUS diffractometer, MoK α radiation, $\mu = 9.85$ cm⁻¹, $F(000) = 1064$, $T = 293$ K. 1972 reflections, 1240 with $I > 2\sigma(I)$ observed ($\omega/2\theta = 1$, hkl : 0.6, 0.15, 0.27. $R = 0.0798$, $R_w = 0.152$, $w = 1/[\sigma^2(F_o)^2 + (0.1757P)^2]$, $S_w = 1.019$ (residual $\Delta\rho < 0.58$ eÅ⁻³). CCDC 182/1695. See <http://www.rsc.org/suppdata/cc/b0029211/> for crystallographic files in .cif format.

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