

SYNTHESES AND NOVEL REACTIONS OF SOME DIENETRICARBONYLIRON COMPLEXES

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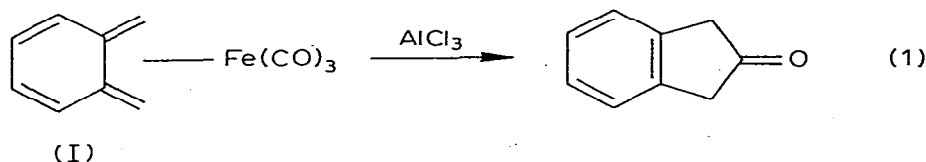
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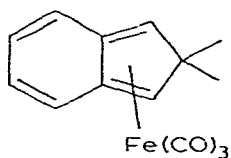
Summary

Five dienetrickarbonyliron complexes were synthesized. Their Mössbauer spectra are discussed. Reaction of 3,3'-biindenyltrickarbonyliron with aluminium trichloride gives anthracene, but 3,3',4,4'-tetrahydro-1,1'-binaphthyltrickarbonyliron, yields different products. This difference in behaviour is briefly discussed.

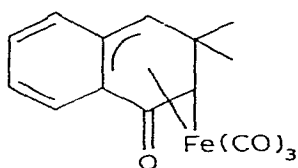
Introduction

Conjugated cisoid dienes can readily form stable trickarbonyliron complexes, and several novel complexes have been prepared [1]. The stability of the conjugated dienetrickarbonyliron group is usually high and sometimes even outweighs the stabilization energy of an aromatic ring, although skeletal reorganizations [2] or double bond migrations [3] have been observed. However, on treatment with Lewis acid some novel rearrangements, occasionally coupled with an insertion of CO moiety, have been reported. For example, cyclooctatetraenetrickarbonyliron reacts with aluminium trichloride to give 2-4- η ,8- σ -9-oxobicyclo-[3.2.2]nona-2,6-dien-8-yltrickarbonyliron [4]. Similar treatment of cyclooctatrienetrickarbonyliron affords 2,3,3a,7a-tetrahydroindenonetrickarbonyliron [4b]. Recently, the *o*-quinodimethane complex (I) was shown to give 2-indanone in fairly good yield on reaction with aluminium trichloride (eqn. 1). However, in the reaction of butadienetrickarbonyliron with aluminium trichloride only a very low conversion was observed. Furthermore, the isoindene complex

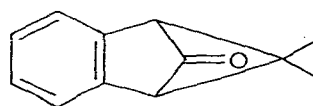




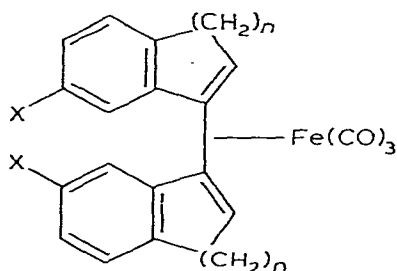
(II)



(III)



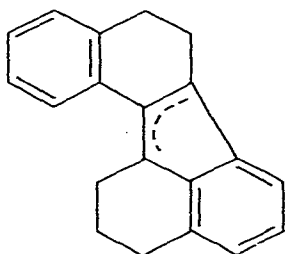
(IV)



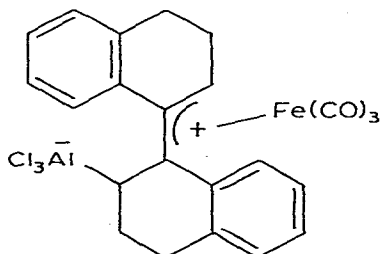
(V)

$$n = 1, 2, 3$$

$$X = \text{H}, \text{CH}_3, \text{CH}_3\text{O}$$



(XI)



(XII)

(II) under similar conditions gave the tricarbonyliron complex (III), but the expected bicyclic ketone (IV) was not isolated. In this paper, we report the synthesis of several dienetricarbonyliron complexes of general structure V and some of their reactions with aluminium trichloride.

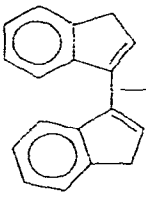
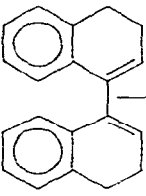
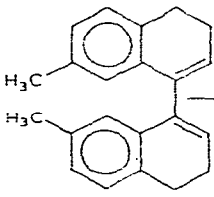
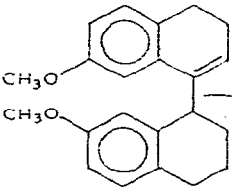
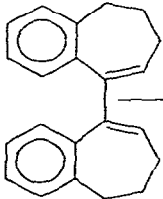
Results and discussion

Synthesis

The dienetricarbonyliron complexes were prepared by treating the dienes with pentacarbonyliron or enneacarbonyldiiron, as indicated in Table 1. The yields are much influenced by steric hindrance in the substrate, being reduced by strong repulsion between the peripheral hydrogens or substituents. Thus, attempts to prepare complexes such as 2,2'-dimethyl-3,3'-biindenyl-, 2,2'-

TABLE 1

YIELDS AND MÖSSBAUER PARAMETERS OF DIENEIRON TRICARBONYL COMPLEXES

Complex	Reagent	Yield ^a (%)	IS (mm/sec)	QS (mm/sec)
 (VI)	$\text{Fe}_2(\text{CO})_9$	27.5	0.446	1.55
 (VII)	$\text{Fe}(\text{CO})_5$	36	0.361	1.35
 (VIII)	$\text{Fe}_2(\text{CO})_9$	5	0.264	1.67
 (IX)	$\text{Fe}_2(\text{CO})_9$	9	0.468	1.74
 (X)	$\text{Fe}(\text{CO})_5$	82	0.361	1.56

^a Yield based on unrecovered starting diene.

dimethyl-3,3',4,4'-tetrahydro-1,1'-binaphthyl-, 5,5',8,8'-tetramethyl-3,3',4,4'-tetrahydro-1,1'-binaphthyltricarbonyliron compounds under various reaction conditions were unsuccessful because of the steric hindrance prohibiting cisoid diene formation.

Mössbauer spectra

The isomer shifts (IS) and quadrupole splittings (QS) of the ironorganic compounds are also summarized in Table 1. As in earlier observations [6], the complexes exhibit strong quadrupole splitting and possess an isomer shift within a fairly narrow region, 0.2 mm/s. Ring size seems to play an important role, with more strained dienes (e.g. VI) giving rise to a positive chemical shift. This observation is understandable, since a more strained olefin ligand would give poorer "forward coordination" which would lead to decrease in electron density, including 4s, at iron, and thereby cause a positive chemical shift. In addition, weaker back donation of *d* electrons into the ligand would also be expected in strained olefin ligands, which would result in a relative increase of 3*d* electron density at iron and so increase the shielding of 4s electron density and cause a positive chemical shift.

Substituents on the ligand also influence the electron density in iron. It is noteworthy that a plot of the isomer shifts of VII–IX versus σ_{meta}^n values [7] gives a straight line with a slope 1.407 ($r = 0.9999$). It clearly demonstrates that the substituents at C(7) (or C(7')) exert an inductive effect at the metal.

Reactions with aluminium trichloride

Treatment of complexes listed in Table 1 with aluminium trichloride, in no case gave a cyclic ketone, in contrast to the results with other complexes [5].

Treatment of VII with aluminium trichloride gave a hydrocarbon, XI, in 62% yield. The structure was assigned by comparing its physical data with those of an authentic compound prepared from the parent ligand diene and acid [8]. It is striking that the same product was isolated from the reaction of aluminium trichloride with the complex and with the uncomplexed ligand. There is no evidence to suggest that aluminium trichloride can catalyze the dissociation of the diene ligand from tricarbonyliron moiety, which in turn undergoes rearrangement. Indeed, the reaction with other substrates which will be discussed later in this paper, tends to rule out this possibility. The detailed mechanism is not clear, but a possible intermediate XII is proposed, which may undergo intramolecular Friedel–Crafts reaction*.

The novel product anthracene was formed from the reaction of the complex VI with aluminium trichloride. A control experiment with parent diene gave a mixture of products, in which no anthracene was detected. This indicates that the metallic part of the complex (VI) can actively participate in this reaction, although the actual mode of transformation is not clear. Similar treatment of aluminium trichloride with the complex X gave no observable product, and about 67% of the starting complex was recovered. This observation further supports the argument that aluminium trichloride does not promote the dissociation of diene ligand from iron under the reaction conditions.

The driving force for these reactions may arise from the fact that steric hindrance is released during the course of the reaction. Indeed, inspection of models shows that the complex X is the least hindered among those in Table 1 and is therefore the least reactive toward aluminium trichloride.

* Pentacarbonyliron has been found to be an active Friedel–Crafts catalyst [9].

Experimental

3,3'-Biindene [10], 3,3',4,4'-tetrahydro-1,1'-binaphthylene, 7,7'-dimethyl-3,3',4,4'-tetrahydro-1,1'-binaphthylene, 7,7'-dimethoxy-3,3',4,4'-tetrahydro-1,1'-binaphthylene [11], and 2,3,2',3'-dibenzo-1,1'-bi(cyclohepta-2,7-diene) [10] were prepared by literature methods. Pentacarbonyliron (E. Merck) was used without further purification. Enneacarbonyldiiron was prepared by the standard procedure [12]. Melting points are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 283 instrument. Nuclear magnetic resonance spectra were measured on a JEOL 60HL spectrometer. Mass spectra were recorded using a Hitachi RMS-4 mass spectrometer or a VG-7070F mass spectrometer. Mössbauer spectra were obtained at ambient temperature on thin samples (40–80 mg/cm²) using a Cu-⁵⁷Co source. Microanalyses were performed by the Australian Microanalytical Service, Melbourne.

3,3'-Biindenyltricarboxyliron (VI)

A mixture of 3,3'-biindene (4.44 g, 19.3 mmol) and enneacarbonyldiiron (12 g, 33.0 mmol) in cyclohexane (180 ml) was refluxed under nitrogen for 40 h. The mixture was cooled and filtered. The filtrate was evaporated in vacuo and the residue was chromatographed on alumina. Starting diene (1.5 g) was recovered, and 3,3'-biindenyltricarboxyliron (VI) was obtained as yellow needles (1.3 g, 27.5% based on unrecovered starting material), m.p. 195°C (dec.) (benzene/petroleum ether); NMR (CS₂): δ 1.75 (d, 2 H, J = 5 Hz), 2.90 (d, 2 H, J = 22 Hz), 3.30 (dd, 2 H, J = 5 Hz, J' = 22 Hz), 7.20 (m, 6 H), 8.35 (m, 2 H); IR (KBr): 2040, 1980 cm⁻¹; MS (70 eV): m/e 370 (M^+). Anal.: Found: C, 68.32; H, 3.85; O, 12.70. C₂₁H₁₄FeO₃ calcd.: C, 68.14; H, 3.81; O, 12.97%.

3,3',4,4'-Tetrahydro-1,1'-binaphthyliron tricarboxyl (VII)

A mixture of 3,3',4,4'-tetrahydro-1,1'-binaphthylene (8.0 g, 31.0 mmol) and pentacarbonyliron (28 g, 143.2 mmol) in di-n-butyl ether (150 ml) was refluxed under nitrogen for 48 h. The mixture was cooled and filtered. The filtrate was evaporated in vacuo and the residue was chromatographed on alumina. In addition to the starting diene (5.8 g, 72%), the desired complex (VII) was obtained as golden prisms (1.2 g, 36% based on unrecovered diene); m.p. 162–163°C (ethanol); NMR (CS₂): δ 1.40 (t, 2 H), 1.97 (m, 4 H), 2.70 (t, 4 H), 7.00 (m, 6 H), 7.50 (m, 2 H); IR (KBr) 2040, 1980, 1960 cm⁻¹; MS (70 eV): m/e 398 (M^+). Anal.: Found: C, 69.15; H, 4.86. C₂₃H₁₈FeO₃ calcd.: C, 69.37; H, 4.56%.

7,7'-Dimethyl-3,3',4,4'-tetrahydro-1,1'-binaphthyltricarboxyliron (VIII)

The complex VIII was prepared similarly. Reaction of 7,7'-dimethyl-3,3',4,4'-tetrahydro-1,1'-binaphthylene (2 g, 55 mmol) and enneacarbonyldiiron (4 g, 13.9 mmol) afforded the desired complex (VIII) as golden yellow crystals (0.3 g, 5%); m.p. 180–181°C (methylene chloride/petroleum ether); NMR (CDCl₃): δ 1.40 (t, 2 H), 2.00 (m, 4 H), 2.17 (s, 6 H), 3.73 (t, 4 H), 7.05 (m, 4 H), 7.52 (s, 2 H). IR (KBr): 2036, 1976, 1959 cm⁻¹; MS (70 eV): m/e 426 (M^+). Anal.: Found: C, 70.54; H, 5.17. C₂₃H₁₈FeO₃ calcd.: C, 70.43; H, 5.20%.

7,7'-Dimethoxy-3,3',4,4'-tetrahydro-1,1'-binaphthyltricarbonyliron (IX)

The method described above was employed. 7,7'-Dimethoxy-3,3',4,4'-tetrahydro-1,1'-binaphthylene (5 g, 15.7 mmol) reacted with enneacarbonyldiiron (2 g, 55 mmol) to give golden yellow crystals of the complex (IX) (0.7 g, 9%); m.p. 180–183°C; NMR (CDCl₃): δ 1.53 (t, 2 H), 1.99 (m, 4 H), 2.67 (t, 4 H), 3.51 (s, 6 H), 6.90 (dd, 4 H), 7.22 (d, 2 H); IR (KBr): 2037, 1978, 1961 cm⁻¹; MS (70 eV): m/e 458 (M^+). Anal.: Found: C, 65.34; H, 4.83. C₂₃H₁₈FeO₅ calcd.: C, 65.50; H, 4.80%.

2,3:2',3'-Dibenzo-1,1'-bi(cyclohepta-2,7-dienyl)tricarbonyliron (X)

A mixture of 2,3:2',3'-dibenzo-1,1'-bi(cyclohepta-2,7-diene) (2.1 g, 7.3 mmol) and pentacarbonyliron was treated as described above to give the desired complex as yellow prisms (2.55 g, 81.6%); m.p. 242°C (dec.) (benzene/petroleum ether); NMR (CS₂): δ 1.00 (m, 4 H), 1.80 (m, 6 H), 2.3–3.2 (m, 4 H), 7.00 (m, 6 H), 7.75 (m, 2 H); IR (KBr): 2044, 1988, 1980 cm⁻¹; MS (70 eV): m/e 426 (M^+). Anal.: Found: C, 70.38; H, 5.25; O, 11.11. C₂₅H₂₂FeO₃ calcd.: C, 70.44; H, 5.20; O, 11.26%.

Reaction of 3,3',4,4'-tetrahydro-1,1'-binaphthyltricarbonyliron (VII) with aluminium trichloride

Freshly sublimed anhydrous aluminium trichloride (0.4 g, 3.0 mmol) was added to a solution of complex VII (0.28 g, 0.7 mmol) in dry benzene (15 ml) at room temperature under nitrogen. The mixture was stirred for 24 h, and water (15 ml) was added. The organic phase was separated and the aqueous phase was extracted with two portions of benzene (15 ml). The combined organic phase was washed with water and dried (Mg₂SO₄). Removal of solvent gave a yellow residue, which was chromatographed on alumina using pentane as eluent. The first yellow band gave the starting complex (VII) (0.08 g, 28%). Further elution gave a white solid upon removal of the solvent. Recrystallization from ethanol/hexane afforded the hydrocarbon XI as colorless plates (0.08 g, 62% based on unrecovered starting material); m.p. 133–134°C (lit. [8]: 129–130°C); NMR (CCl₄): δ 1.0–3.5 (m, 11 H), 7.20 (m, 6 H), 7.60 (m, 1 H); IR (KBr): 1600 cm⁻¹; MS (70 eV): m/e 258 (M^+). Anal.: Found: C, 92.87; H, 7.25. C₂₆H₁₈ calcd.: C, 92.98; H, 7.02%.

Reaction of 3,3'-biindenyltricarbonyliron (VI) with aluminium trichloride

The complex VI (0.45 g, 1.22 mmol) in dry benzene (20 ml) was added dropwise to a stirred suspension of freshly sublimed anhydrous aluminium trichloride (1.0 g, 7.5 mmol) in dry benzene (3 ml) at room temperature under nitrogen. After 4 h, cold water (25 ml) was added. The organic layer was separated and the aqueous phase was extracted with two portions of dichloromethane (15 ml). The combined organic extracts were dried (Mg₂SO₄). The residue after removal of solvent was chromatographed on alumina to afford anthracene (0.12 g, 55%) as white plates, m.p. 212–214°C (lit [13]: 216.1°C).

Reaction of 2,3:2',3'-dibenzo-1,1'-bi(cyclohepta-2,7-dienyl)tricarbonyliron (X) with aluminium trichloride

A solution of the complex X (0.3 g, 0.70 mmol) in dry benzene (15 ml) was

added dropwise to a mixture of freshly sublimed aluminium trichloride (0.25 g, 1.88 mmol) in 2 ml of dry benzene. The mixture was stirred for two days at room temperature under nitrogen, then hydrolyzed by addition of water (15 ml). The organic layer was separated, and the aqueous phase extracted with two portions of benzene (10 ml). The combined benzene solutions were washed with water, dried over anhydrous magnesium sulphate, and filtered. Removal of solvent from the filtrate afforded the starting complex (X) (0.2 g, 67%).

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