Conversion of α,β-Unsaturated Ketone Complexes into α,β-Unsaturated Ketene Complexes

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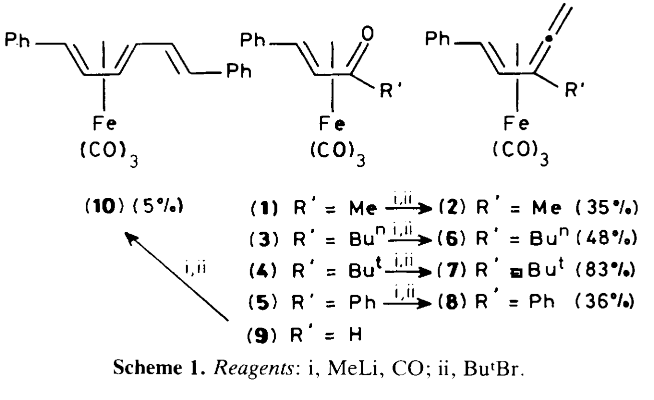
Treatment of (α,β-unsaturated ketone)tricarbonyliron(0) complexes with organolithium reagents under an atmosphere of carbon monoxide gave products which were identified as (α,β-unsaturated ketene)tricarbonyliron(0) complexes based on a crystal structure analysis of [PhCH=CHC(Me)=C=O](CO)$_3$Fe(0) (**2**), the product obtained from (PhCH=CHC=OMe)(CO)$_3$Fe(0) (**1**).

Investigations into the reactivity of α,β-unsaturated ketones attached to the tricarbonyliron(0) moiety have been neglected in the past in favour of investigations into the reactivity of 1,3-dienes attached to the tricarbonyliron(0) unit.[1] Although a small number of reactions of (α,β-unsaturated ketone)tricarbonyliron(0) complexes with electrophiles have been known for some time,[2,3] we recently reported the first examples of nucleophilic attack on these complexes.[4] We demonstrated that reaction of Grignard and organolithium reagents with a range of (α,β-unsaturated ketone)tricarbonyliron(0) complexes under an atmosphere of nitrogen produced 1,4-diketones in good yield, presumably *via* nucleophilic attack on a metal carbonyl ligand. This Communication describes how treatment of (α,β-unsaturated ketone)tricarbonyliron(0) complexes with organolithium reagents under an atmosphere of carbon monoxide results in the reaction following a quite different pathway and leads to the formation of (α,β-unsaturated ketene)tricarbonyliron(0) complexes.



Scheme 1. *Reagents*: i, MeLi, CO; ii, Bu^{t}Br.

(Benzylideneacetone)tricarbonyliron(0) (**1**) is readily prepared from benzylideneacetone and nonacarbonyldi-iron.† A

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† Complexes (**1**), (**3**), (**4**), (**5**), and (**9**) were obtained in 81, 82, 89, 79, and 53% yield, respectively, by heating two equivalents of Fe$_2$(CO)$_9$ with the appropriate α,β-unsaturated carbonyl at 35 °C in diethyl ether for 15—18 h. These conditions were found to be considerably more convenient than conditions used previously[2,4] which involved heating one equivalent of Fe$_2$(CO)$_9$ with the α,β-unsaturated carbonyl at 60—75 °C in toluene for 3—4 h and gave yields of 30—40%.

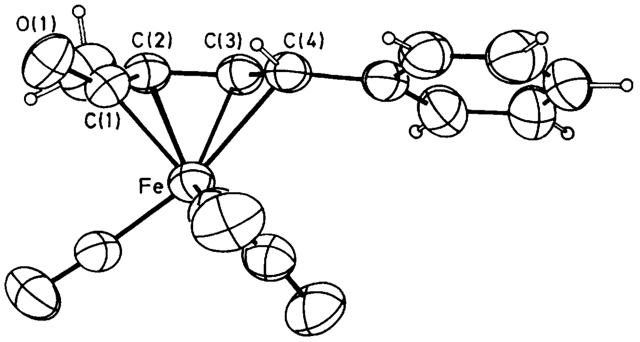
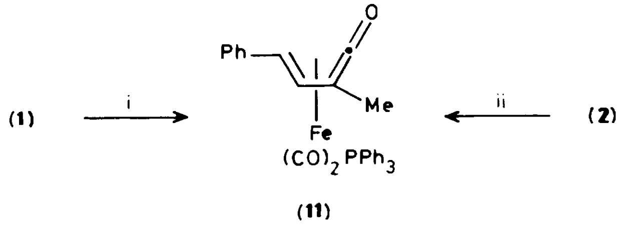


Figure 1. Molecular structure of [PhCH=CHC(Me)=C=O](CO)$_3$Fe^0 (**2**). Principal dimensions: Fe–C(1) 1.926(4), Fe–C(2) 2.103(3), Fe–C(3) 2.092(3), Fe–C(4) 2.181(3), C(1)–O(1) 1.194(5), C(1)–C(2) 1.444(4), C(2)–C(3) 1.397(5), C(3)–C(4) 1.420(4) Å.

solution of complex (**1**) in tetrahydrofuran was cooled to −78 °C under an atmosphere of carbon monoxide and treated with methyl-lithium (Scheme 1).‡ After quenching with t-butyl bromide, the reaction mixture was filtered through alumina to remove iron residues and then chromatographed. This led to the isolation of air-stable yellow crystals which were identified as the novel (α,β-unsaturated ketene)tricarbonyliron(0) complex (**2**) by *X*-ray crystal structure analysis (Figure 1).§

The tolerance of this unusual reaction to variation of the substituent R′ was investigated. The (α,β-unsaturated ketone)tricarbonyliron(0) complexes (**3**),[4] (**4**),[4] and (**5**)[2] were converted to the novel¶ (α,β-unsaturated ketene)tricarbonyliron(0) complexes (**6**), (**7**), and (**8**), respectively, in moderate to good yields, but the α,β-unsaturated aldehyde complex (**9**)[5] failed to undergo an analogous reaction. It proved possible, however, to isolate the triene complex (**10**)[6] from the reaction mixture in low yield. Triphenylphosphine may be used in place of carbon monoxide to promote the conversion of the α,β-unsaturated ketone ligand into the α,β-unsaturated ketene ligand. Thus complex (**1**) gave the novel phosphine-substituted complex (**11**) on treatment with methyl-lithium in the presence of triphenylphosphine (Scheme 2). [Complex (**11**) was also synthesised by heating the tricarbonyl complex (**2**) with triphenylphosphine at 80 °C.] It is of note that although ketone–ketene conversion has been observed using either methyl-lithium or n-butyl-lithium, stoicheiometric quantities of the organolithium reagent are required to drive the reaction to completion.



Scheme 2. *Reagents:* i, (1) MeLi, PPh$_3$, (2) Bu^{t}Br, 31%; ii, PPh$_3$, 91%.

The mechanistic details of this unprecedented reaction are as yet undefined. Reports of the transformation of cyclopropenes,[7] metal vinylcarbene precursors,[8] and metal vinylcarbenes[9] into (α,β-unsaturated ketene)tricarbonyliron(0) complexes, and the isolation of complex (**10**) described above, however, suggest that a metal vinylcarbene complex could be a key intermediate in the reaction.

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‡ Reaction typically involved stirring the α,β-unsaturated carbonyl complex (1.00 mmol) and methyl-lithium (1.10 mmol) in tetrahydrofuran at −78 °C under an atmosphere of carbon monoxide (1.1 atm) for 2 h. Bu^{t}Br (2.0 mmol) was added to the reaction mixture which was stirred for a further 0.5 h at −78 °C and then allowed to warm to room temperature over 1 h under the carbon monoxide atmosphere.

§ *Crystal data* for (**2**): $C_{14}H_{10}O_4Fe$, $M = 298.1$, monoclinic, space group $P2_1/c$, $a = 13.998(6)$, $b = 7.955(5)$, $c = 12.935(5)$ Å, $\beta = 113.04(3)°$, $U = 1325(1)$ Å^3, $Z = 4$, $D_c = 1.49$ g cm^{-1}. Data were collected with a Syntex P2$_1$ four circle diffractometer, maximum 2θ 50°, using Mo-K_α radiation, $\lambda = 0.71069$ Å, μ(Mo-K_α) = 11.4 cm^{-1}, $T = 293$ K, crystal dimensions 0.12 × 0.30 × 0.64 mm. Profile analysis gave 2343 unique reflections ($R_{\text{int.}} = 0.03$); 1854 were considered observed [$I/\sigma(I) \geqslant 2.0$] and used in refinement; they were corrected for Lorentz, polarisation, and absorption effects, the last by the Gaussian method. The Fe atom was located from a Patterson synthesis and the light atoms then found on successive syntheses (including H-atoms). Anisotropic temperature factors were used for all non-H atoms. Hydrogen atoms were given fixed isotropic temperature factors. Phenyl H-atoms were inserted at calculated positions and not refined; the methyl group was treated as a rigid CH$_3$ unit, with its original orientation taken from the strongest H-atom peaks on a difference Fourier synthesis. Other H-atom co-ordinates were refined. Final refinement was on F by cascaded least-squares methods refining 181 parameters. A weighting scheme of the form $w = 1/[\sigma^2(F) + gF^2]$ with $g = 0.0014$ was used and shown to be satisfactory by a weight analysis. Final $R = 0.039$, $R_w = 0.043$. Maximum shift/error in final cycle 0.03. Computing with SHELXTL (Sheldrick, 1983) on a Data General DG30. Scattering factors in the analytical form and anomalous dispersion factors taken from International Tables (1974). Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

¶ The novel compounds (**2**), (**6**), (**7**), (**8**), and (**11**) all gave satisfactory i.r., ^{1}H n.m.r., low resolution m.s., and microanalytical data.

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