of $[C_5H_5Fe(CO)_3]^+$ to give the isocyanate derivative, whereas in the less polar THF, attack by isocyanate was shown clearly by the use of labeled NCO^- to involve direct attack at the metal atom with displacement of CO.[20] Finally, the soft nucleophile iodide gives direct metal attack and formation of the corresponding $BFe(CO)_2I$ ($B = C_6H_7$, C_7H_9)[21] although this occurs in a polar solvent (acetone). In the case of cyclohexadienyliron tricarbonyl cation, soft nucleophiles, except iodide, give ring attack as the final product[22,23] but there is some evidence of carbonyl attack by the hard alkoxide nucleophile.[24] The behavior of the seven-membered ring cation is discussed fully in the following paper, but in summary only metal attack is observed for the iodide ion and a range of substituted hydrazines. For the azide ion, there is an indication of initial metal interaction followed by ring addition to give the stable 5-exo product;[25] however, the reaction with alkoxide ions provides a clear example of the dangers of using the formation of a thermodynamically stable product to infer the site of initial attack. At room temperature, the stable 5-exo ring alkoxy addition product is formed. However, reaction at lower temperatures gives an indication of initial metal interaction followed by carbonyl attack and formation of the dicarbonyl carboalkoxy derivative, which rearranges by a dissociative mechanism to the 5-exo ring product on raising the temperature.[26] Finally, the reaction with phosphines yields either the 5-exo or 5-endo ring product, depending on the steric requirements of the phosphine and solvent polarity. In polar solvents there is again an indication of metal interaction both during substitution and during interconversion of the exo and endo isomer (see the following paper).

It is clear that the prediction of the site of initial attack in these carbonyl complexes is a difficult matter, but the above application of perturbation theory provides a rational theoretical framework in which to discuss the very varied behavior exhibited by these systems.

Registry No. $C_6H_6Cr(CO)_3$, 12082-08-5; $C_5H_5Mn(CO)_3$, 12079-65-1; $C_4H_4Fe(CO)_3$, 12078-17-0; $C_3H_5Co(CO)_3$, 12144-85-3; $[C_5H_5Fe(CO)_3]^+$, 32660-74-5; $[C_6H_7Fe(CO)_3]^+$, 49654-90-2; $[C_7H_9Fe(CO)_3]^+$, 46238-85-1.

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Nucleophilic Substitution and Addition Reactions of the Tricarbonyl(η-1,5-cycloheptadienylium)iron Cation

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The substitution pattern for nucleophilic attack on the tricarbonyl(η-1,5-cycloheptadienylium)iron cation is reported for a series of nucleophiles. Amines attack the ring directly to give 5-exo ring products with no evidence of preliminary interaction at either the metal or the carbonyl carbon atom. Alkoxides give carbonyl attack at low temperatures with formation of carbalkoxy derivatives, which rearrange spontaneously as the temperature is raised to give 5-exo ring alkoxy derivatives. By "tuning" the nucleophilicity of substituted hydrazines it is possible to obtain either metal or carbonyl carbon substituted derivatives. Finally, by careful choice of both phosphine and solvent, both the 5-exo and the 5-endo phosphine ring adducts are obtained. The substitution pattern is discussed in terms of the perturbation theory of reactivity of the preceding paper.

Introduction

The preceding paper[1] discussed the application of the perturbation theory of reactivity[2] to the substitution and addition reactions of two series of (polyene)metal carbonyl complexes, first, the neutral $AM(CO)_3$ series ($AM = C_6H_6Cr$, C_5H_5Mn, C_4H_4Fe, C_3H_5Co, or C_2H_4Ni) and, second, the cationic $[BFe(CO)_3]^+$ series ($B = C_5H_5$, C_6H_7, or C_7H_9). Behavior contrasting to nucleophilic substitution was predicted for the two series. In the former case, substitution by a hard or very soft nucleophile was predicted to involve initial metal attack with no crossover for the chromium and manganese complexes in the curves of ΔE (calculated interaction energies) against $\log \epsilon$ (ϵ = dielectric constant of solvent) between the metal and carbonyl carbon atoms. In no case was initial ring attack predicted for a hard nucleophile whereas the curves for a soft nucleophile such as iodide or phosphine generally indicated ring attack.

In contrast, in the case of attack by a hard nucleophile the cationic series gave much smaller differences between ΔE(metal) and ΔE(carbonyl) with a crossover occurring between these quantities as ϵ increases. Thus the theory predicts for the cations that a hard nucleophile may give initial attack at either the metal atom or carbonyl carbon depending on reaction conditions. Attack by a soft nucleophile is predicted in the sequence

$$\text{ring} > \text{carbonyl} > \text{metal}$$

although initial metal attack may occur in solvents of low polarity. In this paper, we compare the above theoretical predictions with experimental studies of the substitution and addition reaction products of the tricarbonyl(η-1,5-cycloheptadienylium)iron cation for a wide range of nucleophiles.

In general, (cyclic diene)metal carbonyl complexes such as the title compound (I) and the closely related tricarbonyl(η^5-cyclopentadienyl)- and tricarbonyl(η^5-cyclohexadienyl)iron cations may undergo nucleophilic attack at the diene ring,[3]

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the metal atom,[3] or the carbonyl group.[4] In the case of ring attack, the 5-exo product is normally obtained[5] and only very rarely is endo substitution observed[6] so it is generally concluded that in ring substitution or addition the nucleophile approaches the polyene ring on the side opposite from the metal tricarbonyl group, without any involvement of the latter; however, care must be exercized with this argument because if kinetically controlled the initial attack may not lead directly to the thermodynamically stable product; for example, substitution of the title compound (I) by a hard nucleophile such as ethoxide at low temperatures gives the carbethoxy derivative, $C_7H_9Fe(CO)_2(CO_2Et)$, which when the temperature is raised rearranges by a dissociative mechanism to give the 5-exo ring-substituted ethoxy compound $C_7H_9OEtFe(CO)_3$.[7] Recently, it has been shown that for the analogous cyclohexadienyl complexes the 5-endo-methoxide isomer can also be obtained provided the formation of the exo isomer is reversible in the presence of acid and the endo form possesses sufficient thermodynamic stability.[8] Nucleophilic attack at the metal is clearly observed with the iodide ion, and the resulting metal iodide is the stable product;[3] similar behavior occurs with isocyanate.[9] Nucleophiles of intermediate "hardness" such as hydrazines and amines attack at a carbonyl carbon atom of the tricarbonylcyclopentadienyliron cation; in the former case, the carbazoyl intermediates rearrange to form stable metal isocyanates[10] whereas amines form the carboxamide complexes $C_5H_5Fe(CO)_2(CONHR)$.[11] In this paper, we show that for the title seven-membered ring complex it is possible by changing the nucleophilicity of the hydrazine by substitution to vary the point of attack from the metal atom to a carbonyl carbon atom. In contrast, amines attack the ring directly with no evidence for preliminary interaction at either the metal or the carbonyl carbon atom. Finally, by careful choice of both phosphine and solvent, it is possible to obtain both the 5-endo- and the 5-exo-phosphine-substituted isomers with the former possibly being formed via a metal-assisted pathway.

Experimental Section

General Information. Reagent grade chemicals were used without further purification. All solvents were dried and deoxygenated before use. Reactions and workup including chromatography were carried out under oxygen-free nitrogen. Infrared spectra were recorded on Perkin-Elmer 337 and 283 spectrophotometers. ^1H NMR spectra were recorded on a Perkin-Elmer R12B or a JEOL PS100 spectrometer. ^{13}C NMR spectra were recorded on a JEOL PS100 FT spectrometer. UV spectra were recorded on Perkin-Elmer 402 and 552 spectrometers. Microanalyses were performed by the microanalytical laboratory of this department.

Preparation of Carbalkoxy Products, $C_7H_9Fe(CO)_2(CO_2R)$. A typical preparation is as follows. Slow addition of the title compound, $[C_7H_9Fe(CO)_3]BF_4$ (1.06 g, 3.31 mmol), to a well-stirred, ice-cooled NaOEt solution (3.25×10^{-3} mol of Na) in 20 mL of EtOH gave a red color (λ_{max} 470 nm). After it was stirred for 10 min at 0 °C, the pale orange solution was evaporated to dryness, the resulting residue extracted three times with petroleum ether (60–80° C), and the extract washed with degassed cold water and dried with $MgSO_4$. After evaporation of the ether, solution in pentane, concentration, and cooling gave pale yellow crystals: 0.51 g, 55%; mp 56 °C dec. Anal. Calcd for $C_{12}H_{14}FeO_4$: C, 51.80; H, 5.04. Found: C, 51.48; H, 5.03.

Similar methods were employed to obtain corresponding methyl and isopropyl derivatives (see Table I). All the carbalkoxy derivatives should be stored at low temperatures.

Rearrangement to the 5-Exo Product. A typical rearrangement is as follows. $C_7H_9Fe(CO)_2(CO_2Et)$ (0.100 g, 0.36 mmol) in 5 mL of hexane was kept under nitrogen for 12 h and the solution filtered through $MgSO_4$; after concentration and cooling, the filtrate gave a quantitative yield of 5-*exo*-$C_7H_9OEtFe(CO)_3$. This rearrangement in deoxygenated $CHCl_3$ under nitrogen was followed on the JEOL PS100 NMR spectrometer by the rate of growth of the H(2,3) protons at 5.35 ppm due to formation of the ring product and the identical rate of disappearance of the H_3 protons at 6.35 ppm of the carbalkoxy derivative with use of the data-handling system of the above instrument. First-order plots of logarithms of integrated intensities vs. time were obtained.

Rearrangement in the Presence of Added Nucleophile. For example, $C_7H_9Fe(CO)_2CO_2Me$ (0.20 g, 0.76 mmol) was reacted with a fivefold excess of ethanol in 25 mL of $CHCl_3$ under nitrogen at room temperature for 15 h. After evaporation of solvent, solution in pentane, and filtration through $MgSO_4$, pale yellow crystals of 5-*exo*-$C_7H_9OEtFe(CO)_3$ were obtained on concentration and cooling. In contrast, reaction of 5-*exo*-$C_7H_9OMeFe(CO)_3$ (0.31 g, 1.19 mmol) with a fivefold excess of ethanol under the same conditions gave only the unreacted starting compound on workup.

Preparation of the Isocyanate Compound $C_7H_9Fe(CO)_2NCO$. The title compound, $[C_7H_9Fe(CO)_3]BF_4$ (0.52 g, 1.62 mmol), was added to hydrazine hydrate (0.17 g, 3.36 mmol) dissolved in 15 mL of CH_2Cl_2 cooled in an ice–salt bath and shaken vigorously for 5 min. Extraction with 20 mL of ether and removal of solvents gave a reddish brown oil, which was left under reduced pressure for 4 h, washed with pentane, and dissolved in CH_2Cl_2. Chromatography through a 6-in. Florisil (60/100) column and elution of the dark yellow band, removal of solvent, and recrystallization from acetone–ether gave brownish orange crystals (0.20 g, 49.6%), decomposing above 120 °C, of $C_7H_9Fe(CO)_2NCO$. Anal. Calcd for $C_{10}H_9FeO_3N$: C, 48.58; H, 3.64; N, 5.67. Found: C, 48.74; H, 4.10; N, 6.08.

Attempted Preparation of the Carbazoyl Compound $C_7H_9Fe(CO)_2CONHNH_2$. The above preparation was repeated, but after extraction with cold ether the solvent was rapdily removed to give a yellow unstable residue, which gave analyses about 1% from the theoretical for the carbazoyl derivative. However, an infrared spectrum (Fluorolube mull) of a fresh sample gave a broad band at 1622 cm^{-1} and two prominent peaks at 1617 and 1591 cm^{-1} with the presence of a carbazoyl derivative. In the metal carbonyl region a sharp band at 2020 cm^{-1} (in CH_2Cl_2) diminished in intensity as the isocyanate band of $C_7H_9Fe(CO)_2NCO$ at 2228 cm^{-1} increased.

Preparation of the Metal–Substituted-Hydrazine Complexes $[C_7H_9Fe(CO)_2NH_2NR_2]BF_4$ (R = $PhCH_2$, *p*-$MeOC_6H_4CH_2$, *p*-$NO_2C_6H_4CH_2$). A typical preparation is as follows. The title compound $[C_7H_9Fe(CO)_3]BF_4$ (0.64 g, 2 mmol) was stirred at room temperature in 100 mL of CH_2Cl_2 for 7 h with a slight excess of $(PhCH_2)_2NNH_2$ (0.45 g, 2 mmol). Subsequent removal of solvent, repeated washings with 10-mL portions of dry pentane, and recrystallization from CH_2Cl_2–pentane gave yellow crystals (0.84 g, 84%), mp 97 °C dec, of $[C_7H_9Fe(CO)_2NH_2N(CH_2Ph)_2]BF_4$. Anal. Calcd for $C_{23}H_{25}FeO_2N_2BF_4$: C, 54.78; H, 4.96; N, 5.56; F, 15.09. Found: C, 54.29; H, 5.00; N, 5.93; F, 15.44.

Preparation of Substituted Benzylhydrazines. *N,N*-Dibenzylhydrazine was prepared by an improved method of Dewar et al.,[12] the *p*-nitrobenzyl derivative by the method of Carpino[13] followed on a reduced scale, and the *p*-methoxybenzyl derivative according to the method of Iorio and Landi-Vittory.[14]

Preparation of Amine Adducts $[C_7H_9RNH_2Fe(CO)_3]BF_4$ and $[C_7H_9R_2NHFe(CO)_3]BF_4$. These are formed by primary and secondary aliphatic amines and by pyridine. A typical preparation is as follows. To a slight excess of the title compound $[C_7H_9Fe(CO)_3]BF_4$ (0.64 g, 2 mmol) in 30 mL of CH_2Cl_2 was added *n*-$PrNH_2$ (0.11 g, 1.83 mmol) and the mixture stirred at room temperature for 30 min. After removal of solvent and washing with pentane, crystallization from pentane–CH_2Cl_2 gave a white microcrystalline product (0.73 g, 94%),

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mp 123 °C, of [C_7H_9*n*-$PrNH_2Fe(CO)_3$]BF_4. Anal. Calcd for $C_{13}H_{18}FeNO_3BF_4$: C, 41.18; H, 4.75; N, 3.70. Found: C, 40.73; H, 4.62; N, 3.63 (Table I).

Preparation of Neutral 5-Exo Substitution Derivatives $C_7H_9RNHFe(CO)_3$ and $C_7H_9R_2NFe(CO)_3$. These are formed by primary and secondary aliphatic and *aromatic* amines. A typical preparation is as follows. A twofold excess of *n*-$PrNH_2$ (0.249 g, 4 mmol) was added to [$C_7H_9Fe(CO)_3$]BF_4 (0.64 g, 2 mmol) in 40 mL of CH_2Cl_2 and the mixture stirred at room temperature for 20 min. After removal of solvent and excess amine by vacuum pump, extraction with dry pentane and evaporation of solvent gave a yellow oil, [C_7H_9*n*-$PrNHFe(CO)_3$]. Anal. Calcd for $C_{13}H_{17}FeNO_3$: C, 53.61; H, 5.84; N, 4.81. Found: C, 53.72; H, 6.13; N, 4.68.

In the case of aniline and *N*-methylaniline similar deprotonated products were obtained by the above method although much larger mole ratios (e.g., 7:1) of amine:starter cation were required. In the case of *N*-methylaniline, chromatography of the reaction mixture gave both the adduct and (cycloheptatriene)iron tricarbonyl. Similarly, *N*,*N*-dimethylaniline gave only the triene complex as product.

Preparation of the 5-Exo Phosphonium Adducts [$C_7H_9PR_3Fe(CO)_3$]BF_4, R = Et, *n*-Pr, *n*-Bu, Ph, [$C_7H_9PRPh_2Fe(CO)_3$]BF_4, R = Me, Et, and [$C_7H_9PR_2PhFe(CO)_3$]BF_4, R = Me, Ph. To a stirred slurry of the title compound [$C_7H_9Fe(CO)_3$]BF_4 (0.64 g, 2 mmol) in 25 mL of CH_2Cl_2 was added PEt_3 (0.24 g, 2 mmol) with a microsyringe via a serum cap with immediate formation of a clear yellow solution. After it was stirred for 30 min at room temperature and solvent volume was reduced to about 5 mL, the solution was added dropwise through a sintered-glass funnel to 100 mL of pentane with stirring. Pale yellow crystals of [$C_7H_9PEt_3Fe(CO)_3$]BF_4, were collected, washed with pentane, dried, and recrystallized from CH_2Cl_2–pentane (0.82 g, 93.5%); mp 123–125 °C. Anal. Calcd for $C_{16}H_{24}FeO_3PBF_4$: C, 43.87; H, 5.48; F, 17.36. Found: C, 43.90; H, 5.43; F, 17.01.

Preparation of the 5-Endo Phosphonium Adducts [$C_7H_9PR_3Fe(CO)_3$]BF_4, R = Et, *n*-Pr, *n*-Bu, and [$C_7H_9PR_2PhFe(CO)_3$]BF_4, R = Me. The title compound, [$C_7H_9Fe(CO)_3$]BF_4 (0.45 g, 1.41 mmol), was covered with PEt_3 (0.20 g, 1.69 mmol) and 50 mL of CH_3CN added with immediate stirring. A faint red color appeared within 5 min, and after 30 min the solvent was removed in vacuo, leaving a dark red product. After it was washed a number of times with pentane (10 mL), dissolved in 5 mL of CH_3CN, and filtered through sintered glass, addition dropwise to 100 mL of ether gave a brown product (0.42 g, 67%) of 5-*endo*-[$C_7H_9PEt_3Fe(CO)_3$]BF_4, mp 72–74 °C. Anal. Calcd for $C_{16}H_{24}FeO_3PBF_4$: C, 43.4; H, 5.48; F, 17.34. Found: C, 43.80; H, 5.72; F, 17.61.

Results and Discussion

Substitution by Alkoxide. Reaction of the title compound (I) at 0 °C with a slight excess of alkoxide ion OR^- (R = Me, Et, or *i*-Pr) gave an initial red color and rapid formation of the corresponding carbalkoxy complexes $C_7H_9Fe(CO)_2(COOR)$ (II), all of which show two IR metal–carbonyl stretching bands and a normal carbonyl peak at about 1650 cm^{-1} (Table I) in agreement with the above formulation, which is also supported by the low-field ^1H NMR multiplet for H_3 at about τ 3.65–3.90 (Table II). The spectral features are very similar to those reported for the analogous (carbomethoxy)cyclohexadienylosmium dicarbonyl, $C_6H_7Os(CO)_2(COOMe)$.[15] The initial red color (λ_{max} 470) is ascribed to an interaction between the nucleophile and the metal atom by analogy with the observed visible absorption in $C_7H_9Fe(CO)_2I$ (λ_{max} 485 nm). However, these carbalkoxy complexes are not thermodynamically stable, and when the temperature is raised, they rearrange spontaneously both in the solid state and in solution to give the corresponding 5-exo ring-substituted product. It is possible to distinguish between the exo and endo configuration of the H_5 proton by proton NMR. In 5-*exo*-anilino(cyclohepta-1,3-diene)iron tricarbonyl),[15] H_5 forms part of an ABX system (X corresponding to H_5) and occurs as a double doublet with $J_{5,6\text{-endo}}$ = 3.7 Hz and $J_{5,6\text{-exo}}$ = 10.7 Hz. In addition, $J_{4,5}$ is zero. However, in the corresponding 5-endo-anilino system, H_5 is a portion of an ABXYZ system (H_5 is now coupled to H_4) and its signal width is considerably narrowed as compared with that for the 5-exo case, a small plateau resulting at maximum intensity. Our methoxy and ethoxy products are clearly shown to be 5-exo; e.g., with the 5-ethoxy group, $J_{5,6\text{-endo}}$ = 4 Hz, $J_{5,6\text{-exo}}$ = 11 Hz, and $J_{4,5}$ = 0 (see Table II). The rearrangement of both the carbomethoxy and carboethoxy compounds proceed by a first-order process as followed by ^1H NMR ($CDCl_3$), indicating a dissociative mechanism with loss of OR^- and subsequent ring addition giving the exo product. A dissociative mechanism was confirmed by the carrying out of the rearrangement in the presence of another nucleophile, HOR′, and formation of the corresponding 5-exo derivative as main product and also by the fact that reactions between the carbethoxy derivative and tri-*n*-butylphosphine as added nucleophile gave the 5-exo-tri-*n*-butylphosphine adduct as major product. Independent experiments proved that the 5-exo adducts did not interconvert on treatment with added nucleophile.

Reaction with Hydrazines. There have been no previous reports of the reactions of hydrazines with the title compound. In the case of unsubstituted hydrazine hydrate, reaction in CH_2Cl_2 at −10 °C proceeds with an initial red color followed by formation of the intermediate carbazoyl complex $C_7H_9Fe(CO)_2(CONHNH_2)$ as evidenced by the two infrared absorption bands at 1617 and 1591 cm^{-1} due to a carbonyl mode and a δ(NH) bending mode, respectively, closely similar to those reported for the analogous cyclopentadienyl derivative.[10] Attempts to isolate the carbazoyl intermediate were only partially successful, but rapid workup gave a yellow product with approximate micranalysis (1–2% error). When the temperature is raised to 0 °C, the carbazoyl intermediate undergoes a Curtius rearrangement with formation of the isocyanate derivative $C_7H_9Fe(CO)_2NCO$ as the final stable product (Table I). Its structure was confirmed by terminal C–O IR stretching modes at 2041 and 1975 cm^{-1} and an asymmetric ν(NCO) stretch at 2202 cm^{-1}. The ^1H NMR spectrum shows clearly the presence of the ring proton and absence of any hydrazinic protons as observed in the products formed by carbonyl replacement on reaction with substituted hydrazines below.

With an increase of the nucleophilicity of the hydrazine by the introduction of benzyl substituents, e.g., $NH_2N(PhCH_2)_2$, formation of the hydrazine-substituted derivative [$C_7H_9Fe(CO)_2NH_2N(PhCH_2)_2$]$BF_4$ occurs (Table I). The structure was confirmed by the presence of terminal C–O stretching modes at 2051 and 1984 cm^{-1}, a bending δ(NH) mode at 1589 cm^{-1}, terminal NH_2 modes in the 3000–3500 cm^{-1} region, and ν(BF) at 1055 cm^{-1} (Table I).

The ^1H NMR spectra gave further confirmation of this structure. Similar products were obtained with para-substituted benzyl hydrazines, $NH_2N(CH_2C_6H_4$-*p*-$R)_2$ (R = MeO, NO_2), with the rate of reaction lying in the order *p*-MeO > H > *p*-NO_2 in accord with increasing electron donation of the para substitutent increasing the nucleophilicity of the hydrazine and hence the rate of reaction. There was *no* infrared evidence for formation of any intermediate (e.g., carbazoyl) formed by initial attack at the carbonyl carbon atom, suggesting direct metal attack as the reaction pathway (a red color was again present during the reaction). It thus appears possible to vary the reaction pathway in accord with theoretical predictions by "tuning" the nucleophilicity of the attacking hydrazine.

Substitution by Amines. In the case of reaction with amines no evidence was obtained for initial attack at either the metal or a carbonyl carbon atom; e.g., no transient red colors were observed and no infrared absorption in the 1500–1700 cm^{-1} region was observed during the course of reaction even at low temperatures. Although only ring attack is observed, the

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Table I. Decomposition Temperatures, Analyses, and IR Spectra of Carbalkoxyl, 5-Exo-Alkoxy, Isocyanate and Hydrazine, 5-Exo- and 5-Endo-Phosphine, 5-Exo-Amine, and 5-Exo-Deprotonated Amine Derivatives of Cycloheptadienyliumiron Tricarbonyl

R	dec pt, °C	Anal. found (calcd)				IR spectra, cm^{-1}			
		% C	% H	% N	% F	ν(CO)	$\nu(BF_4)$	ν(NH)	δ(NH)
$C_7H_9Fe(CO)_2(COOR)$									
MeO	53	49.69 (50.00)	4.82 (4.55)			2083,^{a} 1656^a 1991,^{a} (ester)			
EtO	56	51.48 (51.80)	5.30 (5.04)			2032,^{a} 1650^a 1988,^{a} (ester)			
i-PrO	oil	53.23 (53.42)	5.22 (5.48)			2032,^{a} 1649^a 1986,^{a} (ester)			
5-*exo*-$RC_7H_9Fe(CO)_3$									
MeO	oil	49.60 (50.00)	4.68 (4.55)			2050,^{a} 1980^a			
EtO	45	51.68 (51.80)	5.05 (5.04)			2045,^{a} 1980^a			
i-PrO	oil	52.71 (53.42)	5.11 (5.48)			2048,^{a} 1980^a			
$C_7H_9Fe(CO)_2R$									
NCO	120	48.74 (48.54)	4.10 (3.64)	6.08 (5.67)		2228^b (ν(NCO))			
$[C_7H_9Fe(CO)_2NH_2N(CH_2R)_2]BF_4$									
Ph	96	54.29 (54.78)	5.00 (4.96)	5.93 (5.56)	15.44 (15.09)	2051,^{b} 1984^b	1055^d	3354, 3290	1589 w^e
p-$NO_2C_6H_4$	108	46.77 (46.48)	4.37 (3.87)	9.72 (9.43)	13.01 (12.80)	2045,^{b} 1971^b	1045^d	3280	1588 w^f
p-$MeOC_6H_4$		49.54 (50.01)	5.29 (5.50)	4.78 (4.67)	12.15 (12.64)	2061,^{b} 1986^b	1033^d	3335, 3282	1583 w^d
$[5\text{-}RC_7H_9Fe(CO)_3]BF_4$									
exo PEt_3	125	43.90 (43.87)	5.43 (5.48)		17.01 (17.36)	2059,^{b} 1989^b	1085^c		
endo PEt_3	74	43.80 (43.87)	5.72 (5.48)		17.61 (17.36)	2051,^{b} 1987^b	1084^c		
exo P-*n*-Pr_3	154	47.21 (47.52)	6.46 (6.25)		15.51 (15.84)	2058,^{b} 1988^b			
endo P-*n*-Pr_3	87	47.09 (47.52)	6.72 (6.25)			2053,^{b} 1984^b			
exo P-*n*-Bu_3	114	50.54 (50.59)	7.14 (6.90)		14.26 (14.56)	2059,^{b} 1990^b	1085^c		
endo P-*n*-Bu_3	91	50.80 (50.59)	7.21 (6.90)		14.84 (14.56)	2055,^{b} 1986^b	1085^c		
exo PMe_2Ph	117	47.03 (47.16)	4.67 (4.37)		16.57 (16.60)	2056,^{b} 1987^b	1086^c		
endo PMe_2Ph	45	47.22 (47.16)	4.77 (4.37)		16.68 (16.60)	2056,^{b} 1988^b	1084^c		
exo $PEtPh_2$	160	54.24 (53.95)	4.75 (4.50)		14.50 (14.24)	2058,^{b} 1986^b			
exo PPh_3		57.71 (57.75)	4.08 (4.13)		13.46 (13.05)	2058,^{b} 1985^b			
[5-*exo*-$RHC_7H_9Fe(CO)_3]BF_4$									
n-PrNH	123	40.73 (41.18)	4.62 (4.75)	3.63 (3.70)		2058,^{b} 1985^b	1081^c	2963^c	
n-BuNH	114	42.58 (42.77)	5.33 (5.09)	3.55 (3.56)		2057,^{b} 1984^b	1055^d		
t-BuNH		42.78 (42.71)	5.25 (5.09)	3.59 (3.56)		2054,^{b} 1977^b			
Et_2N	89	42.50 (42.77)	5.37 (5.09)	3.81 (3.56)		2054,^{b} 1983^b	1051^d	2879^c	
C_4H_8N	111	43.09 (42.92)	4.75 (4.60)	3.70 (3.58)	18.96 (19.44)	2058,^{b} 1988^b	1082^c	3186^c	
$C_5H_{10}N$	128	43.33 (44.47)	5.17 (4.94)	3.30 (3.46)		2063.^{b} 1989^b	1082^c	2942^c	
C_5H_5N (=RH)	124	45.04 (45.12)	3.32 (3.51)	3.47 (3.51)	18.69 (19.05)	2063,^{b} 1965^b	1083^c		
5-*exo*-$RC_7H_9Fe(CO)_3$									
n-PrNH	oil	53.72 (53.61)	6.13 (5.84)	4.68 (4.81)		2045,^{a} 1977^a		3456^g	
n-BuNH	oil	54.77 (55.08)	5.56 (6.23)	3.64 (4.59)		2043,^{a} 1977^a		3458^g	
t-BuNH	oil	54.70 (55.08)	6.44 (6.23)	4.34 (4.59)		2043,^{a} 1973^a		3446^h	
Et_2N	34	54.00 (55.08)	6.35 (6.23)	3.99 (4.59)		2046,^{a} 1977^a			
C_4H_8N	oil	55.72 (55.45)	5.78 (5.61)	4.65 (4.62)		2047,^{a} 1980^a			
PhNH	96	59.56 (59.08)	4.56 (4.62)	4.32 (4.31)		2045,^{a} 1981^a		3394^c	
PhNMe	92	59.90 (60.17)	5.07 (5.02)	4.09 (4.13)		2047,^{a} 1982^a			

[a] Measured in hexane solution. [b] Measured in dichloromethane solution. [c] Measured in KBr disks. [d] Measured in Nujol mull. [e] Measured in Fluorolube mull. [f] Measured in CsBr disk. [g] Measured in carbon tetrachloride solution. [h] Measured as pure liquid.

nature of the product varies considerably with the basicity of the amine.

Primary and Secondary Aliphatic Amines. Reaction between a number of primary and secondary aliphatic amines and the title compound (in 1:1 molar ratios) in dichloromethane or acetonitrile gives the corresponding 5-exo ring-substituted adducts $[C_7H_9RNH_2Fe(CO)_3]BF_4$ and $[C_7H_9R_2NHFe(CO)_3]BF_4$, respectively (see Table I). Their structures were confirmed by the presence of terminal N–H stretching modes in the 3450-cm^{-1} region, terminal metal–carbonyl modes at about 2058 and 1985 cm^{-1} and ν(BF) at 1055 cm^{-1} (Nujol mull) (Table I).

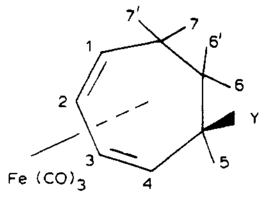
The NMR spectra showed clearly from the examination of H_5 (see previous 5-alkoxide discussion) that 5-exo-substituted products resulted. Representative data are given in Table II.

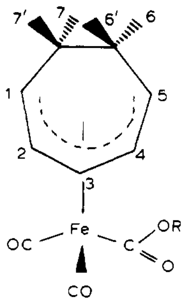
On treatment of the above adducts with a further 1 mol of amine, proton abstraction from the NH_2 (or NH) group occurs with formation of the neutral substituted 5-exo-amino derivatives $C_7H_9RNHFe(CO)_3$ and $C_7H_9NFe(CO)_3$, respectively (see Scheme I). Their structures were confirmed by the presence of a terminal ν(NH) at 3460 cm^{-1} or its absence in the secondary amine product, by the presence of metal–carbonyl modes at about 15 cm^{-1} lower than those in the corresponding adduct, and by the absence of the ν(BF) frequency (Table I).

Tertiary Amines. In this case, reaction with NEt_3 results in formation of the triene complex $C_7H_8Fe(CO)_3$ presumably via initial formation of a ring adduct followed by proton abstraction.

Aromatic Amines. In contract to the primary and secondary aliphatic amines, both aniline and *N*-methylaniline react with the title compound (I) to give the neutral 5-exo-substituted derivatives $C_7H_9NHPhFe(CO)_3$ and $C_7H_9NMePhFe(CO)_3$, respectively, with no spectroscopic (IR or NMR) evidence for the intermediate formation of the cationic adducts. It is important to establish whether bonding to the ring is through the N atom or a para-C atom. In the former mode of bonding, the anilino derivative is a secondary amine and as expected

Table II. Selected ^1H NMR Data (Me_4Si as Internal Standard) of the Complexes





compd	δ	assignt	*J*, Hz 5,6-endo	*J*, Hz 5,6-exo
		$[YC_7H_9Fe(CO)_3]BF_4$		
Y = 5-exo *n*-$PrNH_2$	5.45 (2, m)	H_2, H_3		
	3.59 (1, m)	H_5	3.3	11.2
	3.03 (2, m)	H_1, H_4		
	2.74 (1, d)	ring methylene		
	2.65-1.18 (9, -)	ring methylene NH_2 and CH_2 (alkyl)		
	1.00 (3, t)	CH_3		
5-exo Et_2NH	3.87 (1, m)	H_5	3.4	12.0
5-exo $C_5H_{10}NH$	3.68 (1, m)	H_5	3.8	12.6
5-exo C_5H_5N	5.18 (1, m)	H_5	4.2	15.6
5-exo PEt_3	5.46 (2, m)	H_2, H_3		
	3.17 (1, t)	H_1		
	~2.73 (1, d)	H_5	~5	~11
	~2.50 (1, d)	H_4		
	2.27	$CH_2(P)$, ($J(^{31}P,CH_2) = 13$)		
	1.66 } (19, m)	CH_2 ring		
	1.30 }	$CH_3(P)$, ($J(^{31}P,CH_3) = 18$)		
5-endo PEt_3	5.46 (2, m)	H_2, H_3		
	3.17 (1, m)	H_1		
	2.73 (2, m)	H_4, H_5		
	2.26 } (19, m)	$CH_2(P)$, CH_2 ring		
	1.28 }	CH_3		
		$RC_7H_9Fe(CO)_3$		
R = 5-exo PhNH	3.77	H_5	3.7	10.7
5-exo PhNMe	3.10	H_5	4.8	15.7
5-exo OEt	3.60	H_5	4.4	11.5
		$C_7H_9Fe(CO)_2CO_2R$		
Me	3.65 (1, m)	H_3		
	4.94 (2, m)	H_2, H_4		
	5.78 (2, m)	H_1, H_5		
	6.59 (3, s)	OCH_3		
	7.62 (2, m)	H_6, H_7		
	8.48 (2, m)	H_6', H_7'		
Et	3.67 (1, m)	H_3		
	4.94 (2, m)	H_2, H_4		
	5.79 (2, m)	H_1, H_5		
	6.10 (2, m)	OCH_2		
	7.62 (2, m)	H_6, H_7		
	8.47 (2, m)	H_6', H_7'		
	8.89 (3, t)	CH_3		
i-Pr	3.90 (1, m)	H_3		
	5.15 (2, m)	H_2, H_4		
	5.95 (2, m)	H_1, H_5		
	5.24 (4, m)	$O(CH_2)_2$		
	7.72 (2, m)	H_6, H_7		
	8.66 (2, m)	H_6', H_7'		
	9.05 (3, t)	CH_3		

has one ν(NH) absorption (see Table I) whereas the *N*-methylanilino derivative has no bands ascribable to ν(NH) (Table I) again in accord with bonding through the N atom of the nucleophile. Further confirmation is given by the ^1H NMR spectrum of the anilino derivative showing a broad absorption at 3.58 ppm, which disappears on deuteration, and an aromatic signal (τ 6.92) corresponding to five protons. Similarly, the *N*-methylanilino derivative does not show an NH signal, indicating loss of the proton from the nitrogen atom. This result is in marked contrast to the reported electrophilic attack of the analogous six-membered ring cation, $[C_6H_7Fe(CO)_3]^+$, at the para ring position of *N*,*N*-dimethylaniline.[16] The structures and exo configurations follow again from the observed spectroscopic properties (Table II).

As the basicity of the aromatic amine increases so too does its ability to abstract protons not only from the cationic adduct but also from the polyene ring; thus *N*-methylaniline gives in

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(16) G. R. John and L. A. P. Kane-Maguire, *J. Chem. Soc., Dalton Trans.*, 1196 (1979).

Scheme I. Reaction Mechanism for Saturated Amines

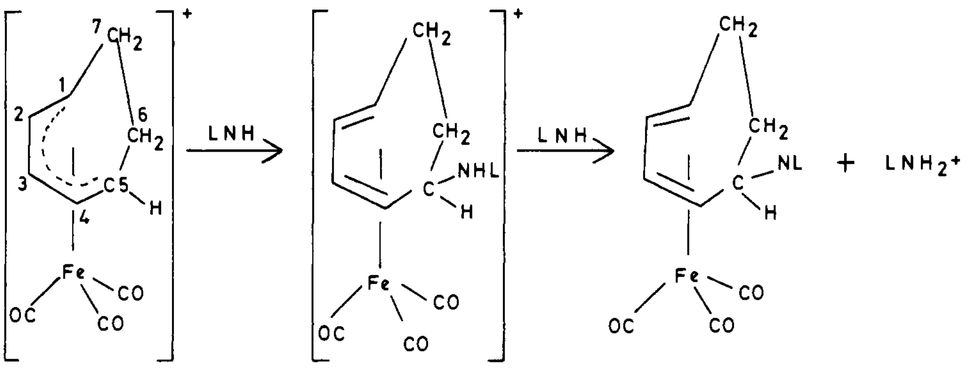

Table III. Proton-Noise-Decoupled ^{13}C NMR Spectra of the Ethylphosphonium Complexes $[RC_7H_9Fe(CO)_3]BF_4^-$ with Me_4Si as Internal Standard[a]

compd	CO	C_2, C_3	C_1	C_4, $J(^{31}P,C_4)$	C_5, $J(^{31}P,C_5)$	C_6, $J(^{31}P,C_6)$	C_7	$CH_2(P)$, $J(^{31}P,CH_2(P))$	CH_3, $J(^{31}P,CH_3)$
R = 5-exo PEt_3^+	210.27 (s)	91.35 (s), 86.69 (s)	58.63 (s)	46.69 (d), 5.0	32.23 (d), 39.1	27.71 (d), 12.2	23.20 (s)	10.63 (d), 46.4	6.31 (d), 4.9
R = 5-endo PEt_3^+	210.07 (s)	91.35 (s), 86.78 (s)	58.73 (s)	46.74 (d), 7.3	32.28 (d), 36.6	27.81 (d), 12.2	23.21 (s)	10.73 (d), 46.6	6.31 (d), 4.9

[a] All shift values are in parts per million; all *J* values are in hertz.

addition to the 5-exo-substituted product above some 1,3,5-trieneiron tricarbonyl, $C_7H_8Fe(CO)_3$, and for the tertiary *N*,*N*-dimethylaniline this is the only product obtained. Finally, it is noteworthy that pyridine reacts with tricarbonyl(η-1,5-cycloheptadienylium)iron to give the adduct only.

Substitution by Phosphines. For substitution of the tricarbonyl(η-1,5-cycloheptadienylium)iron by a soft nucleophile, the preceding theoretical paper predicts the sequence of attack as

$$\text{ring} > \text{carbonyl} > \text{metal}$$

although metal attack may occur in solvents of low polarity. We have previously reported the formation of the yellow 5-exo ring phosphine product on reaction of I with a number of phosphines but suggested that initial metal attack may occur because of the formation of a red color during reaction although an alternative explanation in terms of some type of charge-transfer interaction between nucleophile and substrate cannot be excluded. This report was criticized[17] although the solvent and phosphine quoted in ref 17 were quite different from those given in our preliminary communication. In fact substitution by phosphines is now shown to be markedly dependent on the nature of the solvent used and the steric requirements of the phosphine. Thus treatment of a stirred suspension of I with a 1:1 molar ratio of phosphine (PEt_3, P-*n*-Pr_3, P-*n*-Bu_3, or PMe_2Pr) in dichloromethane gives the yellow 5-exo product without the occurrence of an intermediate red color, contrary to our previous report where the quoted solvent should have been aceonitrile.[18] However, in this latter solvent, treatment of I with a slight excess of phosphine (1.1:2 molar ratio) and *excess* solvent (e.g., 50 mL of acetonitrile for 3 mmol of I) caused the development of the red color within 5 min, and after about 20 min of reaction, reduction of volume and addition of ether precipitates the brown 5-endo product. In this case, the concentrations of reactants are important and, for example, if insufficient acetonitrile is used only the yellow 5-exo isomer is obtained. Phosphines with more than one phenyl substituent give only the 5-exo isomer irrespective of reaction conditions (Table I). For a particular phosphine, both isomers are reasonably stable, but the 5-exo may be converted into the 5-endo isomer by treatment with excess phosphine in acetonitrile, and during the conversion a red coloration is again observed.

The infrared spectra of the 5-exo and 5-endo isomers are very similar except that the higher frequency metal–carbonyl stretching mode of the exo lies about 5 cm^{-1} higher than that for the endo isomer (Table I). However, the ^{1}H and ^{13}C NMR spectra are quite distinctive (Tables II and III).

An intensive series of ^{1}H single-irradiation experiments was performed on the exo- and endo-ethylphosphonium complexes in deuteriochloroform and deuteriodichloromethane. A disadvantage of dichloromethane was that the high-field half of the inner diene system (H_2, H_3) was masked by this solvent. The endo compound was unstable in deuteriochloroform, and the stability of both complexes was enhanced by the absence of Me_4Si.

The inner diene system is at lowest field, 5.5 ppm in the exo-ethylphosphonium complex with H_3 occurring at lower field than H_2. The phosphine group protons give a doublet of triplets at 1.3 ppm, J_{P,CH_3} = 18 Hz, and a doublet of quartets at 2.3 ppm, J_{P,CH_2} = 13 Hz. These signals overlap the area in which H_6 and H_7 occur. H_1 and H_4 are no longer equivalent, and H_1 is observed as an apparent triplet at 3.18 ppm ($J_{1,2} = J_{1,7\text{-exo}}$ = 6 Hz). The position of this signal is the same in both isomers, and since it occurs as a triplet in each case, the possibility of a ring inversion at C_7 in the brown isomer is ruled out. The conclusion is substantiated by the ^{13}C NMR spectra, where C_6 and C_7 occur in almost the same position for both isomers.

The position of H_5 is of major importance. In the spectrum of the exo isomer in deuteriochloroform in the absence of decoupling, H_4 and H_5 overlap: the expected double doublet due to H_5 is not at all clearly evident. However, on irradiation of the $H_{2,3}$ region, the consequent sharpening of H_4 reveals H_5 as a double doublet with $J_{5,6\text{-exo}}$ = 11 Hz and $J_{5,6\text{-endo}}$ = 5 Hz. These values are in accord with the behavior of H_5 in the exo-anilino and exo-alkoxide cases. In addition, although H_4 and H_5 are closely grouped, on irradiation of H_4, H_5 is observed as a doublet, a change in the low-field H_3 diene is observed as a doublet, and H_1 is unaffected. This shows that *no* coupling exists between H_4 and H_5 and is in agreement with

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(17) G. R. John and L. A. P. Kane-Maguire, *J. Chem. Soc., Dalton Trans.*, 873 (1979).

(18) D. A. Brown, S. K. Chawla, and W. K. Glass, *Inorg. Chim. Acta*, **19**, C31 (1976).

the exo-anilino case. Thus, there is no doubt that the yellow product is indeed exo.

The endo-phosphonium isomer, studied in deuteriodichloromethane, shows the narrowing of the H_5 signal, behavior analogous to that in the endo-anilino case. On irradiation of H_5, H_4 collapses and the low-field diene region H_3 is affected. It is clear that the coupling between H_4 and H_5 is not longer zero. Thus the brown product is 5-endo.

The NMR spectra of the other phosphonium complexes can be assigned in a similar manner.

The ^{13}C results (Table III) substantiated the above. Except for very small differences in the chemical shifts, both isomers display similar patterns. However, a variation in the coupling constants of ^{31}P with the neighboring carbon atoms C_4 and C_5 is observed in the ethylphosphine case. Although it is not possible to correlate this result with a particular geometrical configuration, it does indicate the expected change in orientation of the phosphorus group between the isomers.

These results show clearly that substitution of the tricarbonyl(η-1,5-cycloheptadienylium)iron cation by phosphines yields both the 5-exo and 5-endo isomers depending on reaction conditions. The presence of a red coloration during reaction in acetonitrile and during the interconversion of exo to endo isomer is consistent with metal-assisted substitution. The inability of phenyl-substituted phosphines to form the 5-endo isomer is presumably due to steric inhibition of the metal-assisted pathway. In contrast, substitution in dichloromethane proceeds by direct ring attack to give the 5-exo isomer.

In conclusion, the general pattern of nucleophilic substitution of both hard and soft nucleophiles is in good accord with the theoretical discussion of the preceding paper. Thus by varying the nucleophilicity of the attacking group it is possible to observe both metal and carbonyl carbon attack and formation of stable products. It is also possible for hard nucleophiles to attack at the carbonyl carbon atom (and possibly at the metal atom also) even if the final thermodynamically stable product is ring substituted. Finally, for soft nucleophiles such as phosphines, both ring isomers may be obtained although even in this case there may be a metal-assisted pathway in the formation of the endo isomer.

Registry No. I, 12212-05-4; II, R = Et, 81522-88-5; II, R = Me, 81522-89-6; II, R = *i*-Pr, 81522-90-9; 5-*exo*-$C_7H_9OEtFe(CO)_3$, 12109-81-8; $C_7H_9Fe(CO)_2NCO$, 81522-91-0; $C_7H_9Fe(CO)_2CONHNH_2$, 81522-92-1; $[C_7H_9Fe(CO)_2NH_2N(CH_2Ph)_2]BF_4$, 81522-94-3; 5-*exo*-*n*-$PrNH_2C_7H_9Fe(CO)_3]BF_4$, 81522-80-7; 5-*exo*-*n*-$PrNHC_7H_9Fe(CO)_3$, 81522-79-4; [5-*exo*-$PEt_3C_7H_9Fe(CO)_3]BF_4$, 81534-79-4; [5-*endo*-$PEt_3C_7H_9Fe(CO)_3]BF_4$, 81600-18-2; 5-*exo*-$MeOC_7H_9Fe(CO)_3$, 81570-96-9; 5-*exo*-*i*-$PrOC_7H_9Fe(CO)_3$, 81522-81-8; $[C_7H_9Fe(CO)_2NH_2N(CH_2$-*p*-$NO_2C_6H_4)_2]BF_4$, 81522-83-0; $[C_7H_9Fe(CO)_2NH_2N(CH_2$-*p*-$MeOC_6H_4)_2]BF_4$, 81534-81-8; [5-*exo*-P(*n*-$Pr)_3C_7H_9Fe(CO)_3]BF_4$, 81522-85-2; [5-*endo*-P(*n*-$Pr)_3C_7H_9Fe(CO)_3]BF_4$, 81570-98-1; [5-*exo*-P(*n*-$Bu)_3C_7H_9Fe(CO)_3]BF_4$, 81570-86-7; [5-*endo*-P(*n*-$Bu)_3C_7H_9Fe(CO)_3]BF_4$, 81570-88-9; [5-*exo*-$PMe_2PhC_7H_9Fe(CO)_3]BF_4$, 81522-76-1; [5-*endo*-$PMe_2PhC_7H_9Fe(CO)_3]BF_4$, 81570-90-3; [5-*exo*-$PEtPh_2C_7H_9Fe(CO)_3]BF_4$, 81522-78-3; [5-*exo*-$PPh_3C_7H_9Fe(CO)_3]BF_4$, 81570-92-5; [5-*exo*-*n*-$BuNH_2C_7H_9Fe(CO)_3]BF_4$, 81570-93-6; [5-*exo*-*t*-$BuNH_2C_7H_9Fe(CO)_3]BF_4$, 81600-03-5; [5-*exo*-$Et_2NHC_7H_6Fe(CO)_3]BF_4$, 81570-94-7; [5-*exo*-$C_4H_8NHC_7H_9Fe(CO)_3]BF_4$, 81570-95-8; [5-*exo*-$C_5H_{10}NHC_7H_9Fe(CO)_3]BF_4$, 81522-70-5; [5-*exo*-$C_5H_5NC_7H_9Fe(CO)_3]BF_4$, 81570-83-4; 5-*exo*-*n*-$BuNHC_7H_9Fe(CO)_3$, 81522-71-6; 5-*exo*-*t*-$BuNHC_7H_9Fe(CO)_3$, 81570-84-5; 5-*exo*-$Et_2NC_7H_9Fe(CO)_3$, 81522-72-7; 5-*exo*-$C_4H_8NC_7H_9Fe(CO)_3$, 81522-73-8; 5-*exo*-$PhNHC_7H_9Fe(CO)_3$, 67711-11-9; 5-*exo*-$PhNMeC_7H_9Fe(CO)_3$, 81522-74-9.

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Metal Cluster Catalysis. Kinetics and Mechanism of the Catalytic Hydrogenation of Ethylene by the Ruthenium Cluster Complex $H_4Ru_4(CO)_{12}$

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The tetraruthenium cluster hydride $H_4Ru_4(CO)_{12}$ reacts with ethylene at 72 °C to give two molecules of ethane per molecule of cluster. In the presence of excess hydrogen, this cluster complex acts as a catalyst for the hydrogenation of ethylene in heptane solution. Detailed kinetics for the catalytic hydrogenation are presented as functions of catalyst concentration, ethylene pressure, hydrogen pressure, and carbon monoxide pressure. In the reaction of C_2H_4 with D_2, the hydrogen–deuterium exchange between reactants takes place to give C_2H_3D and HD by a more rapid rate than that of ethane formation. A reasonable catalytic cycle for the ethylene hydrogenation is proposed to involve $H_3Ru_4(CO)_{11}(C_2H_5)$ as an intermediate.

Introduction

Mononuclear transition-metal compounds have been extensively used as homogeneous catalysts for the hydrogenation of olefins. The mechanism of olefin hydrogenation on mononuclear transition-metal complexes is well established and has been reviewed by James.[1] Recently, the use of transition-metal cluster compounds as homogeneous catalysts for the olefin hydrogenation has been increasing. Examples include the hydrogenation of olefins with molecular clusters of ruthenium,[2-6] osmium,[7,8] rhodium,[9] and nickel.[10] These metal clusters are considered to provide polymetallic active sites for the catalytic reactions. Recent publications[11-13] have pointed out the analogies between molecular metal clusters and metal surfaces in the processes of chemisorption and of catalysis. At

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