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Functionalization of Cycloheptatriene: The Reaction of Cycloheptatrienyltricarbonylferrate(1−) with Chloroformates

M. Airoldi, G. Barbera, G. Deganello,* and G. Gennaro

Istituto di Chimica Generale[†]*-Facoltà di Scienze dell'Università, 90123 Palermo, Italy*

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Reaction of (1–3-η-cycloheptatrienyl)tricarbonylferrate(1−) (**3**) with chloroformates ($ClCO_2R$; R = Me, Et, Bu) affords, after column chromatography, two isomeric ester-substituted (cycloheptatriene)tricarbonyliron complexes, $[Fe(CO)_3(1\text{–}4\text{-}\eta\text{-}5\text{-}CO_2R\text{-}C_7H_7)]$ (**7**) and $[Fe(CO)_3(1\text{–}4\text{-}\eta\text{-}6\text{-}CO_2RC_7H_7)]$ (**8**), together with $[Fe(CO)_3(1\text{–}4\text{-}\eta\text{-}C_7H_7)]_2$ and small amounts of diester-substituted derivatives. Compound **8** can be converted quantitatively into **7**. Photochemical reaction between pentacarbonyliron and a mixture of isomeric carbethoxycycloheptatrienes, the major component of which is $7\text{-}CO_2EtC_7H_7$, affords mostly **8** and small amounts of **7**, with none of the 7-substituted complex $[Fe(CO)_3(1\text{–}4\text{-}\eta\text{-}7\text{-}CO_2Et\text{-}C_7H_7)]$ detected in the reaction mixture. Experiments designed to elucidate the formation of products support a deprotonation mechanism of the neutral-substituted species $[Fe(CO)_3(1\text{–}4\text{-}\eta\text{-}C_7H_{8-n}(CO_2R)_n)]$ (n = 1, 2) by the anionic complexes $[Fe(CO)_3(\eta^3\text{-}C_7H_{7-n}(CO_2R)_n)]^-$ (n = 0, 1) followed by electrophilic attack. The structure of the monosubstituted anion **10** remains uncertain. The reaction of anion **3** with chloroformates represents a convenient method for the synthesis of cycloheptatrienes bearing an electron-withdrawing substituent specifically at the C-5 and/or C-6 position.

Introduction

Among transition-metal complexes of cycloheptatrienes[1] $[Fe(CO)_3(1\text{–}4\text{-}\eta\text{-}C_7H_8)]$[2] (**1**) is one of the most studied. This interest is due mainly to the presence of an uncoordinated double bond next to a methylenic carbon, which allows for peculiar behavior and reactivity. The interruption of the conjugated π-system of the ring by the $-CH_2-$ group inhibits fluxional behavior by a 1,2 metal shift, which is the usual pathway for the degenerate isomerization of $Fe(CO)_3$ complexes of fully conjugated cyclic polyolefins.[1,3] In principle fluxionality in **1** could occur by a 1,3 metal shift. However, due to the high-energy barrier of this process no evidence for it could be seen by conventional variable-temperature NMR techniques up to the decomposition temperature of the complex.[5] Only recently has the 1,3 metal shift in **1** been detected by the spin saturation transfer method[6] applied to ^{13}C[7] and ^1H[8] NMR data.

Substitution of hydrogen at the methylenic carbon is expected to modify the activation energy of the 1,3 metal shift in **1**. Electron-withdrawing substituents increase[4] the energy barrier of the process while the opposite effect has been suggested[4] and experimentally verified[9] for electron-donating groups.[10] Proton abstraction from **1** can be performed with several bases (LiBu at −60 °C;[11] KO-*t*-Bu,[12] $NaN(SiMe_3)_2$,[13] and KH[9] at room temperature) to give the dark red anion $[Fe(CO)_3(\eta^3\text{-}C_7H_7)]^-$ (**3**). Deprotonation of **1** occurs at the 7-exo-position,[1,14] which is also the usual position of the substituent in the electrophilic addition to **3**.[11–19] The suggestion that **3** can be looked upon as an ambident organometallic nucleophile[9,12] has received much support by the formation of iron–metal bonded complexes.[18,20] Unusual endo deprotonation occurs[21] by the reaction of $[Fe(CO)_3(1\text{–}4\text{-}\eta\text{-}7\text{-}exo\text{-}GePh_3C_7H_7)]$ with KO-*t*-Bu to give the fluxional anion $[Fe(CO)_3(\eta^3\text{-}C_7H_6GePh_3)]^-$. Since the $GePh_3$ group must be considered an electron-donating substituent,[22] endo deprotonation is expected to be even more favored by the electron-withdrawing substituent at the 7-exo-position.

To verify this possibility and to gain more insight concerning the reactivity of anion **3**, we have investigated its reaction with alkyl chloroformates.[23]

Experimental Section

General Information. All experimental procedures were performed under a dry nitrogen atmosphere.

Tetrahydrofuran (THF) and benzene were dried by refluxing with $LiAlH_4$ and Na–K alloy, respectively, and were distilled under nitrogen just prior to use. Petroleum ether (bp 37–47 °C), methylcyclohexane, diethyl ether, *n*-pentane, and *n*-hexane were

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[†] On January 1, 1987, Dipartimento di Chimica Inorganica.

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(23) This reaction was mentioned, some years ago,[19] in a brief communication. [**Note added in Proof.** After submission of this manuscript another brief report appeared on the same reaction (Williams, G. M.; Rudisill, D. F. *Tetrahedron Lett.* **1986**, 3465). Due to the lack of spectroscopic data we cannot comment upon some different results and/or interpretation from ours.] However no details of yields and mechanism were reported. Comparison of our results with previous data can be found throughout the discussion section.

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degassed before use. Pentacarbonyliron (Ventron Corp.) and cycloheptatriene (Fluka) were filtered through a short column packed with neutral alumina (Merk, activity I). Chloroformates (Fluka) were distilled and stored under nitrogen.

Potassium *tert*-butoxide was prepared by adding clean-cut potassium metal to an excess of freshly distilled *tert*-butyl alcohol in a flask, thermostated at 35 °C with an oil bath. After complete dissolution of the metal, excess *tert*-butyl alcohol was removed at reduced pressure and the resulting white powder was dried under vacuum for several hours and stored under nitrogen. Sodium bis(trimethylsilyl)amide (Fluka) was used as received.

(Benzylideneacetone)tricarbonyliron [Fe(CO)$_3$(BDA)] was prepared following a photochemical synthesis outlined in the literature.[24]

Infrared spectra were obtained with a Perkin-Elmer 983-G spectrometer and recorded in expanded form in the region 2500–1500 cm^{-1}.

Proton magnetic resonance spectra were recorded on a deuterium lock Bruker 80 SY instrument, in CDCl$_3$ or THF-d_8. Variable-temperature spectra were obtained in sealed 5-mm tubes. Temperature measurements and calibration were made with a Bruker B–VT 1000 control unit and are believed to be accurate to ±2 K. Chemical shifts are reported in δ (parts per million), relative to Me$_4$Si.

Melting points were determined on a Gallenkamp apparatus and are uncorrected.

Elemental analyses were performed by the Analytical Laboratory of the Department of Chemistry, University of Milan.

Reactions of Potassium Cycloheptatrienyltricarbonylferrate(1–) (3) with Ethyl Chloroformate.[25] A 15-mL THF solution of [Fe(CO)$_3$(1–4-η-C$_7$H$_8$)] (1), prepared according to a literature method[26] (1 mL, 1.44 g, 6.2 mmol), was added dropwise to a slurry of KO-*t*-Bu (0.75 g, 6.7 mmol) in 10 mL of THF. At the end of the addition the deep red solution was stirred for 5 h, until the absorption bands of 1 in the carbonyl region (2048 and 1974 cm^{-1}, in THF) were completely replaced by those of 3 (1942 and 1868 cm^{-1}, in THF). The solution was transferred with a syringe to a dropping funnel, equipped with an equilibration arm and a glass frit (G3), and added dropwise to a solution of ClCO$_2$Et (1.2 mL, 12.5 mmol) in THF (10 mL). The deep red color of the anion 3 rapidly disappeared at the beginning of reaction but, as the reaction proceeded, the color change was much slower. At the end of the addition the cloudy reddish solution was stirred for an additional 4 h and then filtered. Evaporation under vacuum afforded a red-brown oily residue. The material was dissolved in 3 mL of *n*-hexane and transferred to the top of a chromatography column (h = 30 cm; d = 2 cm) packed with neutral alumina (activity III) in petroleum ether. Elution with petroleum ether developed two yellow bands that were separated and collected. At the top of the column a broad orange band remained. Elution with petroleum ether/benzene (2:1) developed a yellow band. Elution with benzene finally gave a red-orange band. After evaporation of the solvent the four fractions afforded respectively (a) an orange-brown oil, identified by ^{1}H NMR spectroscopy as pure [Fe(CO)$_3$(1–4-η-C$_7$H$_8$)] (1), (b) a waxy yellow solid containing (^{1}H NMR test) mostly [Fe(CO)$_3$(1–4-η-5-CO$_2$RC$_7$H$_7$)] (7) contaminated with small amounts of [Fe(CO)$_3$(1–4-η-C$_7$H$_7$)]$_2$[15] and [Fe(CO)$_3$(1–4-η-6-CO$_2$RC$_7$H$_7$)] (8) (a second chromatography on alumina (activity III) using *n*-hexane as eluent allowed the separation of the three components, (c) pure (NMR test) 8, and (d) a red powder that proved to be a mixture of the disubstituted (cycloheptatriene)tricarbonyliron complexes 11 (see Discussion).

Crude 7 and 8 were dissolved in the minimum volume of *n*-pentane, filtered, and cooled overnight at −30 °C to give pure sample of 7 (yellow) and 8 (pale yellow), respectively.[27] Analytical and IR data are reported in Table I. ^{1}H NMR spectra are shown in Figure 1; chemical shifts and coupling constants are listed in Table II.

Interaction of (7-*exo*-Deuteriocycloheptatriene)tricarbonyliron with KO-*t*-Bu and Ethyl Chloroformate. [Fe(CO)$_3$(1–4-η-7-*exo*-DC$_7$H$_7$)], prepared according to the procedure of Brookhart *et* al.,[14] was dissolved in THF and treated with KO-*t*-Bu and after 5 h with ClCO$_2$Et, under the same reaction conditions and reagent ratio as in the preceding synthesis. Usual workup and chromatography separated four fractions containing 1, 7, 8, and 11, respectively. No deuterium was incorporated in any of the isolated products.

Synthesis of Potassium ((Carboxyethyl)cycloheptatrienyl)tricarbonylferrate(1–) (10). [Fe(CO)$_3$(1–4-η-6-CO$_2$RC$_7$H$_7$)] (8) (0.144 g, 0.62 mmol) was dissolved in 5 mL of THF and treated with solid KO-*t*-Bu (0.075 g, 0.67 mmol). The mixture became immediately dark red; nevertheless it was stirred for an additional 2 h. The IR spectrum of the filtered solution showed ν(CO) bands at 1971 and 1899 (+sh) cm^{-1}. The reaction mixture was filtered and used for the successive reactions.

(a) Reaction of 10 with Ethyl Chloroformate. A THF solution of 10 was added dropwise to a THF solution (5 mL) of ClCO$_2$Et (twofold excess). The color of the anion disappeared very slowly, and the reaction mixture was stirred for 5 h. The reaction mixture was filtered, evaporated to dryness, dissolved in minimum petroleum ether, and chromatographed on alumina (activity III). Usual workup of the three fractions, collected by elution with petroleum ether, petroleum ether–benzene (2:1), and benzene afforded respectively 7, 8, and 11. For the preparation of a sample studied by ^{1}H NMR spectroscopy, an analogous, reduced-scale procedure in THF-d_8 was used.

(b) Reaction of 10 with HCl or DCl. Aqueous HCl (1 M) was added dropwise to the solution of 10 until the color of the anion disappeared. After addition of about equal volume of diethyl ether, the organic layer was separated and dried overnight with anhydrous MgSO$_4$. After filtration the yellow ethereal solution was evaporated to dryness, under high vacuum, to give pure 7 (by ^{1}H NMR) as a waxy yellow solid.

In an identical procedure, utilizing a 1 M solution of DCl in D$_2$O (both 99% in D), deuterium incorporation at the 7-exo-position of 7 was observed in about 90% purity (essayed by ^{1}H NMR).

Interaction of Potassium Cycloheptatrienyltricarbonylferrate(1–) (3) with ((6-Carboxyethyl)cycloheptatriene)tricarbonyliron (8). A solution of 8 (0.190 g, 0.62 mmol) in 5 mL of THF was added dropwise to the filtered THF solution of anion 3 obtained from 1 (0.144 g, 0.62 mmol) and KO-*t*-Bu (0.07 g, 0.62 mmol). No color change was noticed. The reaction mixture was stirred for two additional hours and then treated with DCl in 99% D$_2$O (1 M solution) until the red color disappeared. The mixture was extracted with diethyl ether and the organic layer dried overnight with anhydrous MgSO$_4$. Filtration and evaporation of the solvent gave a dark orange-brown oil which was chromatographed on alumina (activity III) with *n*-hexane as eluent. Usual workup afforded 1 and 7-exo-deuteriated 7 in about 90% yield.

Interaction of Potassium Cycloheptatrienyltricarbonylferrate(1–) (3) with (7-exo-Deuterio-5-(carboxyethyl)cycloheptatriene)tricarbonyliron (7-*7-exo-d*). Following the same procedure and the same ratio of 7-*7-exo-d* and 3 as in the preceding reaction, addition of aqueous HCl in place of DCl in D$_2$O gave almost quantitative yield of 7-*exo*-deuteriated 1 and 7.

Synthesis of 7-(Carboxyethyl)cycloheptatriene. Following the procedure outlined by Linstrumelle,[28] ethyl diazoacetate (5.25 g, 43.8 mmol) was dissolved in 300 mL of anhydrous benzene and transferred to a standard photochemical apparatus (Pyrex glass) equipped with a Hanovia mercury lamp (400 W). The solution was photolyzed at room temperature for 20 h, while a stream of nitrogen via a glass frit at the bottom of the reaction vessel was maintained. The solution was evaporated and fractionally distilled. The fraction boiling at 98–101 °C, at 2.3 mmHg, was collected. ^{1}H NMR analysis showed it to be a mixture of three isomeric cycloheptatrienecarboxylates in the ratio 7-CO$_2$EtC$_7$H$_7$

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[24] Brookhart, M.; Koszalka, G. W.; Nelson, G. O.; Sholes, G.; Watson, R. A. *J. Am. Chem. Soc.* **1979**, *101*, 6115.

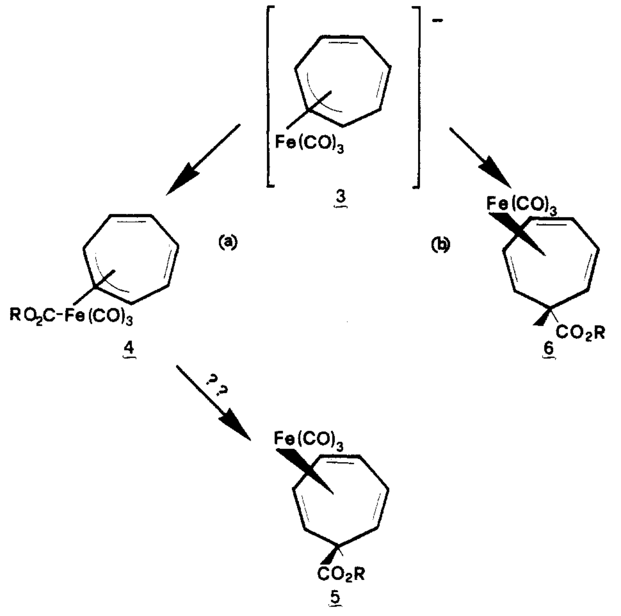
[25] This and the following reactions are based on ethyl chloroformate. Procedures and products of reactions with other chloroformates, described in this paper, are identical.

[26] Kruczynski, L.; Takats, J. *Inorg. Chem.* **1976**, *15*, 3140.

[27] An analogous distribution of products was obtained when the above reaction was carried out by using the Behrens[19] procedure (NaN(SiMe$_3$)$_2$ as a base in benzene) and the same ratio of reagents.

[28] Linstrumelle, G. *Bull. Soc. Chim. Fr.* **1970**, 920.

Scheme I



(62%) to 6-$CO_2EtC_7H_7$ (5%) to 5-$CO_2EtC_7H_7$ (33%).

Reaction of the Isomeric Mixture of Carboxyethyl-Substituted Cycloheptatrienes with Fe(CO)$_3$ Sources. (a) Fe(CO)$_3$(BDA). Treatment of the above mixture of isomeric ester-substituted cycloheptatrienes (2.2 mL) in 120 mL of anhydrous benzene with [Fe(CO)$_3$(BDA)] dissolved in benzene (20 mL) gave, after being stirred at 65 °C for 3 days, a dark solution. Evaporation of the solvent and chromatography of the reddish oily residue gave mostly unchanged starting materials and some free benzylideneacetone. No cycloheptatriene or substituted (cycloheptatriene)carbonyliron complexes were detected.

(b) Photolysis with Fe(CO)$_5$. Filtered iron pentacarbonyl (20 mL) was added to the mixture of ester-substituted cycloheptatrienes immediately after photolysis prior to workup and separation. The solution was photolyzed with a Hanovia (400-W) mercury lamp for 2 days at room temperature. Filtration of the dark red reaction mixture through the glass frit of the apparatus followed by evaporation of the solvent in a rotavapor gave a red oily residue. This material was extracted with petroleum ether and concentrated to 10 mL. Chromatography on Alumina (activity III) with petroleum ether gave two well-separated fractions. The first, orange-red band gave a waxy solid, in poor yield, identified as 7 contaminated by some free ligand. The second, yellow band afforded, after the usual workup, 2 g (59% yield) of pure 8, identified by comparison of its ^{1}H NMR spectrum with that of an authentic sample. The yield of 8 was calculated by assuming that it originated from the corresponding ligand and by isomerization of the [Fe(CO)$_3$(7-$CO_2EtC_7H_7$)] complex.

Results and Discussion

The reaction between [Fe(CO)$_3$(η^3-C_7H_7)]$^-$ (3) and $ClCO_2R$ (R = Me, Et, Bu) gives similar types of products, albeit the relative yields of individual components vary slightly with R. These results appear to rule out changes in reaction pathway as a function of the steric hindrance of the electrophilic chloroformate (Scheme I). So far complexes of type 4 have been obtained only from the reaction of 3 with MPh_3Cl (M = Sn, Pb),[20] yielding (η^3-C_7H_7)Fe(CO)$_3$MPh$_3$. Attempts to promote transfer of the MPh$_3$ group in the latter complexes to the 7-endo-position were unsuccessful. It is notable that although pathway b of Scheme I is the operative mechanism in the present case, we have no evidence for the formation of complex 6. Chromatographic separation of the crude reaction mixture affords, in order of elution, four fractions: (a) [Fe(CO)$_3$(1-4-η-C_7H_8)] (1), (b) [Fe(CO)$_3$(1-4-η-5-$CO_2RC_7H_7$)] (7), (c) [Fe(CO)$_3$(1-4-η-6-$CO_2RC_7H_7$)] (8), and (d) a mixture of isomeric diester-substituted (cycloheptatriene)tricarbonyliron complexes.

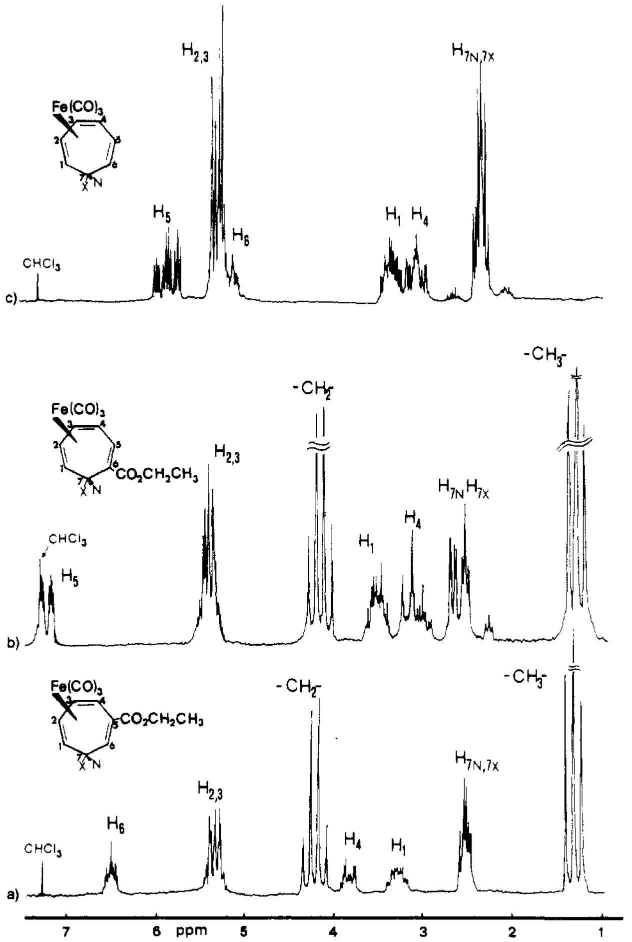


Figure 1. The ^{1}H NMR spectra in $CDCl_3$ solution of (a) [Fe(CO)$_3$(1-4-η-5-$CO_2EtC_7H_7$)] (7), (b) [Fe(CO)$_3$(1-4-η-6-$CO_2EtC_7H_7$)] (8), and (c) [Fe(CO)$_3$(1-4-η-C_7H_8)] (1).

The two isomeric monosubstituted cycloheptatriene complexes 7 and 8 have different physical (Table I) and spectral (Table II) characteristics. The ^{1}H NMR spectra of the complexes clearly shows that they differ only in the position of the $-CO_2R$ substituent on the ring (Table II) and selective decoupling experiments allow unambiguous assignment of their structures. For ease of comparison, the ^{1}H NMR spectra of 1, 7, and 8 (R = Et) are shown in Figure 1. The presence of the electron-withdrawing substituent at C-5 in compound 7 influences the position of the peaks assigned to H_4 and H_7. The resonances now appear at lower fields than the corresponding signals in 1[26,29] and 7-substituted (cycloheptatriene)tricarbonyliron complexes,[8,9,15] and as a result, the relative positions of H_1 and H_4 are reversed. In the isomeric compound 8 the substituent at C-6 produces a downfield shift of ca. 1.5 ppm in the position of H_5 and a greater separation of the methylenic protons H_{7N} and H_{7X} (J_{7N-7X} = 22.7 Hz) which now appear as a well-defined AB quartet further split by H_1 and H_5 and H_1, H_4 and H_5, respectively.

The formation of 7 and 8 contrasts somewhat with the results obtained by Behrens et al.[19] With Na[N(SiMe$_3$)$_2$] as the deprotonating agent, the sodium salt of 3 was reported to react with $ClCO_2R$ (R = Me, Et) with exclusive formation of 8 via isomer 6. The latter was identified as a component of the initial reaction mixture by ^{13}C NMR and IR spectroscopy. The formation of 8 was attributed

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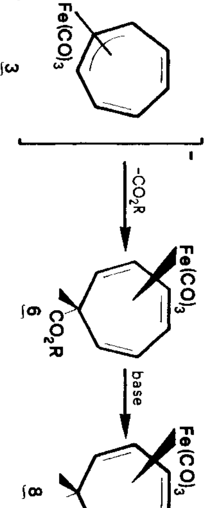
(29) Reference 1, p 51.

Scheme II



to the base-catalyzed isomerization of **6**. In our hands, Behrens' procedure gave the same mixture of products **1**, **7**, **8**, and **11**, as reported above for K[Fe(CO)$_3$(η^3-C$_7$H$_7$)], albeit in slightly different relative yields. Nevertheless, as shown in Scheme II, the initial product of the addition of ClCO$_2$R to **3** should be isomer **6** resulting from attack on the most negatively charged allylic carbon atoms of **3**.

In order to clarify whether the formation of **8** was due to isomerization of the intermediate **6**, caused by the basic reaction medium, we investigated an alternative synthesis of **6**. Photolysis of ethyldiazoacetate with an excess of benzene[28] resulted in a mixture of carbethoxycycloheptatrienes. The isomer composition of the fraction collected was ascertained by ^{1}H NMR spectroscopy and corresponded to 62:5:33 ratio of isomers 7-/6-/5-, respectively. Although the reaction of this mixture with [Fe(CO)$_3$(BDA)] was unsuccessful, irradiation of the isomeric carbethoxy-substituted cycloheptatrienes and excess Fe(CO)$_5$ in benzene gave, after chromatography and usual workup, good yields of **8** (ca. 60%) together with a small amount of **7**. Although 7-carbethoxycycloheptatriene is the major isomer, no traces of complex **6** were detected, confirming its lability.

Nevertheless, the failure in detecting complex **6** in the reaction of **3** with chloroformates and the simultaneous formation of compounds **1**, **7**, **8**, and **11** require some explanation. With this aim we have carried out some additional experiments that in our opinion, elucidate the mechanism of formation of the isolated products and their relative yields.

The observation of **1** cannot be ascribed to an incomplete reaction of **1** with KO-*t*-Bu since the IR spectrum of the reaction mixture in the carbonyl stretching region shows only bands attributable to anion **3** (1942 and 1868 cm^{-1}).[9] Furthermore, **1** is not formed by reaction of unreacted **3** with water during column chromatography. The presence of **1** in the initial reaction mixture prior to chromatography was easily ascertained since H$_5$ of **1** resonates in a region that is free of signals from any other products of the reaction mixture. In addition IR spectroscopy clearly showed that no unreacted **3** remained after the reaction with chloroformates was judged complete. Finally, the production of **1** from back-reaction of **3** with *t*-BuOH, under the new reaction conditions created by the large excess of ClCO$_2$R, can be ruled out also since an analogous reaction with [Fe(CO)$_3$(1–4-η-*exo*-7-DC$_7$H$_7$)][14] in place of **1** did not show incorporation of deuterium in any of the reaction products. Therefore, excluding THF as source of protons,[30] the formation of **1** can be explained only as a consequence of an acid–base reaction between initially formed complex **6** and anion **3** still present at that stage of the reaction (Scheme III). The reaction sequence presented in Scheme III is in agreement with the absence of **6** in the reaction products and with the recovery of **1** in about 50% yield.

Table I. Analytical and IR Data for [Fe(CO)$_3$(1-4-η-CO$_2$EtC$_7$H$_7$)] Complexes 7 and 8

			elemental anal.				IR data[a]		
			calcd		found				
complex	yield, %	mp, °C	C	H	C	H	ν(C≡O)	ν(C=O)	ν(C=C)
7	5	57–59	51.34	3.95	50.98	4.03	2055, 1996, 1984	1725	1648
8	17	63–64	51.34	3.95	51.52	4.02	2057, 1997, 1985	1714	1647

[a] In *n*-hexane solution

Table II. ^{1}H NMR for Complexes [Fe(CO)$_3$(1-4-η-5-CO$_2$RC$_7$H$_7$)] (7) and [Fe(CO)$_3$(1-4-η-6-CO$_2$RC$_7$H$_7$)] (8) in CDCl$_3$

complex	H$_1$	H$_2$	H$_3$	H$_4$	H$_5$	H$_6$	H$_{7N}$	H$_{7X}$	–CH$_2$–	–CH$_3$
7, R = Me	3.15 m	5.24 m	5.27 m	3.74 m		6.42 t of q	2.42 t	2.39 t		3.62 s
7, R = Et	3.26 m	5.34 m	5.38 m	3.81 m		6.50 t of q	2.51 t	2.48 t	4.19 q	1.29 t
coupling consts[a] J, Hz (R = Et)	$J_{1,2}$ = 7.5, $J_{1,3}$ = 4.0, $J_{1,6}$ = 1.4	$J_{2,3}$ = 2.1, $J_{2,4}$ = 3.2	$J_{3,4}$ = 6.6	$J_{4,6}$ = 1.4		$J_{6,7N}$ = 4.1, $J_{6,7X}$ = 4.1	$J_{1,7N}$ = 4.2	$J_{1,7X}$ = 4.2	$J_{CH_2CH_3}$ = 7.1	
7, R = Bu	3.25 m	5.32 m	5.37 m	3.81 m		6.49 m	2.52 t	2.48 t	4.15 m, 1.80–1.15 m	0.97 t
8, R = Me	3.42 m	5.29 m	5.37 m	3.01 m	7.12 d of q		2.60[b]	2.28[b]		3.58 s
8, R = Et	3.49 m	5.35 m	5.41 m	3.09 m	7.19 d of q		2.71[b]	2.39[b]	4.13 q	1.26 t
coupling consts[a] J, Hz (R = Et)	$J_{1,2}$ = 6.5, $J_{1,3}$ = 3.2, $J_{1,4}$ = 0.3	$J_{2,3}$ = 7.0, $J_{2,4}$ = 1.1	$J_{3,4}$ = 6.6	$J_{4,5}$ = 8.8, $J_{4,7X}$ = 0.9	$J_{5,7N}$ = 1.8, $J_{5,7X}$ = 3.0		$J_{7N,7X}$ = 22.7, $J_{1,7N}$ = 5.6	$J_{1,7X}$ = 3.2	$J_{CH_2CH_3}$ = 7.1	
8, R = Bu	3.49 m	5.33 m	5.40 m	3.19 m	7.19 d of q		2.69[b]	2.37[b]	4.07 m, 1.76–1.15 m	0.95 t

[a] Coupling constants have been obtained from selective decoupling and optimization via simulation of the spectra. Coupling constants for R = Me or R = Bu are identical with those for R = Et or differ by less than 0.2 Hz. [b] AB system further split.

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(30) THF-d_8 solution of anion 3, under rigorously purified nitrogen atmosphere, shows the same ^{1}H NMR spectrum after hours at room temperature.

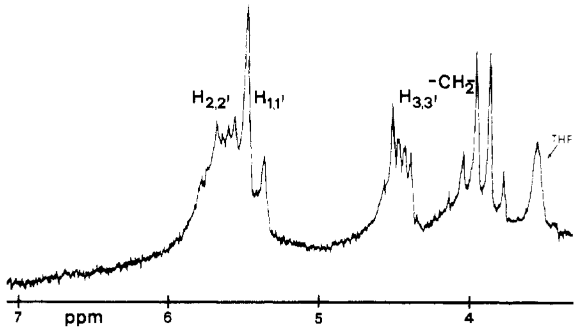
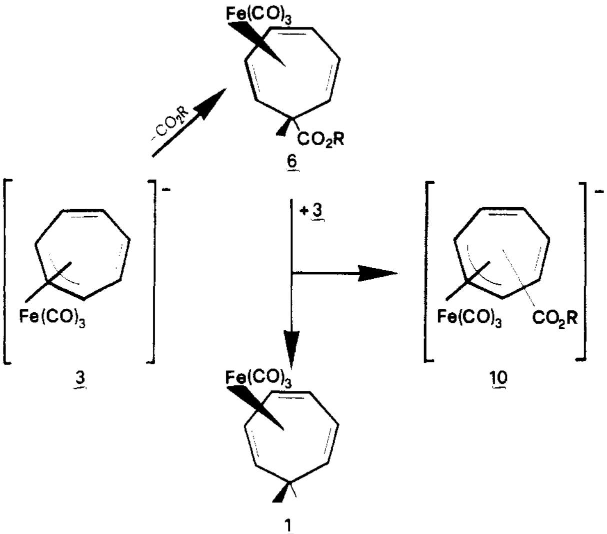


Figure 2. The ^{1}H NMR spectrum in THF-d_8 solution of the anion $[Fe(CO)_3(\eta^3\text{-}CO_2EtC_7H_6)]^-$ (10).

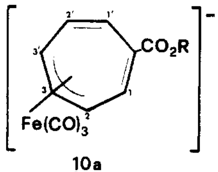
Scheme III



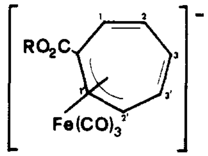
From the above considerations it is clear and in accord with expectations that **3** is a stronger base than **10** or conversely **6** is a stronger acid than **1**.[31]

The IR spectrum of the deep red THF solution resulting upon addition of KO-*t*-Bu to **8** shows two broad bands in the carbonyl stretching region at 1971 and 1899 cm^{-1}.[32] It is indicative of a negatively charged complex. The ^{1}H NMR spectrum (Figure 2), in THF-d_8 at room temperature, shows three groups of signals at 5.68, 5.45, and 4.47 ppm in addition to a quartet at 3.92 ppm (CH_2) and a triplet at 1.16 ppm (CH_3, $J_{CH_2-CH_3}$ = 7.14 Hz); the latter is partially obscured by the protons of *tert*-butyl alcohol. Decoupling experiments indicate that the multiplets at 4.47 and 5.68 ppm and the resonances at 5.45 and 5.68 ppm are coupled together. However, there is little or no coupling between the peaks at 4.47 and 5.45 ppm. As the temperature is lowered, all signals broaden and disappear in the base line at 191 K. The same results are obtained by treating **7** with KO-*t*-Bu in THF.

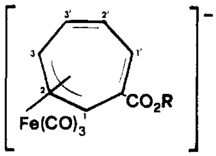
The structure of anion **10** cannot be established. Although the variable-temperature ^{1}H NMR spectrum is not indicative of a fluxional process since broadening might be due to viscosity and ion-pairing effects at low temperature, all the anions of this type so far reported[15-17,20,21] show fluxional behavior, as structures **10a**, **10b**, and **10c** should do. Moreover only structure **10d** is expected to be nonfluxional and consistent with the symmetric room-temperature spectrum of Figure 2.



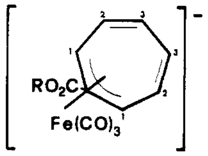
10a



10c



10b



10d

According to extension of the rules developed to rationalize the nucleophilic addition to cationic complexes of unsaturated hydrocarbons,[33] attack of the electrophile on complexes of type **10** is expected to occur at the terminal allylic carbons (C_2 and $C_{3'}$ in **10a**, C_1 and C_3 in **10b**, $C_{2'}$ in **10c**, and C_1 in **10d**). Indeed none of the complexes having the $-CO_2R$ group at the coordinated olefinic carbon atoms have been detected. This observation rules out the possibility of structures **10c** and **10d**. In our case the addition seems to occur preferentially at the terminal allylic carbon atom closer to the carboalkoxy substituent. Such preferential attack, at variance with the formation of both products[21] in the addition of H^+ (or D^+) to $[Fe(CO)_3(\eta^3\text{-}C_7H_6GePh_3)]^-$, could be related to the electron-withdrawing ability of the $-CO_2R$ group that would compete with the metal center for the electron density of the coordinated diene fragment. Nevertheless, it is clear that the same anion **10** is obtained whether **7** or **8** is deprotonated with KO-*t*-Bu or with the anion **3**. The same ^{1}H NMR spectrum as well as identical chemical reactivity behavior is observed. It is interesting to note that, whereas the reaction of **10** with $ClCO_2R$ affords **7**, **8**, and **11**, quantitative and exclusive formation of **7** is seen in the reaction with H^+ (or D^+).

Irrespective of the structure of **10** (**10a** or **10b** or an equilibrium mixture of **10a** and **10b**), progress of the reaction is very likely through further addition of excess of chloroformate to **10** to give disubstituted neutral complexes **11**,[34] which become the source of protons for unreacted **10** to give **7** and **8** and a disubstituted anion (**12**). The limitative basicity of **12** might inhibit further addition of chloroformate. Indeed trisubstituted neutral complexes were not detected in the reaction or by treating anion **10** with chloroformate.

Conclusion

The results presented indicate that endo deprotonation of 7-exo-substituted (cycloheptatriene)tricarbonyliron is

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[31] A qualitative confirmation of this statement can be obtained from the following comparative experiments: (a) The dark red color of a THF solution of **3**, under nitrogen atmosphere, turns immediately yellow (formation of **1**) upon addition of deaerated water, whereas subjected to the same conditions the red color of **10** lasts for hours. (b) A CH_3OD solution of **1** in the presence of $NaOCH_3$ is yellow, whereas that of **8** is a red. Although this experiment cannot be performed with **6**, it is reasonable to consider the acidic character of H_7 in **6** comparable (very likely higher) to that of H_7 in **8**.

[32] The shift toward higher frequency compared to **3** is in agreement with the decreased negative charge on the metal and therefore decreased back-bonding to coordinated carbon monoxide in the carbethoxy-substituted complex.

[33] Davies, S. G.; Green, M. L. H.; Mingos, D. M. P. *Tetrahedron* **1978**, *34*, 3047.

[34] The ^{1}H NMR spectrum of the product obtained from the fourth chromatographic fraction shows partial superposition of CH_2 quartets and CH_3 triplets together with smaller peaks in the low- and high-field regions whose individual integration is less than 1 H, taking the area of the CH_2 resonances as 4 H. Although complicated, the ^{1}H NMR spectrum of the mixture of compounds **11** appears to rule out the presence of complexes bearing $-CO_2R$ substituents at the coordinated olefinic carbons.

a facile process when the substituent is an electron-withdrawing group. Functionalization of cycloheptatriene in these cases is directed at carbon 5 or 6, with carbon 6 being favored. However, exclusive formation of 5-substituted complexes can be achieved by isomerization of **8** to **7** via deprotonation of **8** to **10** and subsequent reprotonation of the resulting anion. Functionalization of cycloheptatriene at carbons 5 and 6 has few precedents in the literature.[35] The available organic synthetic methods invariably produce a mixture of isomers that are difficult to separate.[28] Use of other cycloheptatrienyl metal complexes allows functionalization of the ring at the C-7 position, usually by nucleophilic addition to cationic complexes.[36] Our results may therefore be of interest for specific functionalization of the cycloheptatriene ring at the C-5 and/or C-6 position and thereby increase the scope of metal complexes in organic synthesis.[37] The disengagement of the $Fe(CO)_3$ group is indeed a well-documented and easy reaction.[38]

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Registry No. **1**, 36343-88-1; **3**, 75663-01-3; **7** (R = Et), 106095-07-2; **7** (R = Me), 106095-10-7; **7** (R = Bu), 106095-11-8; **8** (R = Et), 106095-08-3; **8** (R = Me), 106095-12-9; **8** (R = Bu), 106095-13-0; **10** (R = Et), 106114-70-9; **11** (R = Et), 106095-09-4; $Fe(CO)_3(BDA)$, 38333-35-6; $Fe(CO)_5$, 13463-40-6; 7-$CO_2EtC_7H_7$, 27332-37-2; 6-$CO_2EtC_7H_7$, 27332-40-7; 5-$CO_2EtC_7H_7$, 27332-38-3; $ClCO_2Et$, 541-41-3; $ClCO_2Me$, 79-22-1; $ClCO_2Bu$, 592-34-7; ethyl diazoacetate, 623-73-4; benzene, 71-43-2.

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Synthesis and Thermolysis of Dimethylbis(trialkylphosphine)platinum(II) Complexes in Which the Phosphine Ligands Contain Adamantyl, Adamantylmethyl, and Methyl Groups[1]

Marifaith Hackett and George M. Whitesides*

Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138

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This paper describes syntheses of (1-adamantylmethyl)dimethylphosphine (**1**), bis(1-adamantylmethyl)methylphosphine (**2**), tris(1-adamantylmethyl)phosphine (**3**), 1-adamantyldimethylphosphine (**4**), di-1-adamantylmethylphosphine (**5**), and the platinum complexes L_2PtMe_2 (**7**, L = **1**; **8**, L = **2**; **9**, L = **4**). Thermal decomposition of **7** and **8** yields cyclometalated products; **9** decomposes by a complex, poorly defined route. The paper discusses factors that render phosphines susceptible to intramolecular reactions.

Introduction

Although platinum complexes react intramolecularly with the C–H bonds of coordinated ligands, no example of *intermolecular* C–H bond activation by soluble platinum complexes has been reported. In contrast, other transition metal,[2–7] lanthanide,[8] and actinide[9] complexes react with both saturated and unsaturated hydrocarbons. This lack of *intermolecular* reactivity on the part of platinum is due primarily to the facility of the competing *intramolecular* reactions. Metallacycle formation,[10] β-

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