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Alkylation Chemistry of the Exposed Carbon Ligand in $[Fe_4(CO)_{12}C]^{2-}$

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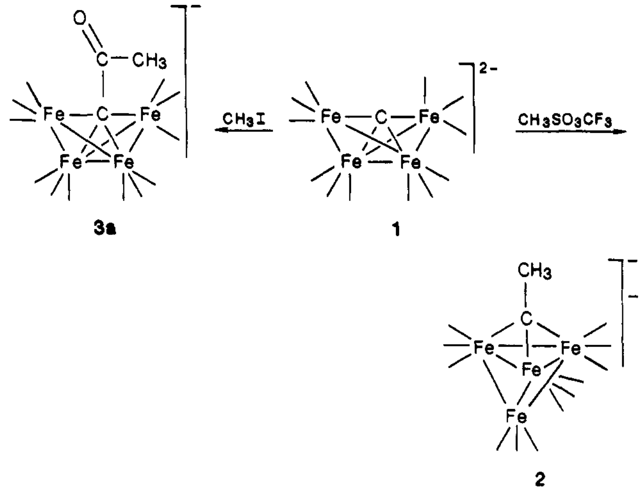
The reactions of the butterfly carbide cluster $[PPN]_2[Fe_4(CO)_{12}C]$ (**1**) were studied with a variety of alkylating agents. For most cases in which reaction was observed, the cluster was alkylated with the formation of a monoanionic cluster having either a four-iron tetrahedral or butterfly framework. Direct electrophilic attack on the carbide ligand appears to occur in the case of highly carbocationic alkylating agents, such as trifluoromethanesulfonate esters, and in these cases the product cluster consists of a tetrahedral Fe_4 array with a face-capping alkylidyne. The reaction of most alkyl halides with **1** occurs with CO uptake to yield $[PPN][Fe_4(CO)_{12}C(CO)R]$ (**3**) (R = Me, $PhCH_2$), and evidence is presented for the involvement of radical species in this reaction.

Introduction

Although carbide clusters (where a carbon atom is attached only to metal atoms) with carbonyl ligands are known for many transition metals, few containing only four metals have been prepared. These butterfly carbide clusters are well-characterized for iron and more recently other metals.[1] The unique features of these compounds are the coordination environment of the carbon atom and reactivity at the carbide center. Reactions in which carbon–carbon bonds are formed with the C ligand are especially interesting, because these may serve as models for the chemistry of the carbide ligand on metal surfaces.

Methylation of the carbide cluster $[PPN]_2[Fe_4(CO)_{12}C]$ results in two different products, depending on the reagent employed. The highly reactive carbocation reagents $CH_3SO_3CF_3$ or CH_3SO_3F give a C-methylated complex consisting of an Fe_4 tetrahedron which is face-bridged by the CCH_3 ligand, **2**.[2] By contrast, reaction of **1** with CH_3I has been reported to produce a CO-insertion product which has an Fe_4 butterfly array with the $C(CO)CH_3$ ligand between the wingtips, **3**.[1a] Cluster **3a** is isolated in 50–60% yield after a 2-day reaction period at room temperature and was identified by NMR and infrared spectroscopy.[1a] Since the product contains one more CO ligand than the reactant, some decomposition must occur to provide CO. The reaction of **1** with $CH_3SO_3CF_3$ is complete to form **2** in 72% yield after 30 min even at −20 °C. Similar results are obtained when $[Me_3O][BF_4]$ is the alkylating agent. Compound **2** has been characterized spectroscopically and also by single-crystal X-ray diffraction.[2]



Product **2** would appear to be the simple result of the attack on an exposed carbide by an electrophilic carbocation; however, the basis for the formation of **3a** is ob-

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(1) (a) Davis, J. H.; Beno, M. A.; Williams, J.; Zimmie, J.; Tachikawa, M.; Muetterties, E. L. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 668. (b) Holt, E. M.; Whitmire, K. H.; Shriver, D. F. *J. Organomet. Chem.* **1981**, *213*, 125. (c) Bradley, J. S.; Ansell, G. B.; Leonowicz, M. E.; Hill, E. W. *J. Am. Chem. Soc.* **1981**, *103*, 4968. (d) Bradley, J. S. *Philos. Trans. R. Soc. London, Ser. A* **1982**, *308*, 103. (e) Beringhelli, T.; Ciani, G.; D'Alfonso, G.; Sironi, A.; Freni, M. *J. Chem. Soc., Chem. Commun.* **1985**, 978. (f) Cowie, A. G.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R. *J. Chem. Soc., Chem. Commun.* **1984**, 710. (g) Kolis, J. W.; Holt, E. M.; Hriljac, J. A.; Shriver, D. F. *Organometallics* **1984**, *3*, 496. (h) Hriljac, J. A.; Swepston, P. N.; Shriver, D. F. *Organometallics*, **1985**, *4*, 158. (i) Sailor, M. J.; Shriver, D. F. *Organometallics* **1985**, *4*, 1476. (j) Cowie, A. G.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R. *J. Organomet. Chem.* **1986**, *306*, C63.

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Table I. CO Stretching Frequencies and ^{13}C NMR Chemical Shifts for the Functionalized Carbide Atom in Tetrahedral and Butterfly Monoalkylated Carbide Clusters

	ν(CO), cm^{-1}	^{13}C NMR δ^e
$[PPN][Fe_4(CO)_{12}CCH_3]$	2041 w, 1993 w, 1980 vs, 1935 m sh[a]	357.0
$[PPN][Fe_4(CO)_{12}CCH_2CH_3]$	2050 w, 2011 m, 1989 vs, 1940 w[b]	373.9
$[PPN][Fe_4(CO)_{12}CCF_3]$	2062 vs, 2001 vs, 1973 m, 1954 sh[c]	314.8 (q, $^2J_{C\text{-}F}$ = 34 Hz)
$[PPN][Fe_4(CO)_{12}C(CO)CH_3]$	2021 m, 1987 s, 1628 w[d]	264.8, 199.2 (acyl)
$[PPN][Fe_4(CO)_{12}C(CO)CH_2C_6H_5]$	2029 m, 1990 s, 1952 sh, 1618 w[b]	264.2, 200.1 (acyl)

[a] Reference 1. [b] CH_2Cl_2 solution. [c] Et_2O solution. [d] Reference 2. [e] CD_2Cl_2/CH_2Cl_2.

scure. We were intrigued by the markedly different reactivities observed in this system and report our study of the factors that influence formation of the tetrahedral and butterfly species.

Experimental Section

General Procedures. All reactions were carried out under anhydrous conditions by using standard vacuum line and Schlenk techniques to exclude air. Solvents were dried before use: CH_2Cl_2 and CH_3CN were distilled from P_2O_5, Et_2O and pentane were distilled from sodium benzophenone ketyl, and ethyl acetate was purified by published procedures.[3a] Alkyl halides were dried and purified by standard methods.[3b] $EtSO_3CF_3$ was distilled in flame-dried glassware. $[PPN]_2[Fe_4(CO)_{12}C]$,[4] $[PPN][Fe_4(CO)_{12}CC(O)CH_3]$[1a] and $[PPN][Fe_4(CO)_{12}CCH_3]$[1b] were prepared by literature methods [PPN = bis(triphenylphosphine)nitrogen(1+)]. Compounds for ^{13}C NMR spectroscopy were obtained by stirring a CH_2Cl_2 solution of $[PPN]_2[Fe_4(CO)_{13}]$[5] for several days under an atmosphere of 99% ^{13}CO.

IR and visible spectra were obtained with Perkin-Elmer 399 and 320 spectrometers, respectively, and NMR spectra were recorded on JEOL FX90Q and FX270 instruments. ESR spectra were recorded on a Varian E5 instrument. Elemental analyses were performed by Galbraith and Schwarzkopf Laboratories.

Preparation of $[PPN][Fe_4(CO)_{12}C(CO)CH_2Ph]$ (3b). To 0.15 g of $[PPN]_2[Fe_4(CO)_{12}C]$ in 10 mL of CH_2Cl_2 was added a CH_2Cl_2 solution of 0.1 g of $PhCH_2I$. The brown solution turned green as the reaction progressed, and the growth of bands at 2029 and 1992 cm^{-1} was monitored by IR spectroscopy. The reaction was complete in a few hours. Solvent was removed under vacuum, the residue was extracted with 12 mL of ethyl acetate, the solution was filtered to remove (PPN)I, and the ethyl acetate was removed by vacuum. The green-black residue was washed with pentane to remove excess alkyl halide. Crystalline product was obtained by dissolving the dried residue in methanol, adding distilled water dropwise with swirling until the product just started to precipitate, cooling in a freezer for several hours, and collecting the black crystals by filtration. The same prodedure was used with 0.1 mL of $PhCH_2Br$ in place of $PhCH_2I$. The reaction with $PHCH_2Br$ takes about 18 h. Recrystallized yields: $PhCH_2I$, 0.02 g, 18%; $PhCH_2Br$, 0.05 g, 45%. Anal. Calcd for $C_{57}H_{37}NO_{13}P_2Fe_4$: C,55.69; H, 3.03; Fe, 18.17. Found: C, 55.52; H, 3.07; Fe, 17.76. ^1H NMR (acetone-d_6): δ 3.52 $(CH)_2$, 7.18 (phenyl protons), 7.59 (PPN^+, also obscures other phenyl protons). ^{13}C NMR (CH_2Cl_2/CD_2Cl_2 at -50 °C): δ 264.5 (carbide), 200.1 (-C(O)-R), 218.8 (6 CO), 210.2 (6 CO).

Preparation of $[PPN][Fe_4(CO)_{12}CCF_3]$ (4b). Excess CF_3I (0.1 mL at −78 °C) was condensed at −196 °C onto a freeze–thaw–degassed CH_2Cl_2 solution of $[PPN]_2[Fe_4(CO)_{12}]$ (0.15 g). The solution was warmed to room temperature and stirred for 2 h. The brown solution turned gray-black, and its infrared spectrum exhibited a strong band at 2000 cm^{-1}. The CH_2Cl_2 was removed under vacuum and the residue extracted with Et_2O. Filtration and concentration of the Et_2O extract followed by layering with pentane produced a black crystalline product. Yield: 0.03 g, 28%. Anal. Calcd for $C_{50}H_{30}NO_{12}F_3P_2Fe_4$: C, 50.93; H, 2.56; Fe, 18.94. Found: C, 50.87; H, 2.72; Fe, 19.49. ^{19}F NMR (acetone-d_6): δ +42.9 (relative to $CFCl_3$). ^{13}C NMR (CH_2Cl_2/CD_2Cl_2 at −90 °C): δ 314.8 (μ_3-C, q, $^2J_{C\text{-}F}$ = 34 Hz), 215.6 (9 CO), 211.2 (3 CO).

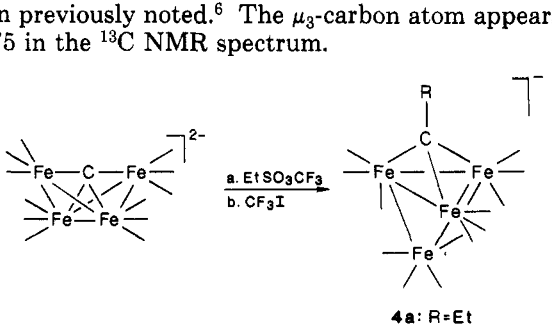
Preparation of $[PPN][Fe_4(CO)_{12}CCH_2CH_3]$ (4a). To 0.15 g of $[PPN]_2[Fe_4(CO)_{12}C]$ in CH_2Cl_2 was added 0.1 mL of $EtSO_3CF_3$. The reaction was stirred for 2 h and judged complete by infrared spectroscopy. The red solution exhibited a strong infrared absorption at 1989 cm^{-1}. Solvent removal, extraction, and layering analogous to that used for $[PPN][Fe_4(Co)_{12}CCF_3]$ produced a red-black product. Yield: 58%. ^1H NMR (acetone-d_6): δ 4.25 (CH_2, q), 1.81 (CH_3, t). ^{13}C NMR (CH_2Cl_2/CD_2Cl_2 at −90 °C): δ 374.0 (μ_3-C), 218.0, (9 CO), δ 213.4 (3 CO). This compound has been previously prepared by a different route.[6]

Results and Discussion

Alkylating agents chosen to investigate the reactivity of $[PPN]_2[Fe_4(CO)_{12}C]$ (1) include compounds which ordinarily undergo S_N2 substitution and those which undergo single electron transfer, SET, reactions. All reactions were performed at room temperature in CH_2Cl_2 and were monitored by infrared spectroscopy. Completion of reaction was judged by disappearance of the infrared bands of 1, and lack of reactivity was judged by the lack of appearance of any product bands after 2 days of stirring. Upon isolation, the products were characterized by infrared and NMR spectroscopy and microanalysis.

The four-iron monoanionic tetrahedral and butterfly carbide clusters of this system can be easily distinguished by ^{13}C NMR spectroscopy. The face-capping μ_3-CR resonance (as in 2) for iron clusters occurs in the range δ 300–400[2,7] whereas the butterfly species (3 for example) have two characteristic ^{13}C resonances. The functionalized carbide atom is at δ 265, and the acyl carbon resonance appears at approximately δ 200. The pattern of the CO stretching bands in the infrared spectral region also is diagnostic. The butterfly clusters have a two-band pattern whereas the tetrahedral clusters show only one major feature. Infrared and NMR data are summarized in Table I.

Formation of Tetrahedral Products. A smooth reaction occurs between 1 and $EtSO_3CF_3$ to form the tetrahedral propylidyne cluster $[PPN][Fe_4(CO)_{12}CCH_2CH_3]$ (4a) analogous to 2. A different route to this cluster has been previously noted.[6] The μ_3-carbon atom appears at δ 375 in the ^{13}C NMR spectrum.



4a: R=Et
b: R=CF_3

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(6) Bradley, J. S., personal communication, 1984.

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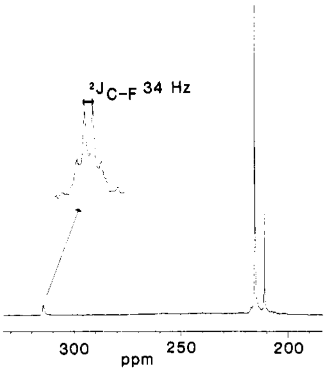
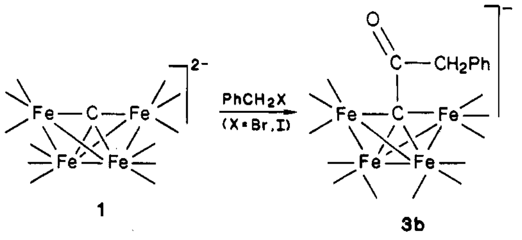


Figure 1. ^{13}C NMR spectrum of **4b** at -90 °C, showing basal and apical terminal CO's and the face-capping carbon resonance. Insert: expansion of the δ 315 resonance displaying fluorine-carbon coupling.

We do not have information of the rate law for the conversion of **1** to **2** because the reaction is quite fast: however, the simplicity of the product suggests direct attack of the alkyl carbocation on the carbon ligand followed by rearrangement of the iron framework to a tetrahedron. One potential objection to this direct attack can be raised from the results of a molecular mechanics calculation which indicates that the approach of an incoming CH_3 to the C ligand would occur with an excessively large activation energy, owing to steric hindrance by surrounding CO ligands.[8] We have reinvestigated this molecular mechanics problem by means of a different model in which the dihedral angle between the wings of the butterfly is allowed to open as the CH_3^+ approaches. This distortion of the butterfly requires very little energy input because the C–Fe and Fe–Fe bonds are highly compliant, and the result of this reorganization is to greatly lower the estimated activation energy for direct attack.[9] Another potential objection to direct attack at the C ligand is that the carbon p_z orbital, which lies along the 2-fold axis of the butterfly and is essential in bond formation with an incoming ligand, has been shown to be highly stabilized by a π-interaction with the d orbitals of the nearly colinear wingtip iron atoms.[10,11] In both studies it is found that the HOMO and nearby occupied orbitals are primarily associated with the metal orbitals. Harris and Bradley also studied the influence of a distortion of the iron framework on the stabilization of the carbon p_z orbital, and they found that as the wingtips are bent down and away from the carbon this interaction diminishes. This is the same distortion which is found to greatly decrease steric crowding between carbonyl ligands and an incoming electrophile. Thus the initial C–C bond formation does not appear to be precluded on steric or electronic grounds. The structure of the final product **2** requires the migration of the CCH_3 ligand toward a basal iron atom as the wingtip iron atoms come together to form an Fe–Fe bond and produce the tetrahedral Fe_4 array of the product.

Reaction of **1** with excess CF_3I also leads to the formation of a tetrahedral cluster **4**. The infrared spectrum of **4b** contains a strong peak at 2000 cm^{-1}. The ^{13}C NMR spectrum of **4b** indicates the formulation $[PPN][Fe_4(CO)_{12}CCF_3]$. The terminal CO region exhibits a 9:3 pattern from -90 to +20 °C (δ 215 and 211) analogous to that observed for **2**,[2] and the μ_3-C appears at δ 315 ppm as a quartet with a two-bond carbon-fluorine coupling of 34 Hz (Figure 1).

Formation of Butterfly Species. As with methyl iodide, reactive alkyl halides such as benzyl bromide and iodide react with **1** to form the butterfly species $[PPN][Fe_4(CO)_{12}C(CO)R]$ (**3**). Species **3** was identified by ^{13}C NMR spectroscopy, with carbide and acyl resonances at δ 264.5 and 200.1, respectively. These reactions are complete in 3–18 h and are therefore faster than that of CH_3I. The spectroscopic yields are about 70%. Again the source of the extra CO ligand appears to be from cluster decomposition.



Possible SET Pathways. The types of alkylating agents that give product **3** are either alkyl bromides or iodides, and, except for CH_3I, these are known to give stabilized radicals or cations upon R–X bond cleavage. (C_3H_5Br also gives a product of type **3**). Benzyl chloride and methyl bromide are unreactive toward **1**, as are methyl and allyl tosylates. The relative rates of reaction observed here is $PhCH_2I > PhCH_2Br > CH_3I$. While the rate of reaction RI > RBr is consistent for both two- and one-electron-transfer pathways, the lack of reactivity of ROTs and sluggishness of the CH_3I reaction point in favor of a SET process. The presence of the halide is an important factor in the reaction because **1** does not react when exposed to alkyl radicals, for example, under photolysis with azomethane.

The electrochemistry of **1** was examined in an attempt to shed light on alkylation processes. Cyclic voltammograms of **1** in CH_3CN or CH_2Cl_2 show four successive oxidations. The first of these appears to be reversible when the potential sweep is reversed immediately after the first wave. The peak to peak separation is 70 mV at a scan rate of 50 mV/s. Bulk electrolyses at the anodic peak potential, E_{pa}, as well as at E_{pa} = +50 mV, E_{pa} = +100 mV, and E_{pa} = +500 mV give values for moles of electrons passed between 3 and 8. These large values may result from an ECE mechanism in which the radical anion produced in the first oxidation rapidly decomposes into electrochemically active species. The decomposition of the original complex was verified by cyclic voltammetry of the electrolyzed solution. When electrochemical oxidation of **1** was carried out in the presence of excess benzyl bromide, no **3b** was observed, as judged by infrared spectra of the solution or comparison of the cyclic voltammogram with that for **3b**. Comparison of measurements at various scan speeds indicate that the electrochemical oxidation of **1** is a two-electron process and that the product, possibly $Fe_4(CO)_{12}C$, is prone to decompose rather than react with RX.

Infrared and visible spectra of a reaction mixture consisting of **1** with $PhCH_2Br$ under pseudo-first order conditions attested to the complexity of the overall reaction. After a 1–2-h induction period, absorption bands of **1** disappear and those of **3b** appear at constant rates. The reaction rate is sensitive to the concentration of $PhCH_2Br$,

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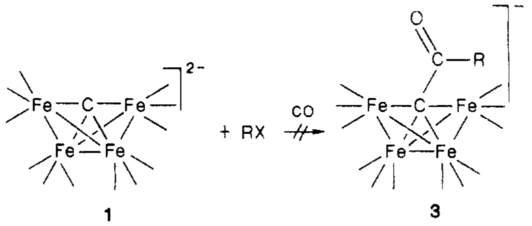
added (PPN)I, Ag^+, and duroquinone and the amount of light to which the reactants are exposed, but the quality of the rate data is low so only relative rates could be determined. The effects of light, duroquinone (a radical inhibitor), and Ag^+ favor radical involvement. A 6-fold rate increase is observed in the presence of a catalytic amount of Ag^+. It is possible the Ag^+ serves to abstract halide from the alkyl group, but Tl^+ does not affect the reaction rate, suggesting that Ag^+ may be functioning as a one-electron oxidant.

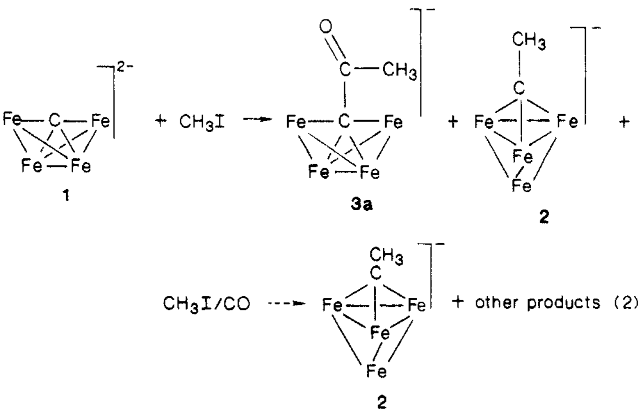
ESR signals were obtained from reaction mixures of 1 and CH_3I, $PhCH_2Br$, or CF_3I that had been frozen at 77 K. The three reactions mixtures exhibited different spectra with broad features and *g* values similar to those of other iron-based radicals.[18] Severe broadening of the NMR resonances is observed with time when the reaction of 1 and alkyl halides is performed in situ in the NMR probe. This broadening may be due to radical species along with Fe^{2+} formed in the reaction.

Reaction of 1 and I_2, ICCI, or CH_2I_2 produces a single paramagnetic cluster that exhibits an intense ESR signal in both solid state and solution. We have been unable to characterize this compound, which possesses cation- and solvent-dependent infrared spectra.

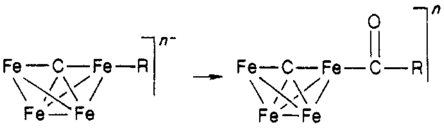
Possible RX Alkylation at Fe and CO Insertion. When the reactions of 1 and CH_3I or $PhCH_2Br$ are performed under a CO atmosphere, no 3 is observed. Instead the infrared spectrum of the reaction solution is very similar to that for the reaction product of 1 with I_2. Upon removal of the CO atmosphere over the reaction mixture of 1 and $PhCH_2Br$, conversion to **3b** occurs. This result suggests that carbon monoxide either stabilizes an intermediate or favors a competing reaction path by inhibiting the alkylation.



An ^1H NMR spectroscopic investigation of the products from the reaction of 1 and methyl iodide shows that some of the tetrahedral cluster 2 also is formed. The ratio of 3 to 2 is about 6:1 Both alkylation pathways thus appear to be accessible for CH_3I, which is known to react both as $CH_3^{\bullet}$ and CH_3^+.[20] Presumably the radical leads to formation of **3a** whereas the CH_3^+ path leads to the small amount of 2 that is experimentally observed of the usual quantity of 2 when 1 is reacted with CH_3I under CO; apparently only the pathway to **3a** is inhibited by CO.

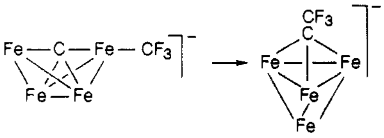


The CO inhibition observed for formation of 3 but not 2 also suggests that an open coordination site at an iron atom may be necessary in the pathway leading to 3. CO loss would not be required if 2 is formed by direct attack at the carbon ligand (eq 3).

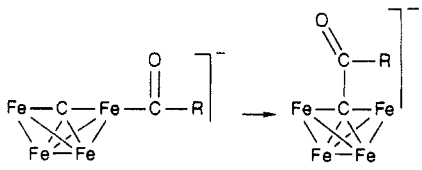


It has already been proposed that the formation of **3a** requires a migratory insertion step,[1a] and migratory insertion reactions are often facilitated by oxidation.[14] Therefore, as suggested by a reviewer, the observed rate enhancement by Ag^+ could be due to oxidative enhancement of the migratory insertion. Alkylation with CO insertion to form an acyl has also been observed for $[Fe_2(CO)_6(PPh_2)_2]$.[2-15] In this dinuclear system, rupture and re-formation of the Fe–Fe bond is considered to be important in assisting the migration. Cluster compounds with σ ligands have been reported recently; the cluster $Os_3(CO)_{10}(CH_3)(\mu\text{-}I)$ inserts CO into the Os–CH_3 bond to give acetyl derivatives.[16] Though the intermediate alkyl complex has not been isolated, $HRu_3(CO)_{10}(\mu\text{-}X)$ reacts with ethylene and CO to give the acyl cluster $Ru_3(CO)_{10}(\mu\text{-}X)(\eta^2,\mu\text{-}C(O)C_2H_5)$.[17] The presence of halides may be important for these types of transformation.

To this point the reaction products appear to correlate well with the nature of the alkylating agents. The production of tetrahedral **4b** with the strong radical reagent CF_3I did not fit the expected pattern. It is possible that the attack is again metal-centered as is postulated for the other alkyl halides but that formation of 3 is blocked because CO insertion into a metal–CF_3 bond is as unfavorable in clusters as it is in mononuclear systems.[21] In the absence of CO insertion, an alkyl migration might occur to the carbide ligand (eq 4). The observation that a CO atmosphere also inhibits formation of **4b** supports the idea that it is mechanistically similar to the RX reactions rather than the reactions of 1 with strong carbocations.



Migration of R_f and C(O)R to the Carbon Ligand. Migration of acyl and perfluoroalkyl ligands to the carbon ligand is proposed to give products 3 and **4b** (eq 5). A



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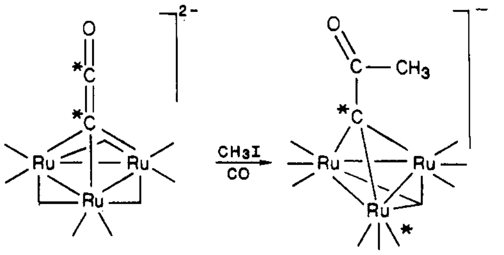
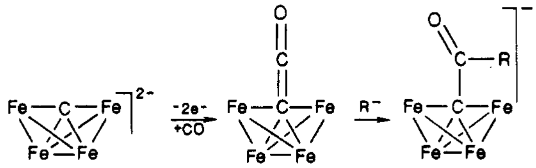
substantial driving force is expected for the postulated migration because carbon–carbon bonds are 30–40 kcal/mol stronger than M–CF_3 bonds and about 40–50 kcal/mol stronger than metal–carbon alkyl bonds.[22] Although alkyl migration to a carbide ligand has not been demonstrated previously in the literature, a recent labeling study in our laboratory supports an acyl to carbon ligand migration in reaction 6.[23] This result suggests prior reaction and CO



(6)

insertion at a ruthenium center, followed by displacement of the labeled ketenylidene CO by a metal-bound acyl ligand.

An alternative mechanism involves a neutral ketenylidene species that is thought to be an intermediate in the reactions of $Fe_4(CO)_{13}C$ with nucleophiles.[24] This mechanism appears unlikely because of the observed carbon monoxide inhibition of the reaction and the lack of product 3 when 1 and RX are mixed together in an electrochemical cell under oxidizing conditions.



(7)

Conclusions. Our observations indicate that different reaction pathways are accessible for the reaction alkyl halides and carbocation alkylating reagents with 1. We suggest that direct attack on the carbon ligand gives the tetrahedral alkylidyne clusters in the case of strong carbocations. In reactions of 1 with alkyl halides, we suggest that the initial site of reactivity is a metal center.

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Silyltitanocene Complexes as Catalysts for the Hydrogenation, Isomerization, and Hydrosilation of Olefins

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The hydrogen evolution that normally accompanies the Cp_2TiMe_2-catalyzed dehydrogenative coupling of organosilanes is completely suppressed in the presence of olefins. Instead, the olefin undergoes hydrogenation. The rates of co-hydrogenation of several olefins (cyclohexene, 1- and 2-pentene, styrene, and norbornadiene) with a variety of silanes ($PhSiH_3$, $PhSiD_3$, $PhCH_2SiH_3$, $C_6H_{13}SiH_3$, c-$C_6H_{11}SiH_3$, and Ph_2SiH_2) parallel the rates of silane coupling in the absence of olefin but are considerably faster. Sterically hindered primary silanes and secondary silanes, which do not catalytically couple in the absence of olefin, dimerize in its presence. The rates of olefin co-hydrogenation are strongly dependent on olefin in the order cyclohexene $<$ 2-pentene $\ll$ 1-pentene $\approx$ norbornene $\approx$ styrene. In the first two cases, a kinetic study reveals that the catalyst is largely in the form of previously described dimeric silyltitanium complexes. The rapidly hydrogenated olefins also give silylated products. In addition to the above reactions the complex $Cp_2Ti(\mu\text{-}H)(\mu\text{-}HSiHPh)TiCp_2$ also catalyzes the isomerization of 2-pentene and the hydrogenation of alkenes by H_2. A kinetic study of the isomerization reaction is also reported.

Introduction

Organotitanium compounds have played a key role in the developed of both synthetic organometallic and catalytic chemistry.[2] It was the discovery of their remarkable activity in the polymerization of 1-olefins that fueled much of the expansion of interest in transition-metal organometallic chemistry that began in the 1950s.[3] In spite of the practical importance of Ziegler–Natta catalysis and the vast amount of research that has been committed to understanding the mechanisms of the polymerization and related catalytic processes, we remain remarkably ignorant of the details of these reactions in comparison to our understanding of similar chemistry involving the later transition groups.[4] For example, very few of the known, iso-

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