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Reductive complexation of cycloheptatrienes by iron pentacarbonyl and catalytic sodium borohydride

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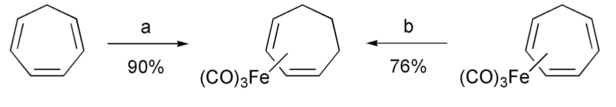
$Fe(CO)_5$ and a catalytic amount of sodium borohydride react with cycloheptatrienes in protic solvents to yield the corresponding tricarbonyl(η^4-1,3-diene)iron complexes in a one-pot procedure, which has been found to be particularly efficient for the synthesis of the useful tricarbonyl(cycloheptadiene)iron complex.

Organoiron compounds are highly versatile substrates with many applications in synthesis.[1] The tricarbonyl(η^4-diene)iron complexes have proven particularly popular due to their ease of preparation, the low cost of the iron carbonyls reagents, their stability to a wide range of reaction conditions, and, most importantly, their synthetically useful transformations. We report herein an exceedingly simple one-pot synthesis of tricarbonyl(1,3-cycloheptadiene)iron complexes from the corresponding conjugated iron-free trienes.

A mixture of cycloheptatriene (**1**), iron pentacarbonyl and sodium borohydride in 1 : 1 toluene–isopropyl alcohol at 100 °C for 38 h has been found to produce the tricarbonyl(cycloheptadiene)iron complex **2** in up to 90% yield[2] (Scheme 1). The results of our study are summarized in Table 1. The optimized transformation requires 3 equiv. of iron pentacarbonyl and 0.125 equiv. of sodium borohydride relative to cycloheptatriene† (Table 1, entry 2). The use of *n*-propyl or *tert*-butyl alcohol instead of isopropyl alcohol (Table 1, entries 6 and 7), proved less effective since small amounts of the tricarbonyl(cycloheptatriene)iron complex (**3**) were also isolated. When the reaction was performed with only 1 equiv. of $Fe(CO)_5$, the yield was halved (Table 1, entries 9 and 10). The reaction of the triene complex **3** with 1.2 equiv. of $Fe(CO)_5$ and 0.25 equiv. of $NaBH_4$ produced the diene complex **2** in good yield (Scheme 1, Table 1, entry 11), but no reaction occurred when **3** was exposed to only $NaBH_4$ (Table 1, entry 12). The optimized conditions for **1** were also applied to 7-methylcyclohepta-1,3,5-triene and 7-phenylcyclohepta-1,3,5-triene, which resulted in the formation of the corresponding tricarbonyl(2-substituted cyclohepta-1,3-diene)iron complexes,‡ but in reduced yields (53% (GC) and 18%, respectively).[3] The reaction with cyclohepta-2,4,6-trienone (tropone)[4a] and the acyclic 1,6-diphenylhexa-1,3,5-triene[4b] under the optimized conditions for **1** gave only small amounts of the diene complexes.



1 **2** **3**

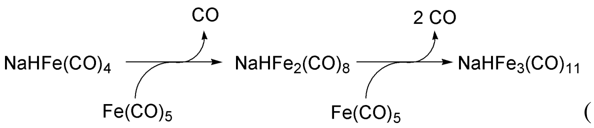
Scheme 1 a, $Fe(CO)_5$ (3 equiv.), $NaBH_4$ (0,125 equiv.), toluene–Pr^iOH, 100 °C, 38 h; b, $Fe(CO)_5$ (1,2 equiv.), $NaBH_4$ (0,25 equiv.), toluene–Pr^iOH, 100 °C, 38 h.

Table 1 Formation of complex **2** from cycloheptatriene (**1**) or from complex **3**

Entry	Substrate	Product	$Fe(CO)_5$ (equiv.)	$NaBH_4$ (equiv.)	Yield (%)
1	**1**	**2**	3	0.05	83[a]
2	**1**	**2**	3	0.125	90
3	**1**	**2**	3	0.25	90
4	**1**	**2**	3	0.50	71
5	**1**	**2**	3	1	61
6[b]	**1**	**2**	3	0.125	76[c]
7[d]	**1**	**2**	3	0.125	79[e]
8[f]	**1**	**2**	2.25	0.25	90
9	**1**	**2**	1	0.25	46
10[g]	**1**	**2**	1	1	49
11	**3**	**2**	1.2	0.25	76
12	**3**	—	—	1	NR

[a] 2% of **3** was isolated. [b] Pr^nOH was used instead of Pr^iOH. [c] 16% of **3** was isolated. [d] Bu^tOH was used instead of Pr^iOH. [e] 3% of **3** was isolated. [f] 0.25 equiv. of $Fe_3(CO)_{12}$ was added prior to introduction of **1** and $Fe(CO)_5$. [g] The mixture was refluxed 2 h before the introduction of **1** to ensure complete consumption of $Fe(CO)_5$.

The reaction of an equimolar amount of $NaBH_4$ with $Fe(CO)_5$ in *n*-butyl alcohol is known to yield the unstable formyl complex $NaFe(CO)_4CHO$ and BH_3, which reacts with the *n*-butyl alcohol to produce $B(OBu^n)_3$ and H_2.[5] Upon warming to reflux, the formyl complex rearranges to the hydride $NaHFe(CO)_4$ with loss of carbon monoxide. In the present case, the deep red color of the reacting mixture suggested the presence of $NaHFe_3(CO)_{11}$, which was confirmed by NMR analysis of the mixture (δ −15.3 ppm ($CDCl_3$); lit.:[5] −14.8 ppm); no $NaHFe(CO)_4$ could be detected (lit.:[5] −9.9 ppm). Furthermore, when $NaHFe_3(CO)_{11}$ was generated independently from $Fe_3(CO)_{12}$ and a stoichiometric amount of $NaBH_4$[6] and then allowed to react with $Fe(CO)_5$ and **1** under the same conditions as in entry 3 (but without $NaBH_4$), the complex **2** was formed in the same yield (Table 1, entry 8), which provides further evidence for the central role of $NaHFe_3(CO)_{11}$ in this reaction. Its formation has been shown to result from the slow decomposition of $NaHFe(CO)_4$ in alcoholic solutions.[5] However, in the present case, its relatively rapid formation might results from initial attack of $NaHFe(CO)_4$ on $Fe(CO)_5$ and subsequent reaction of this new dinuclear species with another equivalent of $Fe(CO)_5$ (eqn. (1)); it has previously been demonstrated that the cluster $Na_2Fe_3(CO)_{11}$ is formed from $Na_2Fe(CO)_4$ and 2 equiv. of $Fe(CO)_5$.[7]



$$NaHFe(CO)_4 \xrightarrow[Fe(CO)_5]{CO} NaHFe_2(CO)_8 \xrightarrow[Fe(CO)_5]{2\,CO} NaHFe_3(CO)_{11} \qquad (1)$$

When the reaction was performed with only 0.05 equiv. of $NaBH_4$, the complex **2** was formed in 83% yield (Table 1, entry 1), clearly demonstrating that the borohydride is not the source of the two new hydrogen atoms in the resulting reduced complex. When **1** was allowed to react with an of excess $Fe(CO)_5$ and independently prepared $NaHFe_3(CO)_{11}$ in refluxing dry toluene under 1 atm of H_2 for 38 h, the triene complex **3** was formed in moderate yield together with only a trace amount of the reduced complex **2**, which indicates that $NaHFe_3(CO)_{11}$ is not a catalyst for the hydrogenation of double bonds under the reaction conditions (under 1 atm of H_2).[8] The source of hydrogen is thus the protic solvant. The trinuclear cluster hydride $NaHFe_3(CO)_{11}$ acts as a homogeneous catalyst

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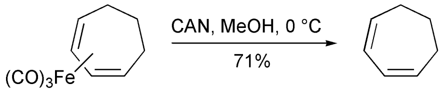
for the transfer of hydrogen from isopropyl alcohol to the activated olefin.[9]

It is tempting to postulate that first the triene is transformed with $Fe(CO)_5$ into the triene complex, which is then reduced (Table 1, entry 11) or, less probably, that reduction[8,9] precedes complexation; however, the efficiency of this one-pot conversion suggests that at least one other pathway may be involved. The nature of the various intermediates involved in this tranformation, as well as the catalytic cycle, remains to be clarified.

The complex **2**, and its traditional synthetic precursor, cycloheptadiene, are two useful building blocks in natural product synthesis.[10] The high price of cycloheptadiene, however, has undoubtedly limited to a large degree their application. In contrast, cycloheptatriene is widely available and cheap.[11] Ceric ammonium nitrate (CAN) has been found to produce 1,3-cycloheptadiene (**4**) cleanly from complex **2** in 71% yield§ (Scheme 2), *thus an efficient, economical two-step protocol for the preparation of 1,3-cycloheptadiene from cycloheptatriene is now available.*



Scheme 2

In summary, we have found that $NaHFe_3(CO)_{11}$, easily generated in isopropyl alcohol from $Fe(CO)_5$ and $NaBH_4$ or from $Fe_3(CO)_{12}$ and $NaBH_4$, is an efficient catalyst for the direct synthesis of the tricarbonyl(cycloheptadiene)iron complex (**2**) from cycloheptatriene. The low cost of the reagents and the efficiency and the simplicity of the reaction make it a highly attractive alternative to the previously reported synthesis of complex **2**,[1] which, *inter alia*, is a very convenient precursor of cycloheptadiene.

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Notes and references

† To a solution of iron pentacarbonyl (3.0 mL, 22.8 mmol) and cycloheptatriene (97%) (0.77 mL, 7.20 mmol) in toluene–isopropyl alcohol (1:1, 10 mL) was added $NaBH_4$ (34 mg, 0.9 mmol) in one portion. The initially orange solution, which turned deep red in a few min at room temperature with production of H_2 and CO, was then refluxed at 100 °C for 38 h (the condenser was equipped with a balloon so as to maintain slightly positive CO pressure). The cooled reaction mixture was placed on a silica gel column, and the product was eluted with pentane to yield 1.51 g (90%) of the pure yellow complex **2**: ^{1}H NMR (200 MHz), δ 5.20–5.33 (m, 2 H), 2.96–3.11 (m, 2 H), 1.75–2.11 (m, 4 H), 1.09–1.53 (m, 2 H); ^{13}C NMR (50 MHz), δ 24.3, 28.4, 59.9, 88.3, 212.3 (broad). A reaction run with 10 times the above quantities provided, after pentane/aqueous sodium hydroxide extraction and filtration over silica gel, complex **2** in 96% yield.

‡ Tricarbonyl(2-phenylcyclohepta-1,3-diene)iron complex: yellow solid, mp 41 °C; IR 2040, 1968 cm^{-1}; ^{1}H NMR (300 MHz), δ 7.50–7.60 (m, 2 H), 7.27–7.40 (m, 3 H), 5.68 (d, J 7.7 Hz, 1 H), 3.46 (pseudo d, J 6.5 Hz, 1 H), 3.05 (pseudo t, J 7.1 Hz, 1 H), 2.16–2.28 (m, 1 H), 1.82–2.15 (m, 3 H), 1.42–1.57 (m, 1 H), 1.18–1.37 (m, 1 H); ^{13}C NMR (75 MHz), δ 24.0, 28.1, 28.6, 55.3, 57.5, 88.9, 105.7, 127.5, 128.4, 128.4, 140.8, 211.2 (broad); MS (DCI) m/z 311 (MH$^+$, 100%). Anal. calc. for $C_{16}H_{14}O_3Fe$: C, 61.97; H, 4.55. Found: C, 62.42; H, 4.72%.

§ To a solution of complex **2** (11.49 g, 49.1 mmol) in methanol (250 mL) at 0 °C was added CAN (54.2 g, 98.9 mmol) in small portions (CAN was added until the starting material was no longer detectable by TLC). Water (100 mL) and pentane (100 mL) were then added and the aqueous layer was extracted three times with pentane. The combined organic layers were washed five times with water, dried over Na_2SO_4 and concentrated at 0 °C under 110 mmHg to give the crude product (85%, essentially pure). Vacuum distillation of this material at 75 °C yielded 3.27 g (71%) of pure 1,3-cycloheptadiene (**4**).

1 A. J. Pearson, *Iron Componds in Organic Synthesis*, Academic Press, London, 1994.

2 The formation of **2** as a minor side product was noticed during the synthesis of **3** from boiling cycloheptatriene and $Fe(CO)_5$. See: H. J. Dauben and D. J. Bertelli, *J. Am. Chem. Soc.*, 1961, **83**, 497.

3 Catalytic hydrogenation of tricarbonyl(methylcycloheptatriene)iron complexes affords the same major isomer. See: Y. Coquerel, J.-P. Deprés, A. E. Greene, P. Cividino and J. Court, *Synth. Commun.*, 2001, **31**, 1291.

4 (*a*) The reaction resulted mainly in decomposition products; (*b*) the unreduced tricarbonyl(η^4-1,6-diphenylhexa-1,3,5-triene)iron complex was the major product (65% yield).

5 R. L. Keiter, E. A. Keiter, K. H. Hecker and C. A. Boecker, *Organometallics*, 1988, **7**, 2466.

6 D. T. Haworth and J. R. Huff, *J. Inorg. Nucl. Chem.*, 1961, **17**, 184; ; we established the formation of $NaHFe_3(CO)_{11}$ by NMR.

7 Y. Zhen and J. D. Atwood, *Organometallics*, 1991, **10**, 2778.

8 $KHFe(CO)_4$ has been reported to reduce isoprene to a mixture of three monoolefins. It has also been shown that $KHFe(CO)_4$ is not a catalyst for hydrogenation of isoprene at 100 °C under 60 atm of H_2. See: Y. Takegami, Y. Watanabe, I. Kanaya, T. Mitsudo, T. Okajima, Y. Morishita and H. Masada, *Bull. Chem. Soc. Jpn.*, 1968, **41**, 2990.

9 In separate experiments, $NaHFe_3(CO)_{11}$ efficiently reduced the conjugated double bonds in carvone and *trans*-methylcinnamate (with $NaHFe(CO)_4$, see: R. Noyori, I. Umeda and T. Ishigami, *J. Org. Chem.*, 1972, **37**, 1542) but left cyclododecene largely unchanged after 2 days at 100 °C.

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11 Aldrich catalog 2000–2001, cycloheptadiene: €239.08 for 5 g and cycloheptatriene €77.71 for 1 L.