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Synthesis of 4-substituted-tricarbonyl(η^4-cyclohexa-2,4-dien-1-one)iron complexes

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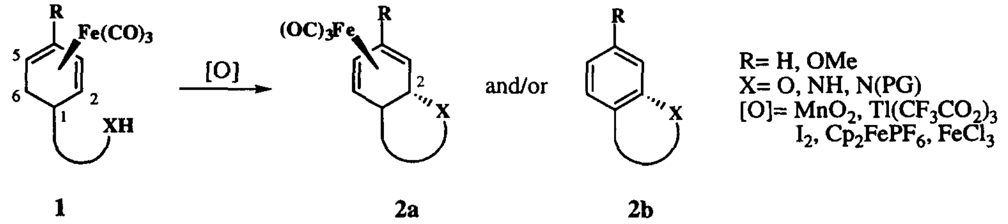
Abstract

The reaction of neutral 1-substituted-tricarbonyl(η^4-4-methoxycyclohexa-1,3-diene)iron complexes **3** with thallium(III) trifluoroacetate in alcoholic solution leads to the corresponding new 4-substituted-tricarbonyl(η^4-cyclohexa-2,4-dien-1-one)iron complexes **4**. A mechanism for this reaction is proposed. © 1999 Elsevier Science Ltd. All rights reserved.

Tricarbonyl(η^4-cyclohexa-1,3-diene)iron complexes have long been recognised as versatile synthetic intermediates for organic synthesis.[1] Their cationic forms react as powerful electrophiles and have found many applications in natural products synthesis.[2] On the other hand, the reactivity of the neutral complexes remains underdeveloped. Only a few useful reactions have been described using the tricarbonyl iron moiety as a protecting group[3] and also as an activator towards nucleophilic addition,[4] Friedel–Crafts acylation,[5] formation of contiguous quaternary centres[6] and especially formation of heterocycles by oxidative cyclisation.[7]

Reagents such as iodine,[8] manganese oxide,[8] iron chloride on silica,[9] ferrocenium hexafluorophosphate[10] or thallium trifluoroacetate[11] were reported as being effective for the demetallation of the complexes and/or for their electrophilic substitution. These reactions always start from 1-alkyl-tricarbonyl(η^4-cyclohexa-2,4-diene)iron **1** (Scheme 1).



Scheme 1.

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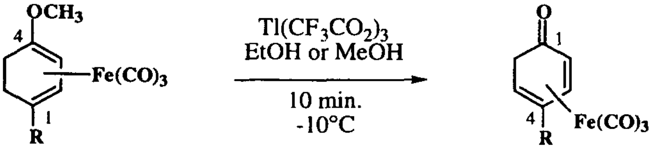
In order to extend our knowledge of their reactivity, we investigated the reaction of 1-substituted-tricarbonyl(η^4-4-methoxycyclohexa-1,3-diene)iron complexes with oxidants.

In this communication, we describe the synthesis of new 4-substituted-tricarbonyl(η^4-cyclohexa-2,4-dien-1-one)iron complexes **4** from 1-substituted-tricarbonyl(η^4-4-methoxy-cyclohexa-1,3-diene)iron complexes **3**[12] using thallium(III) trifluoroacetate in an alcoholic solution (Scheme 2).



3a: R=OCH_3	**4a** (12%)
3b: R=CH_3	**4b** (54%)
3c: R=$(CH_2)_2$-OH	**4c** (52%)
3d: R=$(CH_2)_2$-OCH_3	**4d** (60%)
3e: R=CH_2-CO-OCH_3	**4e** (42%)
3f: R=$(CH_2)_2$-N(PG)$_2$	**4f** (48%)

Scheme 2.

The cyclohexadienone complexes **4** were obtained in moderate yields (12–60%),[13] due to the partial decomposition of the starting complexes **3**, but no aromatic compounds were isolated.

The neutral complexes **4a–f** showed metal carbonyl bands at 2065 and 2002 cm^{-1} and a strong band for the ketone carbonyl (C-1) at 1665 cm^{-1} in their infrared spectra ($CHCl_3$). The ^{13}C chemical shift for the C-1 carbon atom is 197 ppm ($CDCl_3$; 62.9 MHz).

The reaction can be carried out in methanol or ethanol without significant variation of yield. A similar result was obtained by using thallium(III) nitrate.

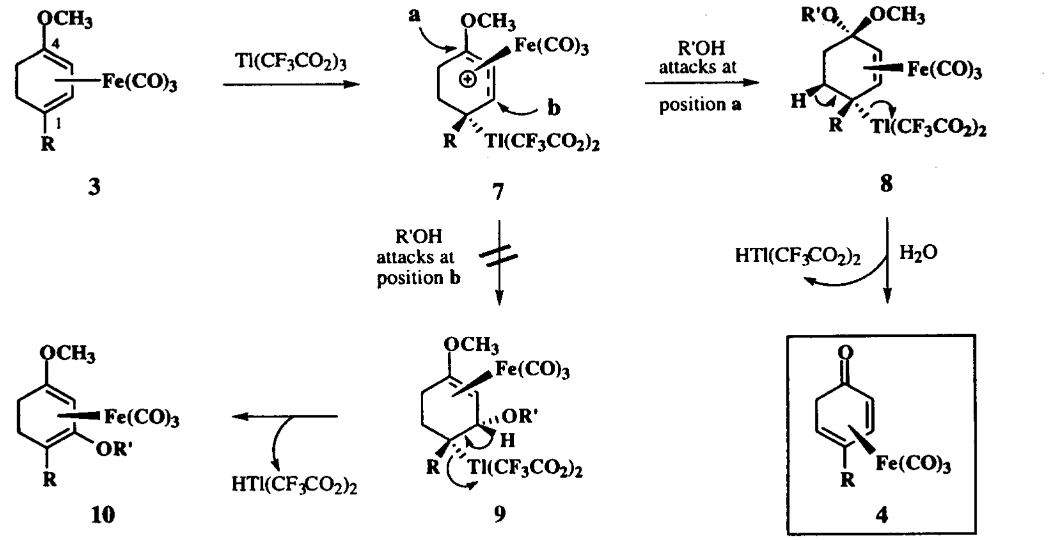
To our knowledge, only two cyclohexadienone complexes **4** substituted at C-4 (R=H and R=OMe) have been previously described. They were synthesised by hydrolysis of the corresponding cationic tricarbonyl(η^5-cyclohexadienyl)iron complexes.[14]

In accordance with the observations of Johnson et al.,[15] the mechanism of this reaction could involve the electrophilic addition of thallium salt to position 1 of complex **3** [*anti* to the $Fe(CO)_3$ moiety] leading to the allyl cation **7**. The polar solvent (MeOH or EtOH) may then attack positions **a** or **b** to afford the unstable complexes **8** or **9**, respectively. *trans*-Elimination of [$HTl(CF_3CO_2)_2$] allows access to complex **4** after hydrolysis of the acetal function or to complex **10** (Scheme 3).

In our experiments, only complexes **4a–f** were obtained. The bulky thallium group is thus likely to inhibit the addition of the solvent to position **b** of the allyl cation **7**. Furthermore, use of complex **3c** (R=CH_2-CH_2-OH) in order to trap the allyl cation **7** by intramolecular attack of the hydroxyl group to position **b**, led to isolation of only cyclohexadienone **4c** when a polar solvent was employed. With other solvents such as diethyl ether or methylene chloride, the reaction led to a complex mixture and no product could be identified.

This mechanism could be extended to the oxidative cyclisation of 1-alkyl-tricarbonyl(η^4-4-methoxycyclohexa-2,4-diene)iron complexes **1**. Indeed, a regioselective addition of the thallium salt to position 5 of complex **1** followed by regioselective addition of the heteroatom to position 2 of the resulting allyl cation and *trans*-elimination of *endo*-H_6 could explain the formation of complexes **2**.[16]

In conclusion, we have demonstrated that thallium(III) salts react with tricarbonyl(η^4-4-methoxycyclohexa-1,3-diene)iron complexes to afford the corresponding new cyclohexadienone complexes **4**. We now wish to examine the synthetic potential of such compounds,[17] particularly with respect to the formation of the corresponding cationic 1-alkoxy and 1-acetoxy substituted tricarbonyl(η^5-cyclohexadienyl)iron complexes.[18]



Scheme 3.

Acknowledgements

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13. A typical procedure is given with complex **3d**: To a solution of 100 mg (325 μmol) of complex **3d** in 5 ml of methanol at −10°C was added 230 mg (422 μmol; 1.3 equiv.) of thallium trifluoroacetate. The reaction mixture was stirred for 10 min, quenched with a solution of $NaHCO_3$ and AcOEt was added. The salts formed were filtered through a short pad of Celite and the filtrate was extracted with AcOEt. The organic layer was washed with water and brine and then dried over $MgSO_4$. Removal of the solvent under reduced pressure left a crude oil which was chromatographed on silica gel to give 57 mg (60%) of **4d** as a yellow oil. ^1H NMR ($CDCl_3$, 250 MHz) δ 5.87 (dd, 1H, $J_{3,2}$=6.1, $J_{3,5}$=2.2 Hz, H_3), 3.70 (t, 2H, J=5.9 Hz, H_8), 3.42 (s, 3H, OCH_3), 3.28 (m, 1H, H_5), 3.09 (d, 1H, $J_{2,3}$=6.1 Hz, H_2), 2.67–2.45 (m, 3H, CH_2 and H_6 *endo*), 2.22 (dd, 1H, J_{gem}=18.7, $J_{6,5}$=1.3 Hz, H_6 *exo*); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 208.9 (CO), 197.3 (C_1), 105.5 (C_4), 86.7 (C_3), 72.5 (CH_2), 60.4 (C_2), 59.0 (OCH_3), 55.5 (C_5), 36.4 (CH_2), 35.3 (C_6); IR ($CHCl_3$): 2064, 2002, 1665 cm^{-1}. Anal. calcd for $C_{12}H_{12}FeO_5$: C, 49.35; H, 4.14. Found: C, 49.35; H, 4.22. MS (C.I., *i*-Bu): 293 $[MH]^+$ (100), 188 (36), 121 (28).

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