

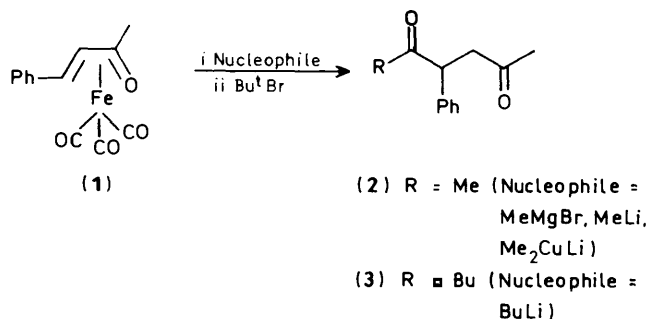
Nucleophilic Addition to Tricarbonyliron Complexes of α,β -Unsaturated Ketones and the Production of 1,4-Diketones

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The first examples of nucleophilic addition to tricarbonyliron complexes of α,β -unsaturated ketones are described. Addition of Grignard, organolithium, and organocuprate reagents to the tricarbonyliron complex of benzylideneacetone (**1**) gives 1,4-diketones. The synthesis and reactivity of the tricarbonyliron complexes of PhCH=CHCOR, R = Bu (**7**), R = Buⁱ (**8**), and R = Bu^t (**9**) are reported.

Tricarbonyliron complexes of α,β -unsaturated carbonyl compounds (which may be regarded as oxa analogues of tricarbonyliron complexes of 1,3-dienes) were first synthesized more than 20 years ago.¹ The properties and reactivity of 1,3-dienes complexed to the tricarbonyliron unit have received much attention in recent years.² In contrast, there have been few reports of the properties and reactivity of α,β -unsaturated ketones complexed to the tricarbonyliron unit. Tricarbonyliron complexes of α,β -unsaturated ketones have been shown to be a mild source of the tricarbonyliron entity and this has been exploited in the synthesis of diene tricarbonyliron complexes³ and the trapping of low concentrations of a diene in an equilibrium mixture.⁴ Complexes of optically active α,β -unsaturated ketones transfer their chirality to give optically active diene tricarbonyliron complexes.⁵ The reactions of electrophiles with tricarbonyliron complexes of α,β -unsaturated carbonyl compounds have been examined. Protonation of the tricarbonyliron complex of benzylideneacetone (**1**) is thought to occur on the oxygen atom of the benzylideneacetone⁶ and reaction of the tricarbonyliron complex of cinnamaldehyde with MeCO⁺BF₄⁻ leads to acylation on the oxygen atom of the cinnamaldehyde.⁷

As far as we are aware, the reaction of tricarbonyliron complexes of α,β -unsaturated carbonyl compounds with nucleophiles has not been reported. We describe here the reaction of tricarbonyliron complexes of α,β -unsaturated ketones with carbon nucleophiles. Part of this work has been the subject of a preliminary communication.⁸



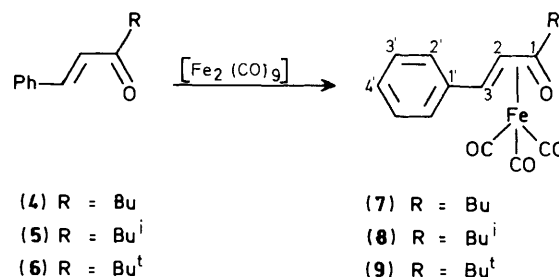
Results

Tricarbonyl(benzylideneacetone)iron(0) (**1**) is an air-stable crystalline solid readily prepared from benzylideneacetone and enneacarbonyliron(0).^{3a} Complex (**1**) was treated with methylmagnesium bromide at -78°C for 7 h and the reaction mixture quenched with an excess of *t*-butyl bromide. The ¹H n.m.r. spectrum of the crude product revealed that it contained

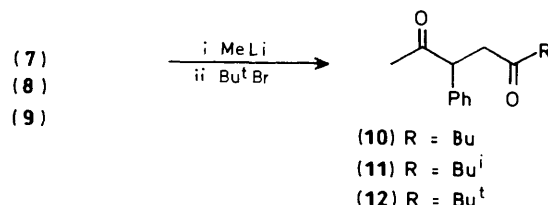
only 3-phenylhexane-2,5-dione (**2**) and benzylideneacetone in a 9:1 ratio. Column chromatography of the mixture led to the isolation of pure compound (**2**)⁹ in 79% yield. Treatment of complex (**1**) with methyl-lithium or lithium dimethylcuprate under identical conditions also led to the isolation of compound (**2**) in 75 and 26% yields respectively. Similarly, addition of butyllithium to complex (**1**) resulted in the production and isolation of 4-phenylnonane-2,5-dione (**3**)⁹ in 53% yield. Addition of phenylmagnesium bromide or phenyl-lithium to (**1**) at -78 or -23°C , however, did not result in the formation of the corresponding 1,4-diketone.

In order to define the scope of this reaction, a range of α,β -unsaturated carbonyl compounds with different substituents at C-1, C-2, and C-3 were prepared and complexed to the tricarbonyliron unit. The reaction of some of these complexes with methyl-lithium was examined.

The α,β -unsaturated ketones (**4**), (**5**), and (**6**) were prepared by heating together sodium hydroxide, benzaldehyde, and the

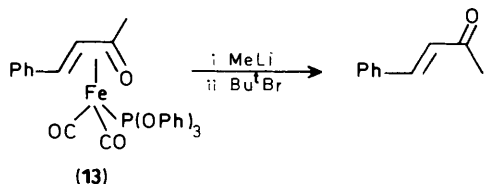


appropriate methyl ketone.¹⁰ Reaction of compound (**4**), (**5**), or (**6**) with enneacarbonyliron(0) at 65°C for 4.5 h led to mixtures of unchanged α,β -unsaturated ketone and the corresponding tricarbonyliron complex. Column chromatography led to the isolation of the air-stable novel complexes (**7**), (**8**), or (**9**) in 33–38% yield. The tricarbonyliron complexes (**7**), (**8**), and (**9**) were each treated with methyl-lithium at -78°C for 7 h. After quenching the reaction mixtures with an excess of *t*-butyl bromide, the novel 1,4-diketones (**10**), (**11**), and (**12**) were isolated in 73, 59, and 64% yields respectively.



Pent-3-en-2-one, non-3-en-2-one, and α -methylcinnamaldehyde were each heated with enneacarbonyliron(0) at 65 °C for 4.5 h in order to produce the corresponding tricarbonyliron complexes. Since the resulting complexes were air-sensitive and difficult to purify, their reactions with nucleophiles were not examined.

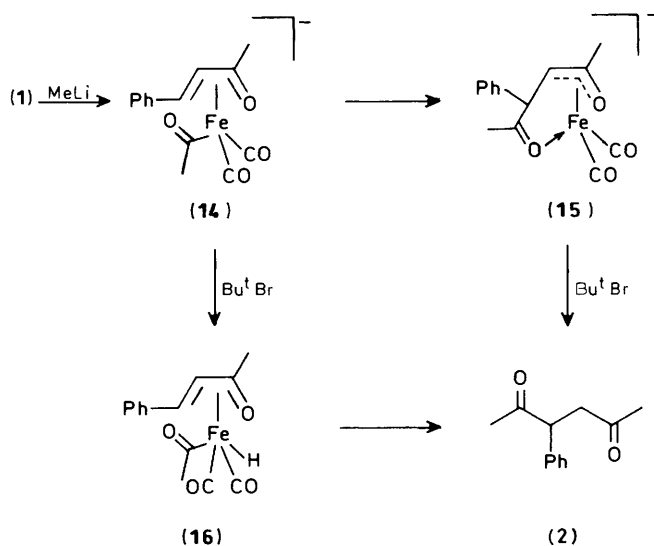
The reaction of methyl-lithium with the triphenyl phosphite complex (13) was examined. Complex (13) is readily available from tricarbonyl(benzylideneacetone)iron(0) (1) and triphenyl phosphite.¹¹ Treatment of complex (13) with methyl-lithium at



−78 °C for 7 h followed by quenching with an excess of *t*-butyl bromide led to a product which contained a trace of 3-phenylhexane-2,5-dione (2) (less than 5%) but was predominantly benzylideneacetone.

Discussion

It has been reported that the metal acyl anions $[\text{NiRCO}(\text{CO})_3]^-$, $[\text{Fe}(\text{RCO})(\text{CO})_3]^-$, and $[\text{Co}(\text{RCO})(\text{NO})(\text{CO})\text{PPh}_3]^-$ react in an intermolecular fashion with α,β -unsaturated ketones to give 1,4-diketones.^{9,12} The formation of 1,4-diketones from the reaction of nucleophiles with the tricarbonyliron complex of benzylideneacetone (1) and the related complexes (7), (8), and (9) is consistent with the formation of a metal acyl intermediate. For example, reaction of compound (1) with methyl-lithium probably leads to the acyl anion (14). Transfer of



the MeCO group to the β -carbon of the benzylideneacetone ligand to give complex (15) followed by protonation leads to (2). Alternatively, protonation of (14) on iron would lead to the iron hydride (16) which, on stepwise transfer of MeCO and H to the carbon-carbon double bond of benzylideneacetone, would also give rise to (2).

It was postulated that replacement of a carbonyl ligand in (1)

with triphenyl phosphite [which leads to more electron density being available to the dicarbonyl(benzylideneacetone)iron(0) fragment] may alter the position of nucleophilic attack on the complex. The increased available electron density, however, only appears to weaken the metal-benzylideneacetone bonding and hence facilitate decomposition of complex (13) under the reaction conditions.

Experimental

All reactions were performed under nitrogen using standard vacuum line and Schlenk tube techniques.¹³ Diethyl ether was dried over sodium wire and light petroleum refers to that fraction boiling in the range 30–40 °C. Enneacarbonyliron(0), methylmagnesium bromide (3.0M in diethyl ether), methyl-lithium (1.4M in diethyl ether), and butyl-lithium (1.6M in hexane) were used as supplied by Aldrich. Chromatography was performed in SiO_2 (Merck, 40–63 μm). M.p.s were obtained in a Gallenkamp capillary m.p. apparatus and are uncorrected. Elemental analyses were performed by Butterworth Laboratories Ltd. I.r. spectra were obtained from solutions on a Perkin-Elmer 580B instrument and calibrated against a polystyrene standard. N.m.r. spectra were recorded in CDCl_3 on Perkin-Elmer R34 (220 MHz ^1H) and Bruker WH 400 (100.6 MHz ^{13}C) spectrometers. Mass spectra were recorded on a Kratos MS 80 instrument using e.i. and f.a.b. techniques.

Reaction of Methylmagnesium Bromide with Tricarbonyl(benzylideneacetone)iron(0) (1).—Methylmagnesium bromide (0.50 ml, 1.5 mmol) was added to complex (1) (143 mg, 0.5 mmol) in diethyl ether (20 ml) at −78 °C and the mixture was stirred at −78 °C for 7 h. The resulting dark green mixture was treated with *t*-butyl bromide (0.56 ml, 5.0 mmol) at −78 °C, allowed to warm to room temperature, and filtered through alumina to remove iron residues. The solvent was removed under reduced pressure to give a crude product which ^1H n.m.r. spectroscopy revealed to be a mixture of 3-phenylhexane-2,5-dione (2) and benzylideneacetone in a 9:1 ratio. Column chromatography (SiO_2 ; light petroleum–diethyl ether, 2:1) gave pure (2) (79%) identified by comparison of its ^1H n.m.r. and i.r. spectra with literature values.⁹

Reaction of Methyl-lithium with Tricarbonyl(benzylideneacetone)iron(0) (1).—Methyl-lithium (0.53 ml, 0.75 mmol) was added to complex (1) (143 mg, 0.50 mmol) in diethyl ether (20 ml) at −78 °C. Following the procedure described above for methylmagnesium bromide led to the isolation of pure 3-phenylhexane-2,5-dione (2) (75%) which was identified by comparison of its ^1H n.m.r. and i.r. spectra with literature values.⁹

Reaction of Lithium Dimethylcuprate with Tricarbonyl(benzylideneacetone)iron(0) (1).—Methyl-lithium (1.06 ml, 1.50 mmol) was added to a suspension of cuprous iodide (143 mg, 0.75 mmol) in diethyl ether (20 ml) at −23 °C and the mixture stirred for 0.5 h at −23 °C. The resulting pale yellow solution was cooled to −78 °C and treated with a solution of complex (1) (143 mg, 0.50 mmol) in diethyl ether (10 ml). Following the procedure described above for methylmagnesium bromide led to the isolation of pure 3-phenylhexane-2,5-dione (2) (26%) which was identified by comparison of its ^1H n.m.r. and i.r. spectra with literature values.⁹

Reaction of Butyl-lithium with Tricarbonyl(benzylideneacetone)iron(0) (1).—Butyl-lithium (0.47 ml, 0.75 mmol) was added to complex (1) (143 mg, 0.50 mmol) in diethyl ether (20 ml) at −78 °C. Following the procedure described above for methylmagnesium bromide led to the production of a crude product, purification of which by column chromatography

(SiO₂; dichloromethane–cyclohexane, 9:1) gave pure 4-phenyl-nonane-2,5-dione (3) (53%) which was identified by comparison of its ¹H n.m.r. and i.r. spectra with literature values.⁹

Preparation of Tricarbonyl(benzylidenemethyl butyl ketone)-iron(0) (7).—Enneacarbonyldi-iron(0) (6.50 g, 17.8 mmol) and benzylidenemethyl butyl ketone (4) (3.35 g, 17.8 mmol) were stirred in toluene (100 ml) for 4 h at 70 °C. The resulting mixture was filtered to remove iron residues and the filtrate concentrated under reduced pressure to give a brown oil. Column chromatography (SiO₂; light petroleum–diethyl ether, 9:1) of this led to the isolation of red crystals of (7) (2.05 g, 35%), m.p. 34–36 °C (Found: C, 58.3; H, 5.05. C₁₆H₁₆FeO₄ requires C, 58.56; H, 4.92%; ν_{\max} (cyclohexane) 2 080, 2 020, and 1 990 cm⁻¹ (C≡O); δ_{H} 1.0 (3 H, t, *J* 7 Hz, CH₃CH₂), 1.45–1.55 (2 H, m, CH₂Me), 1.75–1.85 (2 H, m, CH₂Et), 2.6–2.95 (2 H, m, CH₂CO), 3.1 (1 H, d, *J* 10 Hz, 3-H), 6.05 (1 H, d, *J* 10 Hz, 2-H), and 7.2–7.3 (5 H, m, Ph); δ_{C} 13.7 (CH₃), 22.5 (CH₂Me), 30.1 (CH₃Et), 34.4 (CH₂CO), 60.9 (C-3), 76.7 (C-2), 126.7 (C-2'), 126.9 (C-4'), 128.7 (C-3'), 138.7 (C-1'), and 146.1 (C-1); *m/z* 328 (*M*⁺, 93%), 300 (100, *M* – CO), 272 (31, *M* – 2 CO), and 244 (13, *M* – 3 CO).

Preparation of Tricarbonyl(benzylidenemethyl isobutyl ketone)iron(0) (8).—Enneacarbonyldi-iron(0) (6.50 g, 17.8 mmol) and benzylidenemethyl isobutyl ketone (5) (3.35 g, 17.8 mmol) were stirred in toluene (100 ml) for 4.5 h at 75 °C. The resulting red mixture was filtered to remove iron residues and the filtrate concentrated under reduced pressure to give a brown oil. Column chromatography (SiO₂; light petroleum–diethyl ether, 9:1) of this led to the isolation of red crystals of *title complex* (8) (1.95 g, 33%), m.p. 88 °C (decomp.) (Found: C, 58.85; H, 5.0. C₁₆H₁₆FeO₄ requires C, 58.56; H, 4.92%; ν_{\max} (cyclohexane) 2 080, 2 020, and 1 990 cm⁻¹ (C≡O); δ_{H} 1.05 (3 H, d, *J* 6 Hz, CH₃CH), 1.1 (3 H, d, *J* 6 Hz, CH₃CH), 2.0–2.15 (1 H, m, CHMe₂), 2.45 (1 H, dd, *J* 6 and 14 Hz, 1-H or CH₂CO), 3.0 (1 H, dd, *J* 7 and 14 Hz, 1-H of CH₂CO), 3.1 (1 H, d, *J* 9 Hz, 3-H), 6.05 (1 H, d, *J* 9 Hz, 2-H), and 7.2–7.4 (5 H, m, Ph); δ_{C} 22.3 (CH₃CH), 22.8 (CH₃CH), 28.7 (CHCH₃), 44.1 (CH₂CO), 60.9 (C-3), 78.1 (C-2), 126.7 (C-2'), 126.9 (C-4'), 128.7 (C-3'), 138.7 (C-1'), and 144.5 (C-1); *m/z* 328 (*M*⁺, 78%), 300 (100, *M* – CO), 272 (33, *M* – 2 CO), and 244 (13, *M* – 3 CO).

Preparation of Tricarbonyl(benzylidenemethyl *t*-butyl ketone)-iron(0) (9).—Enneacarbonyldi-iron(0) (2.60 g, 7.1 mmol) and benzylidenemethyl *t*-butyl ketone (6) (1.34 g, 7.1 mmol) were stirred in toluene (50 ml) for 3 h at 70 °C. The resulting red mixture was filtered to remove iron residues and the filtrate concentrated under reduced pressure to give a red oil. Crystallisation of this from light petroleum gave red crystals of *compound* (9) (0.88 g, 38%), m.p. 86–88 °C (decomp.) (Found: C, 58.3; H, 4.8. C₁₆H₁₆FeO₄ requires C, 58.56; H, 4.92%; ν_{\max} (cyclohexane) 2 080, 2 020, and 1 990 cm⁻¹ (C≡O); δ_{H} 1.4 (9 H, s, CH₃), 3.05 (1 H, d, *J* 9 Hz, 3-H), 6.1 (1 H, d, *J* 9 Hz, 2-H), and 7.2–7.35 (5 H, m, Ph); δ_{C} 28.9 [(CH₃)₃C], 36.1 (Me₃C), 60.8 (C-3), 71.6 (C-2), 126.7 (C-2'), 126.9 (C-4'), 128.7 (C-3'), 138.7 (C-1'), 156.1 (C-1'), and 156.1 (C-1); *m/z* 328 (*M*⁺, 75%), 300 (100, *M* – CO), 272 (30, *M* – 2 CO), and 244 (12, *M* – 3 CO).

Reaction of Methyl-lithium with Complexes (7), (8), or (9).—Methyl-lithium (0.53 ml, 0.75 mmol) was added to complex (7), (8), or (9) (164 mg, 0.50 mmol) in diethyl ether (20 ml) at –78 °C

and the mixture was stirred at –78 °C for 7 h. The resulting mixture was treated with *t*-butyl bromide (0.56 ml, 5.0 mmol) at –78 °C, allowed to warm to room temperature, and filtered through alumina. Column chromatography (SiO₂; light petroleum–diethyl ether, 9:1) gave pure compounds (10) (73), (11) (59), or (12) (64%) as colourless oils.

3-Phenylnonane-2,5-dione (10).— ν_{\max} (CCl₄) 1 720 cm⁻¹ (C=O); δ_{H} 0.85 (3 H, t, *J* 7 Hz, CH₃CH₂), 1.2–1.35 (2 H, m, CH₂Me), 1.45–1.6 (2 H, m, CH₂Et), 2.1 (3 H, s, CH₃CO), 2.35–2.5 (2 H, m, CH₂Pr), 2.55 (1 H, dd, *J* 3 and 17 Hz, 1-H or CH₂CH), 3.4 (1 H, dd, *J* 10 and 17 Hz, 1-H or CH₂CH), 4.25 (1 H, dd, *J* 3 and 10 Hz, CHCH₂), and 7.15–7.35 (5 H, m, Ph) (Found: *m/z* 232.1457. C₁₅H₂₀O₂ requires 232.1463).

7-Methyl-3-phenyloctane-2,5-dione (11). ν_{\max} (CCl₄) 1 720 cm⁻¹ (C=O); δ_{H} 1.88 (3 H, d, *J* 6 Hz, CHCH₃), 1.90 (3 H, d, *J* 6 Hz, CHCH₃), 2.1 (3 H, s, CH₃CO), 2.25–2.4 (3 H, m, CH₂CHMe₂), 2.55 (1 H, dd, *J* 4 and 18 Hz, 1 H of CH₂CHPh), 3.4 (1 H, dd, *J* 10 and 18 Hz, 1 H of CH₂CHPh), 4.25 (1 H, dd, *J* 4 and 10 Hz, PhCHCH₂), and 7.2–7.35 (5 H, m, Ph) (Found: *m/z* 232.1471. C₁₅H₂₀O₂ requires 232.1463).

6,6-Dimethyl-3-phenylheptane-2,5-dione (12). ν_{\max} (CCl₄) 1 720 (C=O) and 1 710 cm⁻¹ (C=O); δ_{H} 1.1 (9 H, s, CH₃C), 2.15 (3 H, s, CH₃CO), 2.65 (1 H, dd, *J* 4 and 18 Hz, 1 H of CH₂CH), 3.5 (1 H, dd, *J* 10 and 18 Hz, 1 H of CH₂CH), 4.2 (1 H, dd, *J* 4 and 10 Hz, CHCH₂), and 7.2–7.4 (5 H, m, Ph) (Found: *m/z* 232.1453. C₁₅H₂₀O₂ requires 232.1463).

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