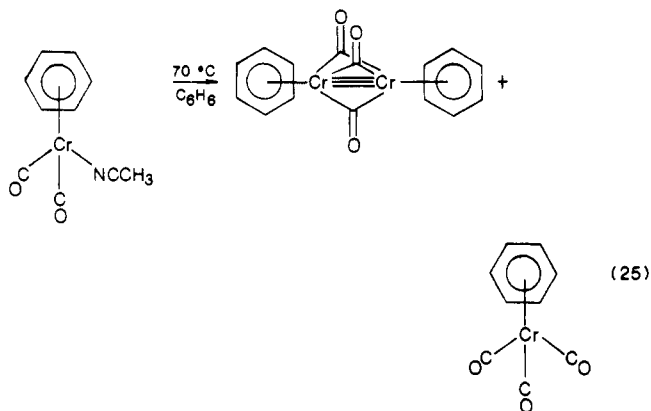
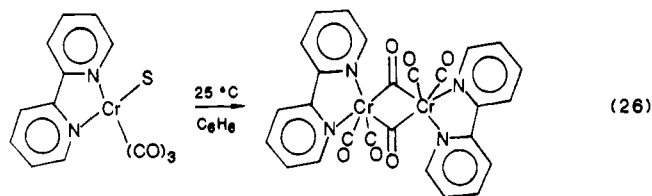


bear some similarity to both II and III. Knoll, Reiss, Schafer, and Klüfers¹⁴ observed a bridged chromium dimer upon heating the monoacetonitrile complex as shown in eq 25. Behrens and co-workers have prepared the doubly



bridged species shown in eq 26 ($M = \text{Cr}, \text{Mo}, \text{W}$).⁶ As written, the latter molecule is a 16-electron metal system.

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Metal-metal bonding would saturate both metals. This suggests a mean of achieving the η^4 intermediates in the dimers which would result in the increased reactivity toward arene exchange.

Conclusion. We have discovered an internal scrambling of CO between (arene)tricarbonyl complexes. This process occurs at about 10 times the rate of the (arene)tricarbonylchromium-catalyzed arene-exchange reaction. These facts lead us to conclude that both scrambling and this catalyzed arene exchange proceed through bis(carbonyl)-bridged intermediates, as shown in eq 16-21.

Acknowledgment. We are grateful to the National Science Foundation, Grant CHE 20612, for support of this research.

Registry No. $\text{BzCr}(\text{CO})_3$, 12082-08-5; $(\text{Bz}-d_6)\text{Cr}(\text{CO})_3$, 38095-88-4; (dibenzo)Cr(CO)₃, 51286-78-3; $\text{MsCr}(\text{CO})_3$, 12129-67-8; $\text{HMBCr}(\text{CO})_3$, 12088-11-8; CO, 630-08-0.

Reactivity of $[\text{HFe}_3(\text{CO})_{11}]^-$ toward Alkynes. 1. Case of Acetylene

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The $[\text{P}(\text{C}_6\text{H}_5)_4][\text{HFe}_3(\text{CO})_{11}]$ cluster (1) reacts at room temperature with acetylene leading to $[\text{P}(\text{C}_6\text{H}_5)_4][\text{Fe}_2(\text{CO})_6(\mu\text{-CO})(\mu\text{-CHCH}_2)]$ (2) and $[\text{P}(\text{C}_6\text{H}_5)_4][\text{Fe}_3(\text{CO})_{10}(\mu_3\text{-CCH}_3)]$ (3) (yield 30 and 40%, respectively). In solution, 3 exists as two forms in equilibrium, $[\text{P}(\text{C}_6\text{H}_5)_4][\text{Fe}_3(\text{CO})_9(\mu\text{-CO})(\mu_3\text{-CCH}_3)]$ (3a) and $[\text{P}(\text{C}_6\text{H}_5)_4][\text{Fe}_3(\text{CO})_9(\mu_3\text{-CO})(\mu_3\text{-CCH}_3)]$ (3b), but in the solid state only 3b is present. In refluxing acetone, 3 generates $[\text{P}(\text{C}_6\text{H}_5)_4][\text{HFe}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-CCH}_2)]$ (4), which immediately reverts to 3 upon addition of carbon monoxide. The reactivity of 3 toward H^+ , C_2H_5^+ , and $\text{C}(\text{C}_6\text{H}_5)_3^+$ has been studied. 3 reacts with H^+ to give $\text{HFe}_3(\text{CO})_{10}(\mu\text{-CCH}_3)$ (5), via the $\text{Fe}_3(\text{CO})_9(\text{CCH}_3)(\text{COH})$ intermediate detected at low temperature. With C_2H_5^+ , $\text{Fe}_3(\text{CO})_9(\mu_3\text{-CCH}_3)(\mu_3\text{-COC}_2\text{H}_5)$ (6) has been formed and isolated while $\text{C}(\text{C}_6\text{H}_5)_3^+$ leads to the formation of $\text{Fe}_3(\text{CO})_9(\mu\text{-CO})(\mu_3\text{-}\eta^2\text{-CCH}_2)$ (7), which has also been produced from 5 in boiling methylcyclohexane. The reactivity of 3, 4, 5, and 6 toward hydrogen under pressure has also been tested. Formation of ethane (3) and ethylene (4) has been observed, and the most interesting result is obtained with 6 for which the main product obtained is $\text{C}_2\text{H}_5\text{OCH}_2\text{CH}_2\text{CH}_3$, i.e., the product resulting from the coupling and the hydrogenation of the two alkylidyne ligands.

Introduction

The reactivity of unsaturated organic molecules with transition-metal clusters is now a well-developed area of investigation¹ and has been mainly studied with clusters of metals of the second and third period. Actually, most of the reactions observed with clusters of the first period are complicated by cluster fragmentation. Nevertheless, a weak metal-metal bond is potentially a propitious factor

of reactivity as metal-metal bond breaking is a way to create a vacant site.² It seemed interesting to find a transition-metal cluster of the first period stable enough to avoid or to limit fragmentation reaction but in which the metal-metal bond would be weak, in order to present a good reactivity. We have thought that the cluster $[\text{P}(\text{C}_6\text{H}_5)_4][\text{HFe}_3(\text{CO})_{11}]$ (1), could achieve this challenge as we could expect that the occurrence of a nonlocalized negative charge could stabilize the metal core. Furthermore, the presence of a hydrido ligand was another potential of reactivity.

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Table I. Spectroscopic Data of the Isolated Complexes

compd	IR $\nu(\text{CO})$, cm^{-1}	^1H NMR, ^a ppm	^{13}C NMR, ^a ppm (CD_2Cl_2 solution)
2	2028 m, 1975 s, 1928 s (br), 1735 m	2.15 (d, $J = 8$ Hz, 1 H), 2.67 (d, $J = 12$ Hz, 1 H), 8.25 (dd, $J = 8$ Hz, $J = 12$ Hz, 1 H)	228.5, 149.8 (d, $J = 153$ Hz), 63.8 (dd, $J_1 = 150$ Hz, $J_2 = 152$ Hz)
3	2045 w, 1995 s, 1962 m, 1940 sh, 1730 vw, 1665 w	4.18 ^b (3 H)	289, 221.8, 44.3
4	2044 m, 2000 s, 1975 s, 1953 s, 1935 sh	4.60 (d, $J = 3$ Hz, 2 H), -17.20 (t, $J = 3$ Hz, ^b 1 H)	253.4, 214.6, 72.9 (t, $J = 157.4$ Hz)
5	2095 w, 2050 s, 2040 s, 2015 m, 1995 m, 1980 m, 1920 w (br)	4.10 (3 H), -19.90 ^c (1 H)	311.3, 209.7, 46.8
6	2084 vw, 2035 vs, 2012 s, 1998 m, 1985 m	4.45 (q, $J = 7.5$ Hz, 2 H), 4.35 (3 H), 1.35 (t, $J = 7.5$ Hz, ^d 3 H)	333, 292.8, 209.4, 83.6, 46.9, 15.1
7	2095 w, 2055 s, 2037 s, 2030 s, 2013 m, 2005 m, 1985 m, 1874 m	5.3 ^c	292.3, 210.9, 74.5 (t, $J = 169.8$ Hz)
8	2094 vw, 2060 s, 2018 s, 2002 m, 1980 w, 1965 w	4.2 (3 H), -23.7 ^d (3 H)	

^a Except phenyl resonances of $\text{P}(\text{C}_6\text{H}_5)_4$. ^b In $(\text{CD}_3)_2\text{CO}$ solution. ^c In CDCl_3 solution. ^d In C_6D_6 solution.

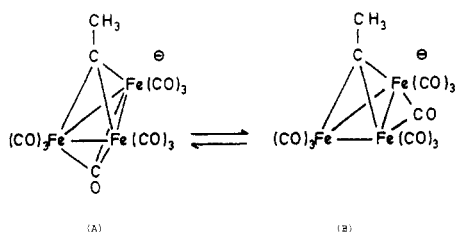
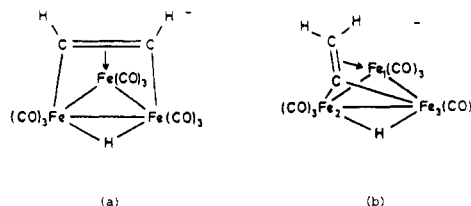
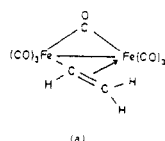


Figure 1. (a) Proposed structure for the complex 2. (b) The two structures in equilibrium for the complex 3 in solution.

In a preliminary communication, we have given results which show that this cluster was very reactive toward alkynes,³ and in this paper, we present detailed results about the action of 1 with acetylene and about the reactivity of the products resulting from this reaction.

Results and Discussion

Reactivity of 1 toward Acetylene. 1 reacts readily at room temperature and atmospheric pressure with acetylene leading to two complexes separated by fractional crystallization. The first complex 2, isolated in 30% yield, shows in the infrared spectrum in the $\nu(\text{CO})$ stretching region, in addition to terminal carbonyl bands, a broad band centered at 1735 cm^{-1} characteristic of a bridging carbon monoxide. Moreover, the proton and ^{13}C NMR spectra give evidence of the presence of a vinylic group (Table I). From the chemical shifts of the vinylic hydrogen atoms, it can be deduced that this group is σ -bonded to one iron atom and π -bonded to another iron atom.⁴ The chemical analysis is consistent with the $[\text{P}(\text{C}_6\text{H}_5)_4][\text{Fe}_2(\text{CO})_7(\text{CHCH}_2)]$ formulation. From all these data, the structure shown in Figure 1 may be proposed for 2. The two iron atoms are shown to be bridged by a vinyl group and carbon monoxide.

For the second complex 3, isolated in 40% yield, the proton NMR study shows only a singlet at 4.18 ppm with an intensity ratio of 3 compared to the phenyl resonances

of the cation. In the proton-coupled ^{13}C NMR spectrum of 3, the presence of a methyl group is confirmed by a quartet centered at 44.3 ppm. Furthermore, two other peaks are observed: one centered at 221.8 ppm attributed to carbonyl groups and one at 289 ppm characteristic of a carbon of an alkyldyne group bonded to several metal centers.⁵

In the infrared spectrum in solution, two weak bands are observed at 1730 and 1665 cm^{-1} , but in the solid state only one is observed, at 1655 cm^{-1} . This suggests that, in the solid state, 3 has a triply bridging carbon monoxide ligand and that, in solution, there is an equilibrium between two forms containing a doubly or a triply bridging carbon monoxide. A similar phenomenon has been observed for the $\text{SFe}_3(\text{CO})_{10}$ cluster.⁶ The chemical analysis is consistent with the $[\text{P}(\text{C}_6\text{H}_5)_4][\text{Fe}_3(\text{CO})_{10}(\text{CCH}_3)]$ formulation, and the structures shown in Figure 1 are proposed for 3 in solution. In these structures the ethynyl ligand triply bridges the triiron triangle, and each iron is bonded to three terminal carbon monoxides. The tenth carbon monoxide is either triply bridging (form A) or doubly bridging (form B). It should be pointed that, for the methylidyne anion $[\text{Fe}_3(\text{CO})_{10}(\mu_3\text{-CH})]^-$, only form B has been detected either in solution or in the solid state.⁷ Considering this equilibrium in solution between forms A and B for 3, we have studied the variable-temperature ^{13}C NMR spectrum of 3, but even at $-80\text{ }^\circ\text{C}$ only a broadening of the carbon monoxide resonance is observed. So the exchange between the two forms is rapid at the NMR time scale.

The chemistry of 3 has been investigated in two ways. The first relates to the concept that organic fragments bonded to metallic molecular clusters can serve as models for the reactivity of the same fragments on metallic surfaces,⁸ and for this reason we have checked the thermal

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stability of **3**. The other way takes into account the anionic nature of this cluster, and we have studied its reactivity toward electrophilic reagents, the proton, and the carbocations $C_2H_5^+$ and $C(C_6H_5)_3^+$.

Thermal Reactivity of 3. In refluxing acetone, **3** is slowly transformed into a new complex, **4**, which analyses for $[P(C_6H_5)_4][Fe_3(CO)_9C_2H_3]$ and which has been fully characterized by IR and NMR spectroscopy. The infrared spectrum in the $\nu(CO)$ stretching region exhibits only terminal carbonyl bands (Table I). In the proton NMR spectrum, one doublet ($J = 3$ Hz) is observed at 4.6 ppm with an intensity ratio of 2 compared to the phenyl resonances and one triplet ($J = 3$ Hz) at -17.2 ppm with an intensity ratio of 1. These observations are in agreement with the two structures shown in Figure 2a,b, but the proton-coupled ^{13}C NMR spectrum of **4** allows us to attribute Figure 2b to **4** since a triplet is observed at 72.9 ppm ($J_{CH} = 157.4$ Hz) and another singlet is observed at 254.3 ppm characteristic of a carbon bonded to two metallic centers.^{5,9} Considering the equivalence of the two hydrogen atoms on the vinylidene ligand, the hydride has been located between the Fe(2) and Fe(3) atoms, but we cannot preclude that this equivalence may be due to the fluxionality of the molecule as evidenced by the observation of only one resonance for carbon monoxide ligands. Here again even at -80 °C it was not possible to observe the slow-exchange limit spectrum by ^{13}C NMR spectroscopy. Complex **4** has also been prepared by deprotonation of $(\mu-H)_3Fe_3(CO)_9(\mu_3-CCH_3)$.¹⁰

To summarize, in refluxing acetone **3** loses one molecule of carbon monoxide. This departure is compensated by carbon-hydrogen activation transforming the ethylidyne ligand into a μ_3 -bonded vinylidene ligand, while the hydrido ligand liberated is bonded to two iron atoms. To check if this reaction was reversible, we submitted **4** to the action of carbon monoxide. **4** quickly reacts with carbon monoxide at room temperature and atmospheric pressure to regenerate **3**. This easy reaction illustrates the great lability of the CH and FeH bonds in **3**.

Study of the Reactivity of **3** toward Electrophiles.

Considering the presence of a bridging carbonyl group in **3**, two sites are a priori potentially accessible to electrophiles such as a proton or a carbocation: the metallic frame and the oxygen atom of the bridging carbonyl ligand. This is specifically the case for the proton where both situations have been observed, but the product resulting from the attack on the carbonyl ligand is stable only at low temperature.^{11,12}

Reactivity of 3 toward the Proton. This study has been performed at two temperatures: room temperature and -80 °C. At room temperature, **3** reacts with a slight excess of trifluoroacetic acid to give a black-red neutral complex, **5**, in nearly quantitative yield. Mass spectrometry is consistent with the $HFe_3(CO)_{10}CCH_3$ formulation. The proton NMR spectrum of **5** exhibits two singlets centered at 4.1 and -19.9 ppm in the 3/1 ratio which shows that protonation results in the fixation of a hydride across a Fe-Fe bond. Except for sharp absorptions of terminal carbonyl groups, the infrared spectrum in the $\nu(CO)$

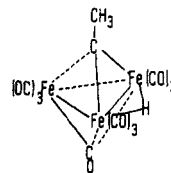


Figure 3. Proposed structure for complex **5**.

stretching region shows (Table I) a broad and weak band centered at 1920 cm^{-1} which could be consistent either with a semibridging carbon monoxide¹³ or with a terminal M-H stretching frequency. Use of deuterated trifluoroacetic acid produces no change in the infrared spectrum which is consistent with the first hypothesis.

Moreover the ^{13}C NMR spectrum gives evidence that **5** is a fluxional molecule since at room temperature only one resonance centered at 209.7 ppm is observed for the carbonyl groups. Upon lowering the temperature to -90 °C this resonance splits into three resonances at 207.8, 206.3, and 205.3 ppm in the 4/3/3 ratio, which seems to indicate that the slow-exchange limit spectrum has not been reached. A similar ^{13}C NMR spectrum has been observed for $HFe_3(CO)_{10}(\mu-CH)$ at -50 °C,⁷ but there is no mention for this compound of the presence of semi bridging carbonyl groups in the infrared spectrum.

From all these results it is difficult to establish firmly the structure of **5**, but since the CO resonances -80 °C are in the 4/3/3 ratio, a triply bridging ethylidyne ligand is not favored. For these reasons we propose for **3** the structure shown in Figure 3 in which the ethylidyne ligand would be bonded to two iron atoms and in interaction with the third one. One of the CO groups of the iron atom bonded to four carbonyl ligands would be in interaction with one of the other two iron atoms. A similar structure has been observed for $HFe_3(CO)_{10}(\mu-COCH_3)$.¹⁴

It can be mentioned that **5** has also been obtained in low yield by two independent complex ways: protonation of $[Fe_3(CO)_9(\mu_3-COCH_3)]^-$ ¹⁵ and reduction of $Fe(CO)_5$ with BH_3/THF .¹⁶ The spectroscopic data are in reasonable agreement.

We also studied the protonation reaction of **3** at low temperature to test if the first attack occurred at the oxygen of the bridging carbonyl. Actually, if the protonation was carried out at -80 °C by adding 1 equiv of trifluoromethanesulfonic acid, the proton NMR spectrum exhibited new resonances at 4.51 ppm for the CH_3 group and a broad signal centered at 12.1 ppm. The latter value is consistent with the formation of a CO-H bond by comparison with the values found for $HFe_3(CO)_9(COH)$ (15 ppm)¹¹ and $HFe_4(CO)_{12}(COH)$ (13.2 ppm).¹⁷ Upon warming to room temperature, resonance signals of **5** slowly appear. We tried to confirm by ^{13}C NMR spectroscopy the $Fe_3(CO)_9(CCH_3)(COH)$ formulation for the product formed at low temperature. At -80 °C, broad signals are observed at 43.3 ppm for the CH_3 group and 214.3 ppm for the carbonyl ligands, and a very broad resonance is centered at 287.6 ppm. Even though the methyl and CO resonances observed are different from those of **3** and **5**, this spectrum is not very conclusive about the mode of bonding of the

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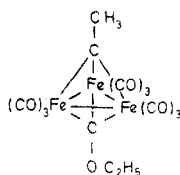


Figure 4. Structure of complex 6.

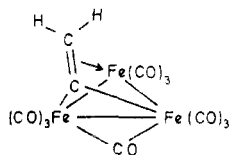


Figure 5. Structure of complex 7.

CCH₃ and COH groups, but the high-field resonance for the ¹³C NMR signal of the COH group suggests a μ_3 -mode of bonding.¹⁸

Reactivity of 3 toward Triethyloxonium Tetrafluoroborate. 3 reacts readily at room temperature with triethyloxonium tetrafluoroborate to give a red neutral complex, 6, whose infrared spectrum shows only terminal CO stretching frequencies (Table I). The proton NMR study indicates the presence of methyl and ethyl groups while the ¹³C NMR spectrum shows, except the resonances of the methyl and ethyl groups and carbonyl ligands, two peaks at 292.8 and 333 ppm characteristic of the carbon atoms of alkyldiene ligands bonded to three metal centers. The chemical analysis is consistent with the Fe₃(CO)₉(C-CH₃)(COC₂H₅) formulation, and the structure shown in Figure 4 is proposed for 6. This structure is similar to that of Fe₃(CO)(μ_3 -CCH₃)(μ_3 -COCH₃) which has been obtained in low yield by the action of methyl fluorosulfate on [NEt₄][Fe₃(CO)₉(μ_3 -C(O)CH₃)].¹⁵

Reactivity of 3 toward Triphenylcarbonium Hexafluorophosphate. The reactivity of the triphenylcarbonium ion toward 3 has been tested to see if it was possible to abstract one hydrogen atom from the ethyldiene ligand. This is the case, and at room temperature the reaction leads to a green neutral complex, 7. In its infrared spectrum, a ν (CO) stretching band at 1874 cm⁻¹ is indicative of the presence of a bridging carbonyl group, and the proton NMR spectrum gives evidence of only one signal at 5.3 ppm. Mass spectrometry and chemical analysis are consistent with the Fe₃(CO)₁₀C₂H₂ formulation. The exact nature of the C₂H₂ group has been inferred from the proton-coupled ¹³C NMR spectrum which shows a triplet centered at 74.5 ppm, a singlet at 210.9 ppm for the carbonyl ligands, and a singlet at 292.3 ppm. These values are in agreement with a μ_3 - η^2 -bonded vinylidene ligand, and the structure shown in Figure 5 is proposed for 7. The observation in the ¹³C NMR spectrum of only one resonance for the carbonyl ligands indicates that this molecule is fluxional. Refluxing 5 in methylcyclohexane affords 7 in 30% yield.

Furthermore 7 was obtained in low yield by the reaction of alcohols with Fe₂(CO)₆(μ -Br)(μ -CHCHBr), but it was incorrectly formulated as containing a coordinated acetylene ligand¹⁹ (same mass spectrum and very similar infrared spectrum to that of 7: 2095, 2054, 2036, 2028, 2009, 1984, and 1878 cm⁻¹ in hexane solution).

Having in hand some examples of trinuclear complexes containing either alkyldiene or vinylidene μ_3 -bonded lig-

ands, it was interesting, with the scope of considering cluster-bonded organic fragments as models for organic fragments bonded to a metallic surface,⁸ to check their reactivity toward hydrogen.

Study of the Reactivity of 3, 4, 5, and 6 toward Hydrogen under Pressure. All the experiments have been conducted under 20 atm of hydrogen, at room temperature and at 70 °C if no reaction was observed at room temperature.

In the case of 3, it was necessary to heat to 70 °C. Gas chromatography analysis only gave evidence of the formation of ethane, and the solution showed extensive decomposition but a small amount of [P(C₆H₅)₄][HFe₃(CO)₁₁] was detected by infrared spectrometry. These observations suggest that the reaction could be catalytic, but no catalytic hydrogenation was observed with excess acetylene. The infrared spectroscopy study of the solution in this case showed no trace of [P(C₆H₅)₄][HFe₃(CO)₁₁], but the spectrum was very complex and no products were isolated or identified.

This constitutes another example of hydrogenation of μ_3 -bonded carbyne ligands.²⁰

With 4, hydrogenation under the same conditions as for 3 gave traces of ethane and ethylene. The infrared spectrum of the solution indicates the formation of [P(C₆H₅)₄][Fe₃(CO)₉(μ_3 -C(O)C₂H₅)]²¹ as the sole complex. Metallic iron is also present in the solution.

The formation of the latter complex can either result from the interaction between the formed [P(C₆H₅)₄][HFe₃(CO)₁₁] and the liberated ethylene or directly from 4 by reaction with the hydrogen atom and the carbon monoxide liberated by partial decomposition of 4, but it is difficult to have evidences concerning the latter hypothesis.

In the case of 5, hydrogenation at 70 °C gives only traces of ethane, and the infrared spectrum of the solution indicates the formation of a new complex, 8, which is isolated by crystallization. The infrared spectrum shows only terminal CO stretching frequencies (Table I). The proton NMR spectrum exhibits two signals of the same intensity at 4.2 and -23.8 ppm. The chemical analysis of 8 is consistent with the H₃Fe₃(CO)₉(μ_3 -CCH₃) formulation, a complex soon prepared and fully characterized during the reduction of Fe(CO)₅ by sodium dihydrobis(2-methoxyethoxy)aluminate.²² It was also obtained by hydrogenation of 5 at lower pressure of hydrogen and lower temperature.¹⁶

The most interesting result of this study is provided by the hydrogenation of complex 7. At 70 °C, 7 is completely destroyed and gas chromatography coupled with mass spectrometry analysis of the solution showed that the major component of the organic products is ethyl propyl ether, i.e., the product resulting from the hydrogenation and the coupling of the two alkyldiene fragments. Only trace quantities of methyl ethyl ether and ethane was detected. This constitutes a further example of reaction in which these two alkyldiene ligands are coupled to each other.²³

In conclusion the results presented here and summarized in Scheme I show that our initial goal was nearly successfully attained: the iron cluster [P(C₆H₅)₄][HFe₃(CO)₁₁]

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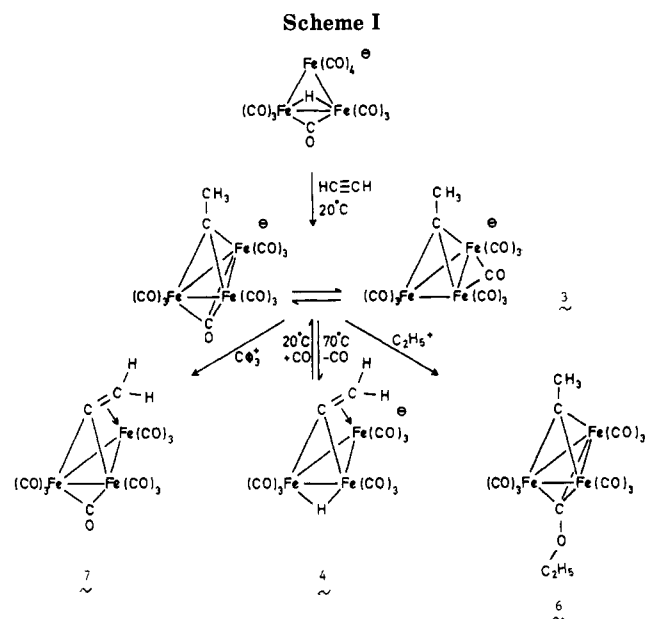
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(1) is a very active compound reacting at room temperature with acetylene, and fragmentation of the cluster is only partially observed in this reaction.

Furthermore, its behavior toward acetylene is very different from that of $\text{H}_2\text{Os}_3(\text{CO})_{10}$ which leads only to $\text{HOs}_3(\text{CO})_{10}(\mu\text{-CHCH}_2)$ at room temperature, the latter complex being converted to $\text{H}_3\text{Os}_3(\text{CO})_9(\mu_3\text{-CCH}_3)$ under forcing conditions and in the presence of hydrogen.²⁴ This is certainly the consequence of more stable bridging hydrogen bonds in the case of osmium.

Experimental Section

All reactions were performed under nitrogen atmosphere by using standard Schlenk tube technique. Infrared spectra were recorded with a Perkin-Elmer 225 spectrometer in dichloromethane solution for ionic complexes and hexadecane solution for neutral complexes. ^1H NMR spectra were obtained with a Perkin-Elmer R12 or a Bruker WH90 spectrometer and ^{13}C NMR spectra with a Bruker WM250 instrument. $[\text{P}(\text{C}_6\text{H}_5)_4][\text{HFe}_3(\text{C}-\text{O})_{11}]$ (1) was prepared by exchange of the cation of $[\text{N}(\text{C}_2\text{H}_5)_3\text{-H}][\text{HFe}_3(\text{CO})_{11}]^{25}$ with $[\text{P}(\text{C}_6\text{H}_5)_4]\text{Br}$.

Preparation of 2 and 3. A solution of 1 (1 g) in 20 mL of acetone was saturated with acetylene and stirred for 5 h at room temperature. The solution was evaporated to dryness. Crystallization in a 1/1 mixture of $\text{CH}_2\text{Cl}_2/(\text{C}_2\text{H}_5)_2\text{O}$ at -20°C gave

2 (0.25 g, 30% yield) as red crystals (mp 119°C). Anal. Calcd for $\text{C}_{33}\text{H}_{23}\text{O}_7\text{PFe}_2$: C, 58.75; H, 3.41; Fe, 16.61. Found: C, 58.74; H, 3.43; Fe, 16.11. The mother solution was evaporated to dryness. The residue was dissolved in a small amount of diethyl ether and the solution cooled to -20°C . 3 was obtained as black crystals (0.4 g, 40% yield) (mp 110°C). Anal. Calcd for $\text{C}_{36}\text{H}_{23}\text{O}_{10}\text{PFe}_3$: C, 53.07; H, 2.82; Fe, 20.63. Found: C, 53.38; H, 2.79; Fe, 20.71.

Preparation of 4. 3 (1 g) was refluxed in boiling acetone for 16 h. The solution was then evaporated to dryness. Crystallization in methanol gave 4 (0.7 g, 72% yield) as red crystals (mp 140°C). Anal. Calcd for $\text{C}_{35}\text{H}_{23}\text{O}_9\text{PFe}_3$: C, 34.54; H, 2.87; Fe, 32.24. Found: C, 34.30; H, 2.87; Fe, 32.34.

Preparation of 5. To 3 (1 g) dissolved in dichloromethane was added trifluoroacetic acid (0.2 mL). The solution was stirred for 10 min and then evaporated to dryness. Extraction of the residue by pentane and cooling the concentrated extract to -20°C gave 5 (0.45 g, 80% yield) as black-red crystals (mp 85°C dec). Mass spectrum: m/z 476 with the successive loss of ten CO. Anal. Calcd for $\text{C}_{12}\text{H}_4\text{O}_{10}\text{Fe}_3$: C, 30.29; H, 0.84; Fe, 35.2. Found: C, 30.06; H, 0.84; Fe, 36.5.

Preparation of 6. To 3 (1 g) dissolved in dichloromethane was added $(\text{C}_2\text{H}_5)_3\text{OBF}_4$ (0.3 g). The solution was stirred for 3 h and then evaporated to dryness. Extraction of the residue with pentane and crystallization of the concentrated extract at -20°C gave 6 (0.5 g, 80% yield) as red crystals. Anal. Calcd for $\text{C}_{14}\text{H}_6\text{O}_{10}\text{Fe}_3$: C, 33.33; H, 1.58; Fe, 33.33. Found: C, 34.21; H, 1.45; Fe, 33.33.

Preparation of 7. (a) To 3 (0.5 g) dissolved in dichloromethane was added $[(\text{C}_6\text{H}_5)_3\text{C}][\text{PF}_6]$ (0.24 g), and the solution was stirred for 2 h. Evaporation to dryness and extraction of the residue with pentane gave after crystallization 7 (0.1 g, 50% yield) as green crystals (mp 130°C). Anal. Calcd for $\text{C}_{12}\text{H}_2\text{O}_{10}\text{Fe}_3$: C, 30.37; H, 0.42; Fe, 35.44. Found: C, 30.38; H, 0.50; Fe, 35.54.

(b) 5 (0.5 g) was refluxed in methylcyclohexane for 5 h. The solution was then evaporated to dryness. Purification by chromatography on a Florisil column followed by crystallization gave 7 (0.15 g, 30% yield).

Hydrogenation Experiments. All the experiments have been performed in a 100-mL stainless-steel autoclave fitted with a glass liner. The dichloromethane solutions of the complexes studied were pressurized under 20 atm of hydrogen and heated to 70°C . Analyses of the gas phase of the solutions were performed on an Instersmat IGC 120F apparatus using a 2-m silica gel column. Gas chromatography coupled with mass spectrometry was performed on a RIBER 10-10 apparatus.

Case of Complex 5: Synthesis of 7. 5 (0.2 g) dissolved in dichloromethane (20 mL) was introduced in the autoclave. The solution was pressurized under 20 atm of hydrogen and heated to 70°C during 16 h. The solution was then cooled and depressurized. Evaporation to dryness and crystallization in pentane gave 7 (0.08 g, 40% yield) as brown crystals. Anal. Calcd for $\text{C}_{11}\text{H}_6\text{O}_9\text{Fe}_3$: C, 29.38; H, 1.34; Fe, 37.33. Found: C, 29.37; H, 1.30; Fe, 36.85.

Registry No. 1, 40806-49-3; 2, 83544-41-6; 3a, 87698-66-6; 3b, 83548-10-1; 4, 83544-42-7; 5, 88610-52-0; 6, 88055-72-5; 7, 103751-58-2; 8, 69440-00-2; acetylene, 74-86-2; Fe, 7439-89-6.

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