Synthesis of Tricarbonyliron(0) Complexes of Itaconic Acid Derivatives

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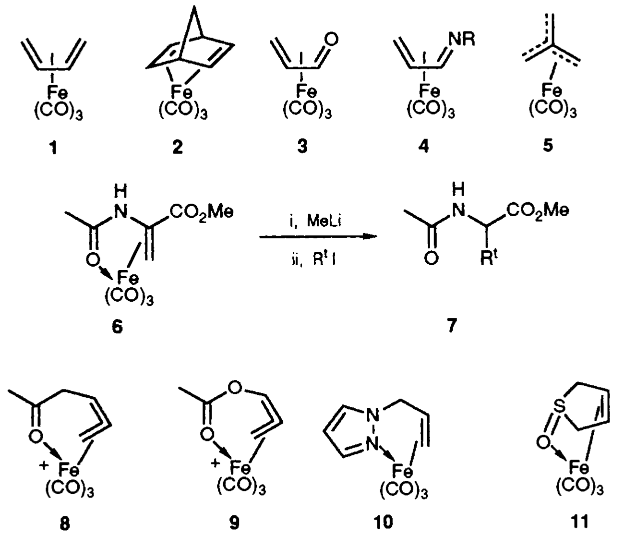
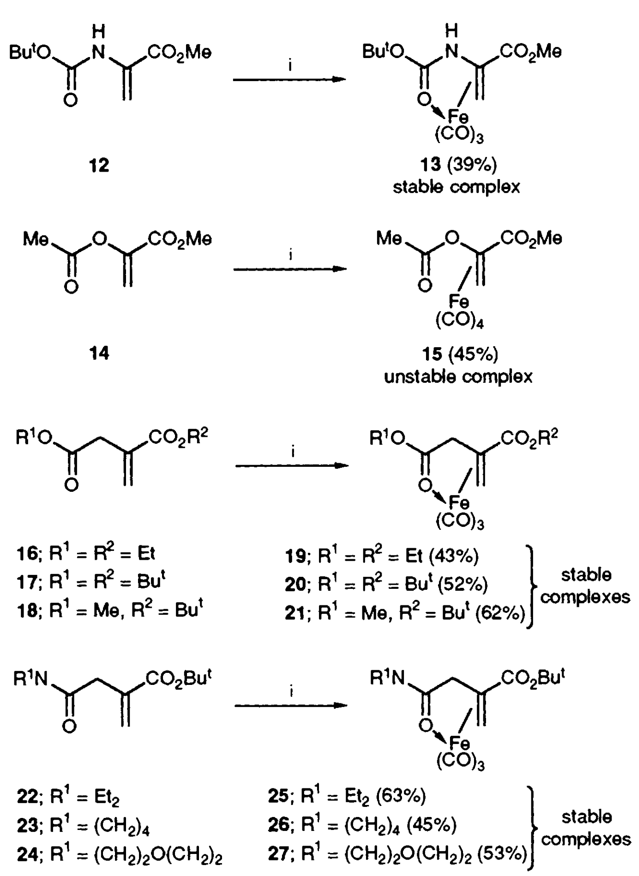
The products derived from $[\mathrm{Fe_2(CO)_9}]$ and alkenes bearing β-carbonyl groups linked to the alkene *via* nitrogen, oxygen and carbon atoms are reported; in particular, derivatives of itaconic acid produce air-stable crystalline tricarbonyliron(0) complexes one of which $[\mathrm{Fe^0(CO)_3\{MeO_2CCH_2C(CO_2Bu^t)CH_2\}}]$ **21** was examined by X-ray crystal structure analysis.

Dewar–Chatt–Duncanson binding between the tricarbonyliron(0) unit and four sp^2 hybridised atoms (as exemplified in structures **1–5**) has been known for many years[1] and is very familiar both to organometallic chemists and to organic chemists interested in the application of transition metal complexes in organic synthesis. With judicious choice of substituents, the complexes formed are stable and easy to handle, and thus they have been the focus of numerous reactivity studies and several applications in organic synthesis.[2] Very recently we have become interested in the relatively unusual and exceptionally stable tricarbonyliron(0) complex **6**, which may be regarded as a complex of a protected form of the unsaturated α-amino acid dehydroalanine.[3] Our initial studies of complex **6** have already led to the discovery of intriguing and unprecedented reactivity. For example, addition of an alkyllithium reagent to the complex followed by addition of a tertiary iodoalkane (R^t–I) produces α-amino acids **7**.[4] In complex **6**, the tricarbonyliron(0) unit is bound to a single carbon–carbon double bond and the remaining coordination site on the iron centre is filled by the oxygen of the adjacent organic carbonyl group. This specific type of bonding between a tricarbonyliron(0) unit and an organic molecule is, to the best of our knowledge, unique and reports of related modes of interaction such as those illustrated by complexes **8–11**[5–8] are isolated and unexploited. In view of its unusual bonding, high stability, and emerging interesting reactivity, we wondered whether or not complex **6** would tolerate significant variation of the atoms around the chelating organic carbonyl group or whether even small substituent variations would disturb a fine electronic balance between ligand and metal and lead to unstable complexes. We report herein preliminary results in this area that (*i*) demonstrate that carbonyl chelation will indeed tolerate significant substituent variation thus suggesting that chelating organic carbonyl groups have been under-exploited in tricarbonyliron(0) chemistry to date, and (*ii*) reveal that itaconic acid derivatives form very stable tricarbonyliron(0) complexes which have considerable potential in organic synthesis.

Initially, the effect of replacing the carbon-centred H$_3$C substituent on the chelating carbonyl group of complex **6** with the oxygen-centred Bu^{t}O group was examined. The required organic substrate **12** was readily synthesised from serine





Scheme 1 *Reagents and conditions*: i, $[Fe_2(CO)_9]$, Et_2O, 25–35 °C, 2–18 h

methyl ester hydrochloride [by sequential treatment with Boc_2O, MsCl and Et_3N (Boc = *tert*-butoxycarbonyl, Ms = methanesulfonyl)] and reacted with $[Fe_2(CO)_9]$ in diethyl ether at 35 °C for 14 h under a nitrogen atmosphere. After work-up, an orange crystalline solid was isolated and identified as the new tricarbonyliron(0) complex **13** on the basis of its spectroscopic and analytical data.† The moderate yield of complex **13** produced in this reaction (39%) contrasts with the excellent yield of complex **6** obtained by complexation of methyl 2-acetamidoacrylate (93%), and probably reflects the greater instability of complex **13** in solution. Nevertheless complex **13** proved to be air-stable in the solid state and could be stored indefinitely without significant decomposition.

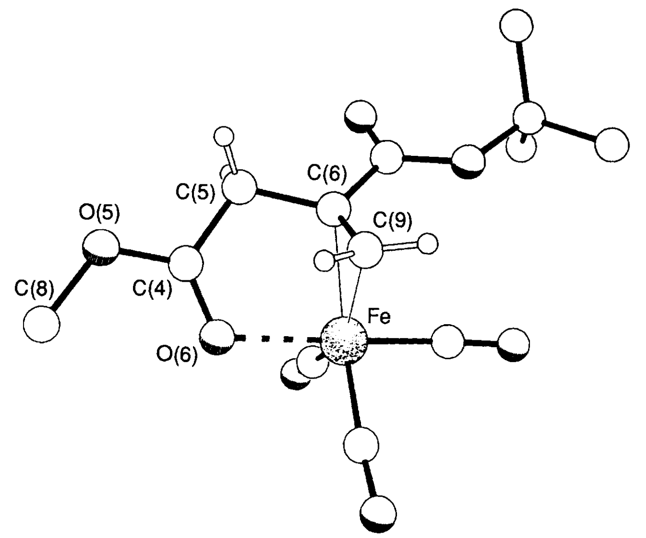


Fig. 1 Molecular structure of one of the pair of crystallographically independent molecules of $[Fe^0(CO)_3\{MeO_2CCH_2C(CO_2Bu^t)CH_2\}]$ **21**. Selected bond lengths (Å), bond angles and dihedral angles (°) (values in [ ] refer to the second independent molecule): Fe–O(6) 2.034(2) [2.038(2)], O(6)–C(4) 1.224(3) [1.231(4)], C(4)–O(5) 1.302(3) [1.305(3)], C(4)–C(5) 1.483(4) [1.474(4)], C(5)–C(6) 1.513(4) [1.521(4)], C(6)–C(9) 1.427(5) [1.419(5)], C(6)–Fe 2.074(3) [2.081(3)], C(9)–Fe 2.039(4) [2.047(4)]; Fe–O(6)–C(4) 114.5(2) [114.9(2)], O(6)–C(4)–O(5) 123.0(3) [122.6(2)], O(6)–C(4)–C(5) 121.6(2) [121.6(2)], C(4)–C(5)–C(6) 108.9(2) [109.9(2)]; Fe–O(6)–C(4)–C(5) 0[0], O(6)–C(4)–O(5)–C(8) 0[0], O(6)–C(4)–C(5)–C(6) 19[16].

Attention then turned to methyl α-acetoxyacrylate **14**, which was predicted to produce a tricarbonyliron(0) complex containing an oxygen bridge between the η^2-bound alkene and the chelating carbonyl group rather than the nitrogen bridges of complexes **6** and **13**. Substrate **14** was synthesised from methyl pyruvate and acetic anhydride[9] and reacted with $[Fe_2(CO)_9]$ in diethyl ether at room temp. for 2 h under a nitrogen atmosphere. Disappointingly, work-up led to the production of an unstable red-brown oil which was subsequently identified as the *tetra*carbonyliron(0) complex **15** on the basis of its spectroscopic data.

The next class of compounds to be examined was selected on the basis that successful tricarbonyliron(0) complex formation would produce complexes containing a methylene carbon bridge between the π-bound alkene and the chelating carbonyl group. Two sub-classes of substrate derived from readily available itaconic acid were investigated. In the first, the non-bridging substituent of the potential chelating carbonyl group was oxygen-centred and in the second, the non-bridging substituent on the potential chelating carbonyl group was nitrogen-centred. Thus diethyl itaconate **16**, di-*tert*-butyl itaconate **17** and the mixed itaconate ester **18** were treated with $[Fe_2(CO)_9]$.‡ Work-up led to the isolation of air-stable red-orange prisms which were identified as the novel tricar-

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† Complexes **13**, **19**–**21** and **25**–**27** gave satisfactory microanalytical, IR, ^1H NMR, ^{13}C NMR and MS data.

‡ The synthesis of complex **20** is representative of all complexation procedures: Di-*tert*-butyl itaconate **17** (0.242 g, 1.0 mmol) and $[Fe_2(CO)_9]$ (0.728 g, 2.0 mmol) were stirred in dry nitrogen-saturated diethyl ether (25 cm³) at 32–35 °C for 16 h under a nitrogen atmosphere. The resulting dark-brown mixture was filtered through a short column of neutral alumina using diethyl ether as solvent to give a bright orange solution. Solvent removal *in vacuo* left an orange-red microcrystalline solid which on purification by column chromatography (SiO_2; dichloromethane) and recrystallisation from hexane afforded complex **20** (0.200 g, 52%) as orange-red prisms.

bonyliron(0) complexes **19**, **20** and **21** respectively on the basis of their analytical and spectroscopic data§ and an X-ray crystal structure analysis of complex **21** (Fig. 1).¶ Similarly, treating [$Fe_2(CO)_9$] with the amide derivatives **22**, **23** and **24** (synthesised by selective hydrolysis of substrate **18** and subsequent 1,1′-carbonyldiimidazole mediated coupling of the resulting monoacid with the appropriate secondary amine) generated the novel tricarbonyliron(0) complexes **25**, **26** and **27** respectively as air-stable red-orange prisms in acceptable yields.

Finally, it is of note that examination of the ^1H NMR spectra of complexes **19–21** and **25–27** reveals that the δ values of the diastereotopic hydrogens attached to the carbon bridge in these compounds differ by between 0.62 and 0.89 ppm. They thus appear to be in quite different environments and methods for using this difference to functionalise derivatives of itaconic acid in a stereoselective manner are currently being examined.

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§ Analytical and spectroscopic data for complex **20**: m.p. 80–100 °C (decomp.); satisfactory C and H analyses were obtained; $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 2046vs, 1964vs (C≡O), 1680 m (free C=O), 1628s (Fe-bound C=O); δ_H (270 MHz; $CDCl_3$) 1.29 (9H, s, Bu^t), 1.44 (9H, s, Bu^t), 1.92 (1H, d, *J* 3.4 Hz, 1H of $C{=}CH_2$), 2.83 (1H, d, *J* 20 Hz, 1H of $CH_2CO_2Bu^t$), 3.30 (1H, d, *J* 3.4 Hz, 1H of $C{=}CH_2$) and 3.70 (1H, d, *J* 20 Hz, 1H of $CH_2CO_2Bu^t$); δ_C {^1H} (125.8 MHz; $CDCl_3$) 27.7, 28.0 [2 × $C(CH_3)_3$], 41.0, 43.0 ($CH_2CO_2Bu^t$ and $C{=}CH_2$), 55.0 ($C{=}CH_2$), 79.9 [$OC(CH_3)_3$ of free ester], 87.1 [$OC(CH_3)_3$ of Fe-bound ester], 174.5 (C=O of free ester) and 185.9 (C=O of Fe-bound ester); *m/z* (EI) 383 (M^+ + H, 2%), 327 (M + H − 2CO, 9), 243 [M + H − $Fe(CO)_3$, 21], 187 [M + H − $Fe(CO)_3$ − isobutene, 56], 131 [M + H − $Fe(CO)_3$ − 2 × isobutene, 39] and 57 (Bu^t, 100).

¶ *Crystal data* for [$Fe^0(CO)_3\{MeO_2CCH_2C(CO_2Bu^t)CH_2\}$] **21**: $C_{13}H_{16}FeO_7$, $M = 340.1$, triclinic, space group $P\bar{1}$, $a = 11.212(3)$, $b = 12.861(3)$, $c = 12.967(3)$ Å, $\alpha = 64.08(2)$, $\beta = 67.74(2)$, $\gamma = 79.14(2)°$, $V = 1556$ Å^3, $Z = 4$ (2 crystallographically independent molecules), $D_c = 1.45$ g cm^{-3}, μ(Mo-Kα) = 9.97 cm^{-1}. Data were measured on a Siemens P4/PC diffractometer with graphite monochromated Mo-Kα radiation using ω-scans. The structure was solved by direct methods and refined anisotropically to give $R = 0.036$, $R_w = 0.039$ for 4287 independent observed reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \leqslant 50°$]. 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.