Behaviour of Cyclo-octatetraene- and Cycloheptatriene-tricarbonyliron under Olefin-metathesis Conditions

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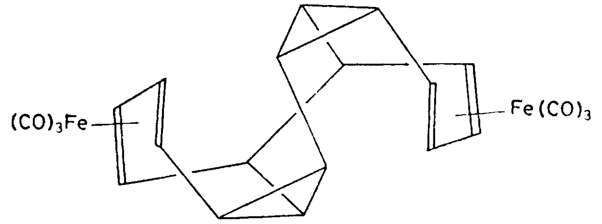
The two title complexes with free double bonds have been used as substrates in the olefin-metathesis reaction. The reaction with [Fe(cot)(CO)$_3$] produces a dimeric complex with a new pentacyclic carbon skeleton; that with [Fe(cht)(CO)$_3$] leads to the dimeric compound tetracarbonylbis(cycloheptadienyl)di-iron, whose stereochemistry is discussed.

THE olefin metathesis reaction has been used with olefins which contain organic functional groups, but there has been no report in which a metal π-complex has been formed in order to block sites in a polyolefin. This paper describes our investigation into the versatility of the olefin metathesis reaction, in particular, with polyolefiniron carbonyl complexes as substrates. As starting materials we chose the well known tricarbonylcyclo-octatetraeneiron [Fe(cot)(CO)$_3$] and tricarbonylcycloheptatrieneiron [Fe(cht)(CO)$_3$] complexes which contain uncomplexed double bonds. Some of this work was reported briefly in a preliminary communication.[1]

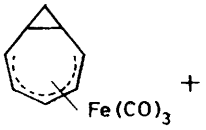
RESULTS AND DISCUSSION

The principal catalyst used was based on the alkylaluminium–tungsten halide–ethanol combination. In common with other workers using this system,[2] we experienced difficulty with the reproducibility of the catalyst. However, using 2 : 1 : 0 as the Al : W : O atomic ratio in the AlEtCl$_2$–WCl$_6$–EtOH catalyst with the [Fe(cot)(CO)$_3$] complex at room temperature in toluene, we obtained a complex mixture of products which were separated by column chromatography.

The column fractions were investigated by i.r., ^{1}H-n.m.r., and mass spectrometry. In many cases the fractions consisted of iron carbonyl complexes, showing that the tricarbonyliron moiety can survive the conditions of the metathesis reaction. Pale yellow crystals were obtained from the first fraction by adding light petroleum (b.p. 30—40 °C, in all cases) after concentration. The only structural features deduced from the ^{1}H n.m.r spectrum of these crystals appeared to be the possibility of cyclopropane rings, and so an *X*-ray structure analysis was carried out,[1] which revealed a new pentacyclic carbon skeleton for a dimer of [Fe(cot)(CO)$_3$], hexacarbonyl(5—8-η:11—14-η-pentacyclo[8.4.1.1^{3,9}.0^{2,15}.0^{4,16}]hexadeca-5,7,11,13-tetraene)di-iron, (1). The compound did not melt below 250 °C and appeared to be very stable, a CDCl$_3$ solution remaining clear after standing for 1 year at 0 °C. This product was only isolated after many attempts, and an Al : W ratio of 2 : 1 was used. Formation of the product was also observed using Al : W = 1.4 : 1; high Al : W ratios do not appear to favour its formation. A complete assignment of the n.m.r. spectrum was possible using the skeleton from the *X*-ray analysis and with the help of spin-decoupling experiments. Although this is stoicheiometrically an exact dimer, and as such could be expected as the product of metathesis of a cyclic olefin, we cannot rationalise the formation of the observed carbon skeleton using known reaction pathways. The coupling of organometallic iron salts has been reported previously by Wilkinson and co-workers[3] using such reagents as zinc dust in boiling tetrahydrofuran (thf), methyl- or phenyl-lithium, or sodium tetrahydroborate in thf in the presence of lithium chloride. However, treatment of (2) with the metathesis catalyst gave no product resulting from C–C bond formation.

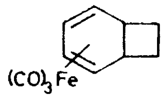


(1)



(2)

Amongst other products which were identified from the metathesis reaction of [Fe(cot)(CO)$_3$] with the AlEtCl$_2$-WCl$_6$-EtOH catalyst (after further chromatography) was the (bicyclo[4.2.0]octa-2,4-diene)tricarbonyliron complex, [Fe(C$_8$H$_{10}$)(CO)$_3$], (3). The ^{1}H n.m.r. spectrum of this compound has been reported previously by Wilkinson and co-workers[4] and thus permitted identification of this fraction. The formation of the skeleton of this compound may possibly involve a bicyclo[5.1.0] intermediate, as the isomerisation of this skeleton to the bicyclo[4.2.0] form has been reported.[5] The formation of a bicyclo[5.1.0] skeleton by the protonation of [Fe(cot)(CO)$_3$] in the acidic medium of the catalyst is not unreasonable. Further elution with light petroleum gave (4). Golden-yellow crystals formed slowly out of a similarly coloured oil and could be separated, after several days, by careful removal of the oil with light petroleum. The crystalline material was characterised as *trans*-[$Fe_2(C_8H_8)(CO)_6$] (4).[6] It would be difficult to assert unequivocally that this was formed in the reaction of [Fe(cot)$(CO)_3$] with the catalyst. The preparation of [Fe(cot)$(CO)_3$] from cyclo-octatetraene and iron pentacarbonyl, which was the method used, can produce [$Fe_2(C_8H_8)(CO)_6$], but careful sublimation *in vacuo* should yield [Fe(cot)$(CO)_3$] without this impurity.



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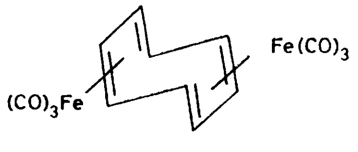
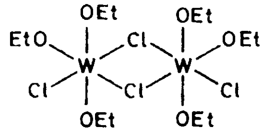


(4)

Starting material and several other pale yellow organoiron complexes were recovered, but in amounts insufficient for full characterisation. The formation of these compounds was generally favoured when using a high O : W ratio in the catalyst.

In addition to the iron complexes described we recovered a maroon dimeric tungsten complex, [$W_2Cl_4(OEt)_6$], (5). This diamagnetic dimer is produced from the interaction of ethanol and tungsten hexachloride and was identified by its ^1H n.m.r. spectrum.[7] Höcker and Jones [8] in their investigation of the $AlEtCl_2$-WCl_6-EtOH catalyst did not isolate this product from metathesis reactions, but they did investigate the possible metathesis activity of some similar quinquevalent tungsten alkoxy-chlorides. The formation of (5) has not been reported previously from use of this catalyst, although this may be due to the different methods of product analysis. The products are usually analysed by g.l.c. and the non-volatile residues are not examined.



(5)

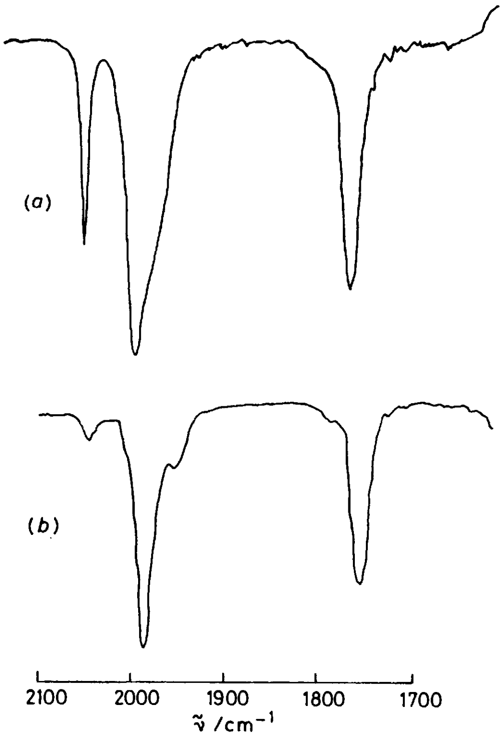
Using [Fe(cht)$(CO)_3$] as substrate under similar reaction conditions to those used for [Fe(cot)$(CO)_3$], but with the significant difference of a high O : W ratio in the catalyst, we obtained two reaction products, which may be separated by very careful column chromatography. The major product is the dicarbonylchloro (1—5-η-cycloheptadienyl)iron complex, (6), previously unreported, but analogous to the iodo-complex, (7), prepared by Dauben and Bertelli [9] from the reaction of [Fe(1—5-η-C_7H_9)$(CO)_3$]-[BF_4] with potassium iodide. Analytical, mass spectrometric, and ^1H n.m.r. data all support this conclusion. The compound is very air-sensitive in solution, but moderately stable to air once crystalline. Both compounds (6) and (7) exhibit remarkably large solvent-induced chemical shifts, in particular the central proton of the dienyl fragment ($\Delta\tau = 1.1$ p.p.m.) (see Experimental section). The complex [Fe(1—5-η-C_7H_9)$(CO)_2$Cl], (6), appears to be the product of addition of hydrogen chloride to [Fe(cht)$(CO)_3$] with loss of carbon monoxide. Formation of the compound is favoured by a high O : W mol ratio in the catalyst, conditions which favour the formation of hydrogen chloride from the reaction of ethanol and tungsten hexachloride. It should be noted that Wilkinson and co-workers [4] report the reaction of hydrogen chloride with [Fe(cht)$(CO)_3$] to lead to the [Fe$(C_7H_9)(CO)_3$]$^+$ cation, and it is likely that this is an intermediate in the formation of [Fe(1—5-η-C_7H_9)$(CO)_2$-Cl]. It is somewhat surprising that the addition of HCl was not observed in the metathesis of [Fe(cot)$(CO)_3$] described above, particularly as this addition has been reported by Lewis and co-workers.[10]

The second product showed i.r. absorptions attributable to terminal and bridging carbonyl ligands, but it was too insoluble for ^1H n.m.r. analysis. With great difficulty, a sample was crystallised sufficiently well for a single-crystal *X*-ray analysis.[11]

The structure whose configuration is shown in (8) did not show an expanded-ring ligand, but a compound in which two C_7H_9 rings were in a *cis* configuration about an iron-bridging carbonyliron plane. The molecular symmetry is C_{2v} and is therefore expected to have four i.r. carbonyl absorptions. The product was not what might have been expected from metathesis but it was interesting in its similarity to the known η-cyclopentadienyliron dicarbonyl dimers (9) and (10).

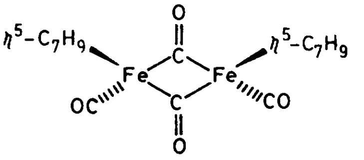
A compound of the same molecular formula, [{Fe$(C_7H_9)(CO)_2$}$_2$], had already been obtained from the sodium-amalgam reduction of [Fe(1—5-η-C_7H_9)$(CO)_2$I] (7), by Pauson and co-workers.[12] Pauson's work was repeated in order to compare the properties of these two compounds. Although Pauson did not investigate the possibility of *cis* and *trans* isomers we found that careful chromatography of the crude reaction product of amalgam reduction gives two isomers. Infrared studies (see Figure) in the 1 700—2 100 cm^{-1} metal-carbonyl stretching region establish that these are *cis* and *trans* isomers, the *trans* form being very much more abundant. The *trans* isomer is assumed to have a planar Fe$(CO)_2$Fe bridging system with C_{2h} symmetry and thus it is expected to have two i.r.-active carbonyl absorptions (one terminal and one bridging). The metathesis product and the minor amalgam-reduction product are identical.

These cycloheptadienyl dimers were carefully studied because of their similarity to the analogous η-cyclopentadienyl dimers (9) and (10) and the *cis*–*trans* interconversions of the latter in solution. Extensive i.r. studies on a number of [{Fe(1—5-η-dienyl)$(CO)_2$}$_2$] systems in various solvents [13-17] have shown how the *cis*–*trans* equilibrium in solution can be altered by a change in the dielectric constant of the solvent, and on the basis of these and variable-temperature ^{13}C n.m.r. experiments[18] a detailed mechanism was proposed by Cotton and co-workers[19] to explain the *cis–trans* interconversion of the dimeric dicarbonyl(η-cyclopentadienyl)iron conformers and the related simultaneous bridging–terminal carbonyl-ligand interchange.



Infrared spectra of (*a*) *cis*- and (*b*) *trans*-[$\{Fe(C_7H_9)(CO)_2\}_2$], complexes (8) and (11) respectively, in dichloromethane

However, in the cycloheptadienyl systems, the isomers do not appear to interconvert. In dichloromethane solution, the i.r. spectra of *cis*- and *trans*-[$\{Fe(C_7H_9)(CO)_2\}_2$] showed three and two intense absorptions



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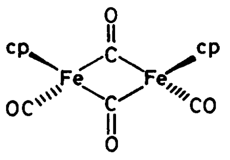

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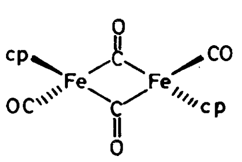

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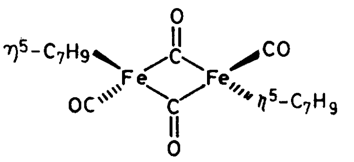
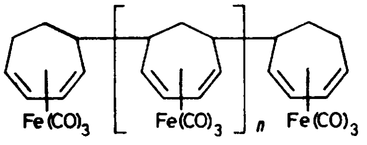


(11)

respectively in the carbonyl region (Figure). This is the same as is found in the cyclopentadienyl case,[13] where the fourth band of the *cis* isomer due to symmetric stretching of the bridging carbonyls is very weak [*cis*-(8): 2 042vs, 1 984vs, and 1 754vs cm^{-1}; *trans*-(11): 2 048vw,[*] 1 984vs, and 1 754vs cm^{-1}]. Measurement of the spectrum of the *trans* isomer, immediately on dissolution, and after 17 h, showed no change in intensity of the very weak band at 2 048 cm^{-1}. In a polar solvent such as dichloromethane one would expect the equilibrium to favour the presence of the more polar solute, *i.e.* the *cis* isomer. No evidence for this was observed and separation of the *cis*- and *trans*-[$\{Fe(C_7H_9)(CO)_2\}_2$] isomers by chromatography suggests no interconversion between isomers. The two isomers were too insoluble for ^{13}C n.m.r. measurements.

The restricted interconversion of the [$\{Fe(C_7H_9)(CO)_2\}_2$] isomers is not easily explained. The common feature of the η-cyclodienyl systems studied by McArdle and Manning,[13,14] and Cotton and co-workers,[19] is that the bonding 'dienyl' is always η-cyclopentadienyl. In the 1—5-η-cycloheptadienyl isomers, the dienyl bonding fragment cannot be considered 'cyclic', but rather 'open'. Attempts to corroborate these observations by *X*-ray crystallography have been unsuccessful. Studies of the *trans* isomer have given a diffraction pattern which cannot be distinguished from that of the *cis* isomer.[11]

In addition to the $AlEtCl_2$–WCl_6–EtOH catalyst we experimented with the [$MoCl_2(NO)_2(PPh_3)_2$]–$AlEtCl_2$ catalyst prepared by Zuech *et al.*[20] Neither of the iron complexes appeared to react with this catalyst under a variety of conditions. The WCl_6–$LiBu^n$ catalyst prepared by Wang and Menapace[21] was tried with both complexes. No reaction was observed with [$Fe(cot)(CO)_3$] but [$Fe(cht)(CO)_3$] reacted at 80 °C in toluene. Work-up gave a product with absorptions at *ca.* 2 000 cm^{-1} in the i.r. spectrum, characteristic of a tricarbonyliron complex. The powdery material could not be crystallised successfully, and was very stable, resisting oxidation by Ce^{4+} and iron(III) chloride–hydrochloric acid. The analytical data suggested a compound of empirical formula $Fe(C_{8.7}H_{10.7})(CO)_3$. The ^1H n.m.r. spectrum showed broad ill defined absorptions suggesting a polymeric material, and broad absorptions were also observed in the ^{13}C n.m.r. spectrum at 88.6, 61.6, 48.5, and 28.7 p.p.m. downfield from $SiMe_4$; the carbonyl resonance was observed as a sharp signal at 211.9 p.p.m.



(12)

These results suggest that the WCl_6–$LiBu^n$ catalyst has polymerised the [$Fe(cht)(CO)_3$], but in an unknown manner. More recently, McArdle and Sherlock[22] have reported the polymerisation of [$Fe(cht)(CO)_3$] with tricarbonyltropyliumiron cation to give (12). The ^{13}C

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[*] Also present in solid-state spectrum.

n.m.r. resonances of polymer (12) at 211.5, 88.8, 61.3, 48.5, and 29.4 p.p.m. downfield from $SiMe_4$ suggest the polymer obtained from the reaction with the metathesis catalyst has retained the cyclic structure of $[Fe(cht)(CO)_3]$. Polymer (12) is very soluble, as is ours, but reportedly has ' decomposition problems ' whereas ours is very stable. Olefin-metathesis catalysts are known polymerisation catalysts, although with cyclic olefins, ring-opening polymerisation is the more common occurrence. It seems likely that the end groups of the polymer produced by the WCl_6–$LiBu^n$ catalyst are different from those in (12).

EXPERIMENTAL

Hydrogen-1 n.m.r. spectra were recorded on a Perkin-Elmer model R12B spectrometer at 60 MHz with $SiMe_4$ (τ 10.00) as internal reference, or at 90 MHz on a Bruker WH90 Fourier-transform instrument. Carbon-13 n.m.r. spectra were obtained on a Bruker WP60 spectrometer at 25.1 MHz with $SiMe_4$ as internal reference. Infrared spectra were recorded on a Perkin-Elmer model 325 spectrophotometer and mass spectra on an A.E.I. MS30 spectrometer operating at 70 eV.*

All reactions and manipulations were carried out under an atmosphere of dry N_2 using Schlenk-tube techniques. All solvents were dried, and distilled under N_2. Solutions of catalyst components were prepared in either benzene or toluene. The reactions may be carried out in either solvent. Chromatography was carried out on silica using columns fitted with an external cooling jacket kept at 10 °C.

The complexes $[Fe(cot)(CO)_3]$ [23] and $[Fe(C_7H_9)(CO)_3][BF_4]$ [24] were prepared by standard methods; $[MoCl_2(NO)_2(PPh_3)_2]$ was prepared by the method of Cotton and Johnson [25] from $[MoCl_2(NO)_2]$,[26] and $[Fe(cht)(CO)_3]$ was prepared in high yield by irradiation of iron pentacarbonyl and cycloheptatriene using a procedure kindly supplied by G. L. P. Randall,[27] rather than the thermal procedure previously reported.[4]

Preparation of $[Fe(cht)(CO)_3]$.—Irradiation [100-W medium-pressure mercury discharge lamp (Hanovia), principal wavelength 366 nm] of a solution of $[Fe(CO)_5]$ (100 g, 0.51 mol) and cycloheptatriene (100 cm^3, 0.96 mol) in benzene (100 cm^3) at reflux temperature for 36 h, followed by evaporation *in vacuo*, gave a yellow-brown oil. Distillation at reduced pressure gave the product as an orange oil (80 g, 68%), b.p. 55—65 °C (0.05 mmHg). The product was stored at −5 °C. The irradiation was carried out in a specially constructed Pyrex flask with the lamp fitting in an insert in the bottom of the flask to allow irradiation of the solution through Pyrex glass and also provide the heating.

Reaction of $[Fe(cot)(CO)_3]$ *with* $AlEtCl_2$-WCl_6-EtOH *Catalyst.—General procedure.* A solution of $[Fe(cot)(CO)_3]$ (1.3 g, 5.3 mmol) in benzene (10 cm^3) was added to a catalyst mixture, prepared by the addition of ethanol (0.2 cm^3, 3.4 mmol) and ethylaluminium dichloride solution (17.5 cm^3, 0.2 mol dm^{-3}, 3.5 mmol) to a solution of WCl_6 (35 cm^3, 0.05 mol dm^{-3}, 1.75 mmol), stirring in a Schlenk tube. The latter was sealed with a rubber bung, and the mixture left stirring for 24 h when more premixed catalyst (identical quantities) was added. After stirring for another 17 h, the mixture was filtered and chromatographed on a column (100 × 1.5 cm). Collection of the aromatic solvent and the polar solvent-front fraction on elution with diethyl ether–light petroleum (1 : 9), gave, on evaporation of the solvent under reduced pressure and treatment of the residue with light petroleum, $[Fe_2(C_{16}H_{16})(CO)_6]$, fraction 1, as a yellow powder which was washed repeatedly with light petroleum; the washings were collected for further chromatography. The product was recrystallised from toluene–methanol (3 : 2) at −20 °C to give golden yellow crystals, m.p. >250 °C, blackening above 190 °C (Found: C, 54.05; H, 3.35; Fe, 22.65. $C_{22}H_{16}Fe_2O_6$ requires C, 54.15; H, 3.30; Fe, 22.9%). Mass spectrum: *m/e* 460, $[M - CO]^+$, with consecutive loss of 5 CO. I.r. spectrum: ν(CO) ($CHCl_3$) at 2 040 and 1 980 cm^{-1}. Hydrogen-1 n.m.r. ($CDCl_3$): τ 4.9 (m, 4 H), 6.74 (m, 2 H), 7.0 (q, 2 H), 7.5 (t, 2 H), 8.19 (q, 2 H), 9.25 (q, 2 H), and 9.57 (t, 2 H). Maximum yield *ca.* 15 mg (<1.5%) at Al : W : O = 2 : 1 : 0.79.

Elution with diethyl ether–light petroleum (3 : 7) gave maroon fraction 2, which on evaporation yielded a deep red crystalline compound, $[W_2Cl_4(OEt)_6]$, (5) (Found: C, 18.3; H, 4.00; Cl, 18.25. Calc. for $C_{12}H_{30}Cl_4O_6W_2$: C, 18.5; H, 3.90; Cl, 18.2%). In air, blackening of the complex occurred above 180 °C; no melting was observed. Further elution with diethyl ether did not yield any other iron complexes.

Careful chromatography of the washings of fraction 1 on a column (100 × 1.5 cm) gave on elution with light petroleum the following fractions. (*a*) Yellow oil, $[Fe(C_8H_{10})(CO)_3]$, (3). Maximum yield *ca.* 20 mg (<1.5%) (Found: C, 54.85; H, 4.60. Calc. for $C_{11}H_{10}FeO_3$: C, 53.7; H, 4.1%). The mass spectrum showed a parent ion at *m/e* 246, with successive loss of three carbonyl groups. Hydrogen-1 n.m.r. ($CDCl_3$): τ 4.53 (m, 2 H), 6.58 (m, 2 H), 7.45 (m, 2 H), 8.15 (m, 2 H), and 8.85 (m, 2 H). Infrared data: ν(CO), at 2 050 and 1 970 cm^{-1}, in good agreement with reported literature values.[4] (*b*) Yellow crystalline compound, *trans*-$[Fe_2(C_8H_8)(CO)_6]$, (4), m.p. *ca.* 180 °C (decomp.) (Found: C, 43.3; H, 1.90. Calc. for $C_{14}H_8Fe_2O_6$: C, 43.8; H, 2.1%). The mass spectrum showed a parent ion at *m/e* 384 with successive loss of six carbonyl groups. Infrared spectrum (cyclohexane); ν(CO) at 2 046, 1 990, and 1 982 cm^{-1}. Hydrogen-1 n.m.r. ($CDCl_3$): τ 4.4 (m, 4 H) and 6.8 (m, 4 H) (lit.,[6] τ 4.2 and 6.7). Co-eluting with this complex was an unidentified oil, which showed ^1H n.m.r. resonances $[(CD_3)_2CO]$ at τ 3.78(d), 3.95(d), 4.5(m), 6.8(m), and 7.2(m). Infrared spectrum: ν(CO) at 2 040 and 1 975 cm^{-1}. (*c*) Further elution with light petroleum gave unchanged $[Fe(cot)(CO)_3]$ as the next product, and the remaining iron carbonyl complexes that were subsequently eluted could not be characterised sufficiently for identification.

Reaction of $[Fe(cht)(CO)_3]$ *with* $AlEtCl_2$–WCl_6–EtOH *Catalyst.—General procedure.* A solution of $[Fe(cht)(CO)_3]$ (5.4 g, 23.3 mmol) in benzene (15 cm^3) was added to a catalyst mixture, prepared by the addition of ethanol (0.41 cm^3, 7 mmol) and ethylaluminium dichloride solution (12.6 cm^3, 2.5 mmol) to a solution of tungsten hexachloride (35 cm^3, 1.75 mmol), stirring in a Schlenk tube. The container was sealed with a rubber bung, and the mixture stirred for 24 h, when more premixed catalyst (identical quantities) was added. After another 17 h, the reaction mixture was filtered and transferred to a chromatography column (100 × 1.5 cm). Unchanged $[Fe(cht)(CO)_3]$ was eluted with the benzene solvent and light petroleum, leaving a red band at the top of the column. This was collected by elution with diethyl ether, discarding the very small frac-

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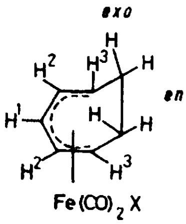
* Throughout this paper: 1 eV ≈ 1.60 × 10^{-19} J; 1 mmHg ≈ 13.6 × 9.8 Pa.

tion on the polar solvent front. The red products were redissolved in hot toluene after evaporation of the volatile solvent under reduced pressure, and very carefully rechromatographed on a column (35 × 1.5 cm). After removal of the aromatic solvent with light petroleum, careful elution with diethyl ether–light petroleum (1 : 3) gave fraction 1, *cis*-[$\{Fe(C_7H_9)(CO)_2\}_2$], (8), as a pink powder, which was recrystallised with difficulty from ethyl acetate or ethyl acetate–light petroleum at −20 °C, to give red-pink crystals, m.p. 160—165 °C (decomp.). Maximum yield, 8—10 mg (<1%); *M* = 409.991 6 (calc. 409.990 3).

Elution of the above column with diethyl ether–light petroleum (1 : 1) gave fraction 2, [$Fe(1—5-\eta-C_7H_9)(CO)_2Cl$], (6), which was recrystallised from diethyl ether at −20 °C to give orange crystals, m.p. 60—65 °C (decomp.). Yield 130—150 mg (2—3%) (Found: C, 44.55; H, 3.95; Cl, 14.45. $C_9H_9ClFeO_2$ requires C, 44.95; H, 3.75; Cl, 14.75%). The mass spectrum showed prominent ions at *m/e* 298, 270, 242, 186, 148, 93, and 91. Infrared spectrum: ν(CO) (KBr) at 2 110w, 2 040vs, and 1 975vs, br cm⁻¹.



(6) X = Cl

(7) X = I

Hydrogen-1 n.m.r. data

Solvent	Chemical shift (τ) H^1	H^2	H^3	H_{endo}	H_{exo}
(6; X = Cl)					
C_6H_6 [a]	3.7	5.4	7.1	8.5	9.6
$CDCl_3$	2.6 [b]	4.6	6.3	7.6	8.7
(7; X = I) [c]					
$CDCl_3$	2.99	4.28	6.01	7.59	8.55
C_6D_6	3.98	4.98	6.73	8.33	9.4

[a] Chemical shifts are relative to C_6H_6 (τ 2.8). [b] Resonance is obscured by $CHCl_3$ resonance. [c] Dauben and Bertelli [9] report resonances at τ 3.1 (2 H), 6.1 (2 H), 7.7 (2 H), and 8.5 (2 H) in hexachloroacetone.

Separation of cis- *and* trans-[$\{Fe(C_7H_9)(CO)_2\}_2$], (8) *and* (11).—The amalgam-reduction products were separated by chromatography on silica under conditions similar to those used above. Fraction 1 was eluted with diethyl ether–light petroleum (3 : 7) and is the *cis* isomer, (8). Fraction 2 is the *trans* isomer, (11), and was eluted using dichloromethane.

Reaction of [Fe(cht)$(CO)_3$] *with* WCl_6–LiBu^n *Catalyst.—General procedure.* A solution of tungsten hexachloride in toluene (40 cm³, 2 mmol) stirring in a Schlenk tube was treated with n-butyl-lithium (1.508 mol dm⁻³, 2.6 cm³, 3.92 mmol) in hexane, and [Fe(cht)$(CO)_3$] (2.6 g, 11.2 mmol) in toluene (10 cm³) was added. The reaction mixture was heated to 80 °C for 17 h and gave, after filtration and chromatography on a column (35 × 1 5 cm), a pale cream compound, which in toluene, co-eluted with unchanged [Fe(cht)$(CO)_3$]. Evaporation of the solvent gave an oil which on treatment with light petroleum gave the product, which was filtered off and washed with light petroleum. Yield 114 mg (Found: C, 54.75; H, 4.2; O, 19.25%), indicating an approximate composition $Fe(C_{8.7}H_{10.7})(CO)_3$, m.p. 200 °C. The complex is very soluble in benzene, toluene, chloroform, dichloromethane, and diethyl ether. Infrared spectrum (C_6D_6): ν(CO) at 2 040 and 1 970 cm⁻¹. The ^1H n.m.r. spectrum (C_6D_6) showed broad absorptions at τ *ca.* 5.1, 7.4, 8.2, and 8.8—9.15 with intensity ratio *ca.* 2 : 2 : 3 : 3.25.

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