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SYNTHESIS AND REACTIONS OF TETRACARBONYL- AND TRICARBONYLIRON COMPLEXES OF α,β-UNSATURATED KETONES

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SUMMARY

A series of iron tricarbonyl derivatives of α,β-unsaturated ketones have been prepared. These are of special interest to organometallic chemists concerned with the production of iron tricarbonyl derivatives since they offer not only a convenient source of the $Fe(CO)_3$ moiety but also several advantages over the more conventional methods employing the iron carbonyls.

INTRODUCTION

We wish to report the syntheses and reactions of several tetracarbonyl- and tricarbonyliron complexes of α,β-unsaturated ketones. The tricarbonyl iron complexes have been found to be very useful in the synthesis of tricarbonyl(diene)iron derivatives, serving as a convenient source of the $-Fe(CO)_3$ moiety and offering advantages over the more conventional routes employing the iron carbonyls.

These conjugated heterodiene metal complexes are formally derived from butadiene–metal π-complexes by replacing one of the sp^2 carbon atoms by an sp^2 heteroatom. Besides α,β-unsaturated ketones, tricarbonyliron complexes are known of several other heterodiene systems, namely O=C–C=N–[1], –N=C–C=N–[2], and –N=N–N=N–[3].

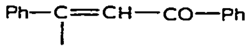
Among the tetracarbonyl(π-olefin)iron complexes prepared by Weiss *et al.*[4] was tetracarbonyl(cinnamaldehyde)iron, which was found to convert, on heating at 60° for 15 h, to tricarbonyl(cinnamaldehyde)iron[5], formulated on the basis of infrared and NMR evidence as the π-bonded isomer.

RESULTS AND DISCUSSION

We have studied the reactions of $Fe_2(CO)_9$ with:

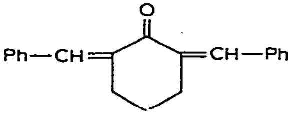
Benzylideneacetone (BDA)	$Ph—CH{=}CH—CO—CH_3$
Chalcone	$Ph—CH{=}CH—CO—Ph$

Dypnone



$$\mathrm{Ph{-}\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CH{-}CO{-}Ph}$$

2,6-dibenzylidenecyclohexanone



Chalcone readily forms a tetracarbonyl complex, which can be converted into tricarbonyl(chalcone)iron by heating in toluene at 60° for 9 h. Benzylideneacetone also forms a tetracarbonyl complex. This is less stable than the corresponding chalcone derivative and readily converts under ambient conditions to the tricarbonyl derivative. With dypnone and 2,6-dibenzylidenecyclohexanone, the tetracarbonyl complexes were not observed during the production of the tricarbonyl derivatives.

The complexes have been fully characterised by the usual analytical and spectroscopic techniques (Tables 1 and 2). In the ^{1}H NMR spectra the upfield shifts observed for the "inner" and "outer" protons of the diene unit (τ 0.5 and ~4 respec-

TABLE 1

Complex	*IR* $\nu(CO)$ (cm^{-1})	*^1H NMR (τ)*			
		H_i^a	H_o^a	*J (Hz)*	*Other protons*[b]
(Chalcone)Fe(CO)$_4$	2095, 2060, 2030, 1995 (ketone; 1630)				4.69 (Olefin proton, AB) 5.15 (Olefin proton, J 11 Hz) 2.0–2.9 (Ph, m)
(Benzylideneacetone)-Fe(CO)$_3$	2065, 2005, 1985	3.98	6.90	9.0	7.50 (CH$_3$, s) 2.73 (Ph, m)
(Chalcone)Fe(CO)$_3$	2060, 2000, 1980	3.22	6.54	9.5	2.0–2.8 (Ph, m)
(Dypnone)Fe(CO)$_3$	2040, 1980, 1950	3.92			8.0 (CH$_3$, s) 2.0–2.8 (Ph, m)
(2,6-Dibenzylidene-cyclohexanone)Fe(CO)$_3$	2065, 2010, 1985		6.90		2.92 (Ph, m) 7.3, 8.15 (CH$_2$, m)

[a] H_i is the proton α to the carbonyl group; H_o is the other olefinic proton. [b] s Singlet; q quartet; m multiplet.

TABLE 2

ANALYTICAL DATA

Compound	*Analysis found (calcd.) (%)*		*Mol. wt. found*[a] *(calcd.)*
	C	*H*	
(Benzylideneacetone)Fe(CO)$_3$	54.7 (54.6)	3.8 (3.5)	286 (286)
(Chalcone)Fe(CO)$_3$	62.6 (62.1)	3.9 (3.5)	348 (348)
(2,6-Dibenzylidenecyclohexanone)Fe(CO)$_3$	65.8 (65.9)	4.7 (4.4)	
(Chalcone)Fe(CO)$_4$	61.1 (60.8)	3.4 (3.2)	

[a] Mass spectrometric method.

tively) are similar to those observed in tricarbonyldieneiron complexes (τ 0.5 and 2–3)[6].

In common with tricarbonyl(cinnamaldehyde)iron[5], these complexes exhibit no ketonic absorption in the range 1900–1600 cm^{-1}. There are absorptions in the range 1485–1460 cm^{-1}, which are not present in the free ligand. Tricarbonyl(diene)-iron complexes exhibit similar vibrations, which have been assigned to the stretching mode of the coordinated double bond[7,8].

The mass spectra characteristically show the parent ion (p^+), and the daughter ions $(p\text{–}CO)^+$, $(p\text{–}2\ CO)^+$ and $(p\text{–}3\ CO)^+$; no other metal-containing ions are observed.

Reactions

These reactions were carried out using tricarbonyl(benzylideneacetone)iron [$(BDA)Fe(CO)_3$], the most readily available of the complexes.

Triphenylphosphine readily displaces the organic ligand at 30° over two hours in benzene to give $(PPh_3)_2Fe(CO)_3$. Tricarbonyl(butadiene)iron reacts slowly under more vigorous conditions to form $(PPh_3)_2Fe(CO)_3$[9]. The reaction of tricarbonyl-(cinnamaldehydeanil)iron results in displacement of CO to form the $L\cdot Fe(CO)_2(PPh_3)$ derivative[1].

$(BDA)Fe(CO)_3$ is also useful as a source of the iron tricarbonyl moiety in the preparation of dieneiron tricarbonyl complexes. Previous syntheses have relied mainly on the reaction of $Fe(CO)_5$, $Fe_3(CO)_{12}$, or $Fe_2(CO)_9$ with the free diene, using elevated temperatures and/or UV irradiation. We have found $(BDA)Fe(CO)_3$ to be useful for dienes sensitive to heat and irradiation, or where the iron carbonyls are unsatisfactory.

For example, in the preparation of tricarbonyl(8,8-diphenylheptafulvene)iron from the free ligand[10] the iron carbonyls, $Fe(CO)_5$ and $Fe_3(CO)_{12}$ could not be used because of the sensitivity of the diene to both heat and ultra-violet irradiation, while reaction with $Fe_2(CO)_9$ under mild conditions gave an unstable diiron hexacarbonyl derivative. In contrast, reaction of the same heptafulvene with a slight excess of $(BDA)Fe(CO)_3$ in toluene at 50° for 6 h, followed by chromatography, gave a 70% yield of tricarbonyl(8,8-diphenylheptafulvene)iron (see Table 3), identical to that prepared by an alternative route[11]. Heptafulvene complexes are also the products of the reaction of $(BDA)Fe(CO)_3$ with 7-(hydroxymethyl)cycloheptatriene[12] and dimethyl-7-cycloheptatrienylmethanol[13].

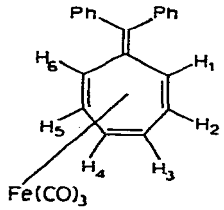
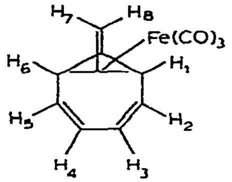
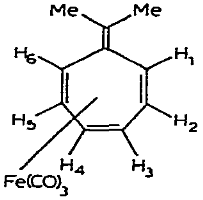
Reaction of equimolar amounts of $(BDA)Fe(CO)_3$ and 7-(hydroxymethyl)-cycloheptatriene in refluxing benzene for 8 h, followed by chromatography, gave a 27% yield of the trimethylenemethane bonded isomer of tricarbonyl(heptafulvene)-iron (see Table 3), identical with a sample prepared from the alcohol and $Fe_2(CO)_9$[14].

Reaction of $(BDA)Fe(CO)_3$ with dimethyl-7-cycloheptatrienylmethanol under the same conditions gives tricarbonyl(8,8-dimethylheptafulvene)iron (see Table 3), bonded in this case via the more usual diene linkage, and identical to that reported previously[11].

This reagent possesses several advantages over the other iron carbonyl reagents. The reactions can be carried out under mild conditions and are clear, in that no colloidal iron or other iron carbonyls [$Fe_3(CO)_{12}$ or $Fe(CO)_5$] are formed as by-products. The work up is thus much easier, and the reactions can be followed easily by infrared spectroscopy. For example, in the reaction between $(BDA)Fe(CO)_3$ and

TABLE 3

IR AND NMR DATA OF (8,8-DISUBSTITUTED HEPTAFULVENE)IRON TRICARBONYLS

Compound	*IR* *ν(CO) (cm^{-1})*	*NMR*[b] (τ)
	1978 (broad)[a] 2025 (sharp)	2.9 (Ph, m, 10H) 4.3–4.9 (H_{3-6}, m, 4H) 6.1 (H_1, d, 1H; $J_{1,2}$ 7.9 Hz) 7.1 (H_2, m, 1H)
	1973[c] 1982 2050	3.9–4.4 (H_{2-5}, m, 4H) 8.64 ($H_{7,8}$, s, 2H) 6.38 ($H_{1,6}$, d, 2H; $J_{1,2}$ 6.8 Hz)
	1975[c] 1985 2055	4.25–4.90 (H_{3-6}, m, 4H) 6.05 (H_1, d, 1H; $J_{1,2}$ 7.6 Hz) 7.05 (H_2, m, 1H) 8.25 (Me, d, 6H)

[a] Thin film. [b] s singlet; d doublet; t triplet; m multiplet. [c] Cyclohexane solution.

7-(hydroxymethyl)cycloheptatriene, the extent of reaction can be followed by the disappearance of the 2065 cm^{-1} absorption of (BDA)Fe(CO)$_3$ and the appearance of the absorption at 2050 cm^{-1} due to tricarbonyl(heptafulvene)iron. It is interesting to note that in the reactions of both alcohols with (BDA)Fe(CO)$_3$, there is no evidence in the infrared for the intermediate formation of the tricarbonyl(alcohol)iron complexes. Another advantage is the well defined stoichiometry of the reaction, with one mole of (BDA)Fe(CO)$_3$ yielding one mole of the Fe(CO)$_3$ moiety. This is in contrast to the uncertain stoichiometry of the reactions of the other iron carbonyls, which are commonly used in large excess. Thus, problems arising from dimer formation when using highly unsaturated ligands are minimized.

These advantages make tricarbonyl(benzylideneacetone)iron the reagent of choice in many syntheses of tricarbonyldieneiron complexes, and further work is in progress.

EXPERIMENTAL

1. *Tetracarbonyl(chalcone)iron*

Chalcone (1.19 g) and $Fe_2(CO)_9$ (2.20 g) were heated in toluene (20 ml) at 40°

for 1 h. The solution was filtered and the solvent removed under vacuum. Chromatography on silica gel, eluting with toluene, gave the product as yellow crystals (0.55 g, 26%) m.p. 88–90°.

Tetracarbonyl(chalcone)iron is converted to the tricarbonyl derivative by heating in toluene at 60° for 9 h.

2. *Tricarbonyl(benzylideneacetone)iron*

Benzylideneacetone (10.4 g) and $Fe_2(CO)_9$ (26 g) were heated in toluene (100 ml) for $4\frac{1}{2}$ h at 50–60°. The deep red reaction mixture was filtered, and the solvent removed under vacuum. Chromatography on silica gel, eluting with 10% ethyl acetate/toluene, gave the product as orange-red crystals (6.07 g, 32%), m.p. 88–89°

The tricarbonyliron complexes of chalcone, dypnone, and 2,6-dibenzylidenecyclohexanone[15] can be prepared similarly.

A higher temperature (70–80°) and a longer reaction time (8 h) are necessary for the chalcone complex. All compounds gave satisfactory elemental analyses (Table 2).

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