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# A rapid and convenient method for the formation of (diene)Fe$(CO)_3$ complexes

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**Abstract**

The formation of (diene)Fe$(CO)_3$ complexes has been achieved in the absence of solvent by the action of mild heat on a mixture of the diene and a preformed mixture of $Fe_2(CO)_9$ and silica gel. The yield of complex obtained compares well with literature examples especially for polar substrates. The first complexation of Danishefsky's diene, 1-methoxy-3-trimethylsilyloxybuta-1,3-diene, to Fe$(CO)_3$ has been achieved using this method. The speed of the reaction (typically complete after 2 h at 85°C) and the ease of work-up make this solid-state procedure the method of choice for the preparation of complexes of many polar dienes and heterodienes. © 1998 Elsevier Science S.A. All rights reserved.

*Keywords:* Iron; Diene; Solid state synthesis

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## 1. Introduction

For 25 years after its preparation by Reihlen et al. in 1930 [1], butadienetricarbonyliron remained in the chemical literature as a curiosity. Its reinvestigation only became attractive after the discovery of the metallocenes and the work of Dewar [2] and of Chatt and Duncanson [3] which provided the theoretical basis for formulating such substances as $\pi$-complexes. Repetition of Reihlen's synthesis from pentacarbonyliron and butadiene and extension of this method to the synthesis of tricarbonylcyclohexadieneiron [4] opened the door leading to a vast number of diene-iron compounds and further to the whole field of alkene-transition metal complexes.

Among such compounds the diene-iron complexes have a special place as useful intermediates in organic synthesis. Their stability allows them to smoothly undergo Friedel–Crafts type substitution as well as reversible hydride abstraction to give cationic dienyl complexes. The attached tricarbonyliron group controls reactions at the diene ligand and can provide a high degree of regio- as well as stereo- and even enantioselectivity–yet is easily removed by photolysis or oxidation when the desired organic moiety has been built up. Typical examples of such transformations have been reviewed in textbooks and journal articles e.g. [5–7].

The original method for the preparation of the diene-iron complexes requires elevated temperatures (typically 100–150°C) and fairly long reaction times–conditions under which pentacarbonyliron also catalyses double bond migration; sensitive substrates may be destroyed and pressure vessels must be used for the more volatile dienes. Hence there is continuing interest in the replacement of pentacarbonyliron by more reactive starting materials which allow diene complexes to be formed at, or below, room temperature. Nonacarbonyldiiron, in spite of its insolubility, meets this requirement in most cases, e.g. [8]. Its main drawback is the utilisation of only one of the iron atoms:

$$Fe_2(CO)_9 + \text{diene} \rightarrow (\text{diene})Fe(CO)_3 + Fe(CO)_5 + CO$$

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Even better results are achieved [9] by using the diene to displace one of the less firmly held heterodienes, e.g. PhCH=CHCH=NPh or PhCH=CHCOMe:

$$(\mathrm{PhCH{=}CHCOMe})\mathrm{Fe(CO)_3} + \mathrm{diene}$$
$$\rightarrow (\mathrm{diene})\mathrm{Fe(CO)_3} + \mathrm{PhCH{=}CHCOMe}$$

Alternative methods rely on activation of pentacarbonyliron by either ultrasound [10] or amine-*N*-oxides [11] to remove one CO group. The same procedures have also been found to be effective in reactions of (carbene)$Cr(CO)_5$ [12] and of (alkyne)$Co_2(CO)_6$ [13]. Smit and co-workers [14] introduced a dry-state adsorption technique for reaction of alkenes with the alkyne–cobalt complexes and demonstrated that the reactions were greatly accelerated and proceeded cleanly and in high yield. This approach was also found useful in displacement of CO from carbenepentacarbonylchromium [12] and we now describe its use as a rapid and convenient method for reactions of nonacarbonyldiiron with dienes.

Various adsorbents including alumina and magnesium carbonate have been used, but silica has proved most consistently successful. The earliest examples involved intramolecular Khand reactions of (enyne)hexacarbonyldicobalt; solutions of these complexes were added to the adsorbent and the solvent was then removed on a rotary evaporator. Gentle heating then sufficed for complete reaction and the product could be purified by adding the reaction mixture to the top of a prepacked chromatography column of the same adsorbent. Extensions to intermolecular reactions were possible [14] by adding the pure alkenes (if liquid) to the adsorbed alkyne metal complex.

## 2. Discussion

To find whether a related dry-state method could be devised for the synthesis of diene–iron complexes we chose the binuclear carbonyl as the most appropriate precursor. Its insolubility prevents its deposition from solution, but by careful and thorough grinding together of a mixture of this carbonyl with the adsorbent in a mortar we seem to have achieved sufficiently close contact to enhance the reactivity of the carbonyl. Addition of dienes as pure liquids or, in the case of solids, as solutions in easily removable volatile solvents then yielded diene–iron complexes on heating. Useful yields were however only obtained from highly polar dienes; the results are summarised in Table 1 [15–17]. In most cases the reactions were much faster than by other techniques, being complete after 2 h at 85°C. They were very clean and the chromatographic method described above provided pure products easily and quickly.

Among the more polar dienes used, several of the yields are at least comparable to those reported using other techniques. In the best case, the complex of (*E*,*E*)-hexa-2,4-dien-1-ol, the yield (77%) is significantly greater than any reported values. Notably, the method also succeeds well for heterodiene complexes.

Hexa-2,4-dienal was selected as a convenient example to compare the efficacy of silica with other adsorbents and also to study different iron carbonyl to silica ratios. When ground without 'inert' adsorbent, $Fe_2(CO)_9$ reacted at 85°C in 2 h to give the complex in a 49% yield. In contrast to $SiO_2$ (73%), all other adsorbents tried lowered this value ($Al_2O_3$, 28%; Florisil, 37%; $K_2CO_3$, 37%; $MgSO_4$, 45%). The yield quoted for silica was achieved with an apparently optimal 5:1 ratio of $SiO_2$:$Fe_2(CO)_9$. Both an increase to 12.5:1 or a decrease to 2.5:1 lowered the yield (to 66 and 59%, respectively).

In summary, we believe that for many polar dienes and heterodienes, the use of the essentially low toxicity, non-volatile, $Fe_2(CO)_9$–$SiO_2$ mixtures, their speed of reaction at modest temperatures and the ease of work-up will make this solid-state procedure the method of choice and especially when suitable ultrasound and photochemical equipment (needed for other methods) is not readily available.

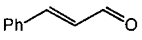
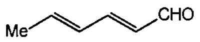
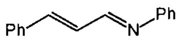
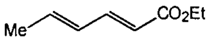
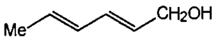
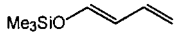
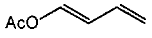
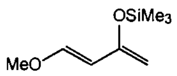
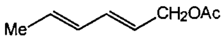
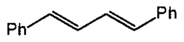
## 3. Experimental

### 3.1. General procedure for diene complexation

The diene (0.5 g) is added to a carefully ground mixture of nonacarbonyldiiron (1.1 equivalents) and silica (230–400 mesh; 5 g per g of $Fe_2(CO)_9$). The flask is shaken to obtain an even dispersion and then heated under nitrogen under the conditions specified in the table. After cooling, the mixture is added to the top of a prepacked column of dry silica gel; the products are separated by gradient elution using hexane/ether. If the silica is dried overnight at 140°C the yield of diene complex is diminished, but this was necessary to permit isolation of the unstable complex of 1-methoxy-3-trimethylsilyloxybuta-1,3-diene.

The following new spectroscopic data have been obtained: (*E*,*E*)tricarbonyl(hexa-2,4-dienal)iron $\delta_C(C_6D_6)$ 19.1, 55.5, 60.6, 81.7, 89.7, 195.3, 210.5; tricarbonyl (1-trimethylsilyloxybuta-1,3-diene)iron $\nu_{max}$(hexane) 1992, 2059 $cm^{-1}$; $\delta_H(C_6D_6)$ 0.01(9H, s), 0.85(2H, m), 1.58(1H, broad s), 5.4–6.0(2H, m); tricarbonyl(1-acetoxybuta-1,3-diene)iron $\nu_{max}$(hexane) 1999, 2060 $cm^{-1}$; $\delta_H(C_6D_6)$ 1.49(1H, broad s), 1.80(3H, s), 1.95–2.06(1H, m), 4.17(1H, d), 5.03–5.20(2H, m); tricarbonyl(1-methoxy-3-trimethylsilyloxybuta-1,3-diene)iron $\nu_{max}(C_6D_6)$ 1985, 2069 $cm^{-1}$; $\delta_H(C_6D_6)$ 0.01(9H,s), 1.25(1H, d), 1.56(1H, d), 2.86(1H, m), 3.56(3H, broad s), 4.74(1H, broad s); tricarbonyl(hexa-2,4-dien-1-yl ac-

Table 1
Reactions of dienes with $Fe_2(CO)_9/SiO_2$

| Diene | Temperature /°C | Time | Yield/% | Lit. Yield/%, method | Reference |
|---|---|---|---|---|---|
|  | 85 | 2 h | 49 | 26, $Fe_2(CO)_9$/35°C | [8] |
|  | 140 | 10 m | 61 | | |
| | 85 | 2 h | 73 | 96, (bda)$Fe(CO)_3$/72 h | [9a] |
| | 30 | 20 h | 48 | 45, $Fe(CO)_5$ | [9b] |
| | 15 | 18 d | 17 | 58, $Fe(CO)_5$, $Me_3NO$ | [11b] |
|  | 85 | 2 h | 74 | 81, $Fe_2(CO)_9$/)))<br>28, $Fe_2(CO)_9$/40°C | [10a]<br>[15] |
|  | 85 | 2 h | 50[a] | 43, $Fe(CO)_5$ | [16] |
|  | 85 | 90 m | 77 | 51, $Fe_2(CO)_9$/))) | [10b] |
|  | 85 | 2 h | 40 | no yield reported | |
|  | 85 | 2 h | 30 | 100, $Fe_2(CO)_9$/))) | [10b] |
|  | 85 | 2 h | 17 | new complex | |
|  | 85 | 2 h | 12 | no yield reported | |
|  | 120 | 24 h | 43 | 51, over 2 cycles | [17] |
| Cyclohepta-1,3,5-triene | 30 | 96 h | 5 | 50, (bda)$Fe(CO)_3$ | [9b] |

etate)iron $\nu_{max}$(hexane) 1750, 1984, 2049 $cm^{-1}$; $\delta_H(C_6D_6)$ 1.15–1.24(2H, m), 1.57(3H, d), 1.74(3H, s), 4.54(2H, d), 5.4–5.6(2H, m).

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