Stuart R. Berryhill,* Gary L. Clevenger, and F. Yucel Burdurlu

Department of Chemistry, California State University, Long Beach, California 90840

Received March 7, 1985

Reaction of compounds of the type $CpFe(CO)_2SiMe_2R$ with *n*-BuLi or LDA results in migration of the silyl group from iron to the Cp ligand. Crossover experiments show the reaction to be intramolecular, and a mechanism involving deprotonation of the Cp ligand followed by silyl group migration utilizing a silicon d orbital is presented. A ring-deprotonated species cannot be observed or trapped, but an independent experiment with CpFe(CO)₂Me shows that compounds of this type can be deprotonated. Treatment of $CpFe(CO)_2Me$ with LDA followed by TMSCl gives $(TMSCp)Fe(CO)_2Me$ $(TMS = Me_3Si)$ which is also the product of a migration sequence involving treating $CpFe(CO)_2SiMe_3$ with *n*-BuLi followed by MeI. The regiochemistry of silyl group migration to a substituted Cp ligand is found to be affected by the size of the substituent. Both 1,2- and 1,3-disubstituted products are obtained when the substituent is methyl, while only a 1,3-disubstituted product is obtained when the substituent is trimethylsilyl or dimethyl-phenylsilyl. Several anions of the type $(RMe_2SiCp)Fe(CO)_2Li$ are characterized by IR spectroscopy. Only carbonyl-bridged ion pairs are present in a solution of (1,3-(TMS)₂Cp)Fe(CO)₂Li in THF.

Introduction

The chemical reactivity of the iron-silicon bond in the compound $CpFe(CO)_2SiMe_3$ ($Cp = \eta^5 - C_5H_5$) has been investigated in a number of studies. Electrophilic cleavage of the bond is observed with reagents such as Cl₂ and HCl.³ Several nucleophilic reagents including alkoxides,⁴ a phosphorus ylide,⁵ and fluoride ion⁶ attack at silicon liberating the $CpFe(CO)_2$ anion. A recent report from this laboratory described an interesting migration of the trimethylsilyl group from iron to the complexed cyclopentadienyl ligand that occurs when CpFe(CO)₂SiMe₃ is treated with strong bases.⁷ The migration product is $(TMSCp)Fe(CO)_2Li^+$ $(TMSCp = \eta^5-C_5H_4SiMe_3)$.

This paper describes a study of the scope and mechanism of the silvl migration reaction. An anionic rearrangement similar to the one outlined here involving initial deprotonation of a cyclopentadienyl ring may also be operating in some other reported base-induced migrations of metal-bonded groups to π -bonded cyclopentadienyl ligands: triphenylgermyl from molybdenum to Cp,⁸ aryl from cobalt to Cp,⁹ acetyl from iron to Cp,¹⁰ and acetyl from rhenium to Cp.²⁸ Studies of the scope of the reaction show that several other silyl groups besides trimethylsilyl do migrate and that silvl groups migrate to cyclopentadienyl rings already substituted with methyl, trimethylsilyl, or dimethylphenylsilyl groups.

Results and Discussion

When $CpFe(CO)_2SiMe_3$, 1a, is treated with either n-BuLi or LDA in THF solution at -78 °C, an immediate

- (4) (a) Nasta, M. A.; MacDiarmid, A. G. J. Organomet. Chem. 1969,
 (8) (a) Nasta, M. A.; MacDiarmid, A. G. J. Organomet. Chem. 1973, 55, 177.
 (5) Malisch, W. J. J. Organomet. Chem. 1973, 61, C15.
 (6) Marten, D. F.; Wilburn, S. M. J. Organomet. Chem. 1983, 251, 71.

 - (7) Berryhill, S. R.; Sharenow, B. J. Organomet. Chem. 1981, 221, 143.
 (8) Dean, W. K.; Graham, W. A. G. Inorg. Chem. 1977, 16, 1061.
 (9) Werner, H.; Hofmann, W. Angew. Chem., Int. Ed. Engl. 1978, 17,
- 464
- (10) Liebeskind, L. S.; Welker, M. E. Organometallics 1983, 2, 194.

Table I. Infrared Spectral Bands for Iron Anions

ОС	
R, R ¹ , M ⁺	$\nu_{\rm CO},^a {\rm cm}^{-1}$
H, TMS, Li H, TMS, Na H, DMPS, Li	1875, 1861, 1806, 1743 1874, 1861, 1805, 1770 1881, 1867, 1812, 1751
H, DMPS, Na TMS, TMS, Li	1881, 1864, 1805, 1773 1871, 1757

^a In THF. Referenced to polystyrene (1601 cm⁻¹).



reaction occurs as evidenced by a color change of the reaction mixture from pale yellow to a deep orange-red. The reaction is conveniently monitored by IR spectroscopy which shows complete conversion of 1a to (TMSCp)Fe- $(CO)_2$ Li within a few minutes. The spectrum of (TMSCp)Fe(CO)₂Li in the carbonyl stretching region is almost identical with that reported for $CpFe(CO)_2Li^{11}$

⁽¹⁾ A part of this work was presented at the 11th International Conference on Organometallic Chemistry, Pine Mountain, GA, Oct. 1983.
(2) Piper, T. S.; Lemal, D.; Wilkinson, G. Naturwissenschaften 1956,

^{43. 129.} (3) Bichler, R. E.; Clark, H. C.; Hunter, B. K.; Rake, A. T. J. Organomet. Chem. 1974, 102, 367

⁽¹¹⁾ Nitay, M.; Rosenblum, M. J. Organomet. Chem. 1977, 136, C23.

(Table I). The bands at 1861 and 1743 cm^{-1} may be assigned to a carbonyl-bridged ion pair and those at 1875 and 1806 cm^{-1} to a tight ion pair.^{11,12}

(TMSCp)Fe(CO)₂Li is readily alkylated in high yield by alkyl⁷ and benzyl halides (Scheme I). When n-BuLi is the base and the entire reaction sequence including alkylation is carried out at -78 °C, a trace amount of ferrocene is observed when the crude product is examined by ¹H NMR. If the temperature for the entire sequence is raised to 0 °C, the yield of the alkylation produce is considerably lower,⁷ and the ferrocene in the crude products amounts to 3-4% based on iron. Since ferrocene must be produced in some sort of bimolecular reaction in which Cp is transferred, approximately 8% of the starting material undergoes this side reaction under these conditions. The lower yield also suggests other side reactions whose products are not easily identified. When LDA is used as the base and the entire reaction sequence is carried out at -78°C, the yield of alkylation product is generally lower than in the low-temperature n-BuLi reaction,⁷ but ferrocene is not observed in the crude product. These facts suggest that 1a and n-BuLi can be involved in an electron-transfer process whose product is ferrocene. This point will be considered at greater length below in the discussion of the mechanism of the silvl migration.

An independent synthesis of compounds of type 2 was carried out in order to help confirm their identity and to supply compounds for investigations of the chemistry of the $(TMSCp)Fe(CO)_2R$ system. Accordingly, the iron dimer $[(TMSCp)Fe(CO)_2]_2$, 5a,¹³ is reductively cleaved with sodium amalgam, and the resulting $(TMSCp)Fe-(CO)_2Na$ (for IR spectrum see Table I) is alkylated in good yield (eq 1). The sequence shown in eq 1 also allowed

$$[(TMSCp)Fe(CO)_2]_2 \xrightarrow{1.Na/Hg} 2a,d,e,f,g \qquad (1)$$

5a 59-96%

preparation of $(TMSCp)Fe(CO)_2(\eta^1-CH_2CH=CH_2)$, 2e, $(TMSCp)Fe(CO)_2(\eta^1-CH_2C(CH_3)=CH_2)$, 2f, and $(TMSCp)Fe(CO)_2TMS$, 2g, in yields of about 70%. None of these compounds could be prepared in reasonable yield by treating $(TMSCp)Fe(CO)_2Li$ (from treatment of 1a with *n*-BuLi) with the appropriate electrophile. Apparently with allyl and methallyl chlorides and trimethylsilyl chloride oxidation of $(TMSCp)Fe(CO)_2Li$ is preferred because considerable quantities of 5a were isolated in each case. Spectroscopic data for the compounds of type 2 is found in the Experimental Section. In addition, compounds 2d and 2g proved stable enough to be shipped for combustion analysis.



Compounds 2e and 2f are further characterized by conversion into cationic π -alkene complexes 6a and 6b on treatment with HPF₆ as shown in eq 2. The alkene complexes are stable, crystalline solids. Interestingly, while the four cyclopentadienyl protons of 6b appear as a singlet in the ¹H NMR spectrum, those of 6a appear as a pair of apparent triplets. Compounds $1b^{14}$ and 1c were prepared and treated with *n*-BuLi at -78 °C in order to test the generality of the silyl migration. In both cases silyl migration occurs rapidly and iron alkyl compounds **3a**, **3b**, **4a**, and **4b** are isolated in high yield after treating the reaction mixtures with either MeI or EtBr. IR spectral data for (DMPSCp)Fe(CO)₂Li (DMPSCp = η^5 -C₅H₄SiMe₂Ph) is given in Table I. Four carbonyl stretching bonds are observed as in the spectra of CpFe(CO)₂Li and (TMSCp)Fe(CO)₂Li. However, the bands for the carbonyl-bridged ion pair at 1867 and 1751 cm⁻¹ are at higher frequency than those for the carbonyl-bridged ion pairs in solutions of the other two anions. This implies a somewhat weaker oxygen–lithium interaction¹¹ in the carbonyl-bridged ion pairs of (DMPSCp)Fe-(CO)₂Li.

During the course of this study it was reported that the aminosilyl groups in compounds of the type CpFe- $(CO)_2SiMe_2NR_2$ migrate to the cyclopentadienyl ring when the compounds are treated with the corresponding lithium dialkylamide.¹⁵ Although the reaction was run under quite different conditions (benzene solvent, room temperature) and the final alkylated product was isolated in only about 20% yield, this result taken with those presented in this paper demonstrates the generality of the base-induced migration of the silyl group from iron to cyclopentadienyl ring in cyclopentadienyldicarbonyliron silanes.

While considering the scope of the migration reaction, it was of interest to determine whether a silyl migration will occur in compounds having an already substituted cyclopentadienyl ligand. Compounds 2g, 7, and 8 were prepared for this study as shown in eq 3 and 4. When

$$[(RMe_2SiCp)Fe(CO)_2]_2 \xrightarrow[2.CISiM_3]{1.Na/Hg}} (RMe_2SiCp)Fe(CO)_2SiMe_3 (3)$$

$$2g, R = Me$$

$$7, R = Ph$$

$$[(MeCp)Fe(CO)_2]_2 \xrightarrow[2.ClSiMe_3]{1.Na/Hg} (MeCp)Fe(CO)_2SiMe_3 \quad (4)$$

each of these compounds is treated with *n*-BuLi followed by alkylation, products are isolated whose spectroscopic properties demonstrate that the silyl groups have migrated. The migration of the silyl group of 8 occurs rapidly at -78°C, but good yields of the final alkylated product can only be obtained from 2g and 7 when the reaction mixture is stirred for 5–6 h at -78 °C prior to alkylation or when *n*-BuLi is added at -78 °C and the reaction mixture is allowed to warm to 0 °C prior to alkylation. This qualitative difference in reaction rate must be a result of the considerably greater steric bulk of the silyl groups of compounds 2g and 7 than of the methyl group of compound 8.

The difference in size of the ring substituents might be expected to influence the regiochemistry of the migration product in these reactions. The substitution pattern of the cyclopentadienyl rings was deduced by analysis of the ¹H NMR spectra of compounds 9, 10, and 11 (Scheme II). The spectra of the cationic π -ethylene complexes proved easier to interpret. Hydride abstraction from ethyliron complex 2b using trityl cation has already been reported to proceed smoothly.⁷ The spectrum of 9 shows two methyl group resonances at δ 2.03 and 2.12 and two TMS group resonances at δ 0.41 and 0.46. If the major product

⁽¹²⁾ Pannell, K. H.; Jackson, D. J. Am. Chem. Soc. 1976, 98, 4443.
(13) (a) Kraihanzel, C. S.; Conville, J. J. Organomet. Chem. 1970, 23, 357.
(b) Abel, E. W.; Moorhouse, S. J. Organomet. Chem. 1971, 28, 211.

⁽¹⁴⁾ Mance, A. M.; Van Dyke, C. H. Inorg. Nucl. Chem. Lett. 1979, 15, 393.

⁽¹⁵⁾ Thum, G.; Riews, W.; Greissinger, D.; Malisch, W. J. Organomet. Chem. 1983, 252, C67.



Figure 1. The 200-MHz ¹H NMR spectrum of the cyclopentadienyl protons of complex 10 (acetone- d_6 , 25 °C).



is assumed to be 1,3 disubstituted for steric reasons, its resonances can be assigned as the upfield peak of each pair. Integration values show that the ratio 9 (1, 3)/9 (1, 2) is 1.85. The chemical shifts of the Me, TMS, and Cp protons for the complex (MeCpTMS)Ti(NMe₂)₃ are reported in the literature,¹⁶ and the authors have inferred the presence of both the 1,2- and 1,3-disubstituted isomers. In the case of complex 10 only one regioisomer is detected. The spectrum shows a singlet for the TMS groups at δ 0.48 and a singlet for the ethylene protons at δ 3.94. Two ring proton resonances split by 1,3 coupling (δ 5.99 (d, 2 H, J = 1.4 Hz), 5.91 (t, 1 H, J = 1.4 Hz)) show that the cyclopentadienyl ring is 1,3-disubstituted (Figure 1). A very similar pattern has recently been reported for the ambient temperature spectrum of the ring protons of 1,1',3,3'-tet-



ra-tert-butylferrocene.¹⁷ Compound 12 could not be crystallized, so the spectrum of the ethyl compound 11 is presented here as evidence that only the 1,3-disubstituted isomer is formed when the TMS group of compound 7 migrates. Singlets at δ 0.38 and 0.67 may be assigned to the TMS group and the dimethylphenylsilyl methyl groups, respectively, while the ethyl and phenyl groups give rise to multiplets centered at δ 1.40 and 7.44. Interestingly, although compound 11 does not have the symmetry of compound 10, there is apparent equivalency of the ring protons adjacent to the two different silyl groups so there are two ring proton resonances split by 1,3 coupling (δ 4.82 (d, 2 H, J = 1.5 Hz), 4.66 (t, 1 H, J = 1.5 Hz)).

While investigating the TMS group migration with compound 2g, the IR spectrum of anion 13 was obtained (Table I). The spectrum shows only two carbonyl



stretching bands for a carbonyl-bridged ion pair. The absence of carbonyl bands for a tight ion pair may be due to steric interference to the solvation of lithium by the two silyl groups. Additionally, the high frequency of the 1757 cm⁻¹ band implies a weaker oxygen-lithium interaction than in the carbonyl-bridged ion pairs of (TMSCp)Fe-(CO₂)Li.

Finally, compounds 14a and 14b were prepared by β -hydride abstraction from compounds 3a and 4b, respectively. The hydride abstraction typically requires about



1.5 h at 0 °C and can be readily monitored by IR spectroscopy. The cationic ethylene complexes are quite stable, and acceptable elemental analyses were obtained.

A proposed mechanism⁷ for the silyl group migration is shown in Scheme III. Initial deprotonation of the cyclopentadienyl ligand is followed by migration of the silyl group to give the iron anion. Formation of the coordinatively saturated 18-electron anion must provide a driving force for the rearrangement. This reaction may be regarded as an organometallic example of a Brook-type rearrangement.¹⁸

It is perhaps surprising that *n*-BuLi does not directly displace the $CpFe(CO)_2$ anion from silicon since the migration appears to involve the displacement of an analogous anion from silicon. The kinetic acidity of the cyclo-

⁽¹⁶⁾ Dammgen, J.; Burger, H. J. Organomet. Chem. 1975, 101, 307.

⁽¹⁷⁾ Luke, W. D.; Streitwieser, A. J. Am. Chem. Soc. 1981, 103, 3241.
(18) Colvin, E. "Silicon in Organic Synthesis"; Butterworths: London, 1981; Chapter 5.



pentadienyl ring protons (vide infra) must be reasonably high to account for the observed course of the reaction. A somewhat analogous situation exists when trimethylsilylcyclopentadiene is treated with *n*-BuLi. In this case also the kinetic acidity of the cyclopentadienyl proton must be the important factor because the product formed is the (trimethylsilyl)cyclopentadienide ion¹⁹ rather than the aromatic cyclopentadienide ion which would be formed by displacement at silicon. The preference for deprotonation rather than reaction at silicon in these two cases may also be related to the fact that both the CpFe(CO)₂ anion and the Cp anion would be soft leaving groups.

Two different crossover experiments were conducted in order to determine whether the silvl migration is inter- or intramolecular. Scheme IV shows the two reactions carried out and the products obtained. In each case only the products of intramolecular migration of the silvl groups were isolated. The products were separated by using column chromatography and characterized by ¹H NMR and mass spectrometry. The ethyl complexes were chosen for this study because the previous work had shown that they give a very characteristic mass spectral fragmentation pattern. Typically, the important fragments observed are $M^+ - 28$, $M^+ - 56$, $M^+ - 84$, and $M^+ - 85$ corresponding to loss of CO or ethylene, both CO ligands or one CO and ethylene, both CO ligands and ethylene, and both CO ligands and the ethyl group (see Experimental Section). The NMR and mass spectra obtained of the crossover products were identical with those of compounds 3b and 11 prepared by the other routes described. Each crossover experiment was run at two different concentrations of reactants (see Experimental Section), and in no case were products of an intermolecular reaction observed.

The Brook rearrangement has been shown to involve an intramolecular attack on silicon forming a pentacoordinate silicon species²⁰ as shown in eq 5. An empty d orbital on



⁽¹⁹⁾ Lappert, M. F.; Singh, A.; Englehardt, L. M., White, A. H. J. Organomet. Chem. 1984, 262, 271 and references therein.
(20) Brook, A. G. Acc. Chem. Res. 1974, 7, 77.



Figure 2. Participation of a silicon d orbital in the silyl migration.

silicon is presumably involved. Since the rearrangement of a silyl group from iron to carbon is intramolecular, an analogous pentacoordinate species is probably also important in this reaction (eq 6). As mentioned above,



formation of the coordinatively saturated 18-electron anion may drive the rearrangement. In the Brook rearrangement formation of the stable silicon-oxygen bond drives the reaction.

One question that remains to be considered is whether deprotonation (metalation) of the Cp ring is actually the first step in the reaction. Although no direct evidence has been obtained for this step with the iron silanes because of the extremely facile silvl migration, metalation of the Cp ring is observed under the proper conditions with the related iron alkyl compound $CpFe(CO)_2Me$, 15. The behavior of 15 when treated with *n*-BuLi followed by ethyl bromide has been previously reported.⁷ Electron transfer seems to dominate because ferrocene and CpFe(CO)₂Et are identified in the tractable portion of the product. No evidence has been obtained for any product resulting from Cp ring metalation when 15 is treated with n-BuLi. On the other hand, treatment of 15 with LDA at -30 °C results in smooth metalation as evidenced by the isolation of compounds 2a and 3a in good yield after treating the reaction mixture with the appropriate chlorosilane (eq 7).



It is thus demonstrated that with the proper choice of base ring metalation of a cyclopentadienyl dicarbonyliron derivative is favored over other possible reactions such as electron transfer or nucleophilic attack at a coordinated CO ligand. Use of this reaction has allowed preparation of a number of ring-silylated $CpFe(CO)_2R$ (R = alkyl) compounds.²¹

During the course of the present study a Russian group has reported the ring metalation of $CpFe(CO)_2Ph$ and $CpFe(CO)_2CH_2Ph$ using *n*-BuLi.²² In addition, they performed kinetic acidity measurements from which they estimated the pK_a of the ring hydrogens to be 29 for the phenyl compound and 30 for the benzyl compound.^{22b} It is likely that the kinetic acidity of the ring hydrogens of 1a is in this range or possibly even greater based on the observation that (TMSCp)Fe(CO)₂Li is present immediately when 1a and *n*-BuLi are mixed at -78 °C.

⁽²¹⁾ Berryhill, S. R.; Burdurlu, Y.; Richardson, R., manuscript in preparation.

^{(22) (}a) Orlova, T. Y.; Setkina, V. N.; Sizoi, V. F.; Kursanov, D. N. J. Organomet. Chem. 1983, 252, 201. (b) Orlova, T. Y.; Setkina, V. N.; Kursanov, D. N. J. Organomet. Chem. 1984, 267, 309.

Iron to Cyclopentadienyl Ligand Silyl Group Migration

Figure 2 shows the participation of a d orbital on silicon in accepting charge from the cyclopentadienyl ring carbon. This picture is an orbital representation of the pentavalent silicon species shown in eq 6. The lifetime of the presumed intermediate $(\eta^5-C_5H_4Li)Fe(CO)_2SiMe_3$ (Scheme III) must be extremely short because 2a is isolated when a mixture of 1a and CH_3I is treated with LDA at -78 °C. Indeed, it is possible that deprotonation and silyl group migration occur essentially concomitantly.

In summary, the work reported here shows that the facile rearrangement of a silyl group from iron to a coordinated cyclopentadienyl ring is intramolecular, and a Brook-type mechanism involving a pentavalent silicon species is reasonable. This type of anionic rearrangement from metal to coordinated cyclopentadienyl ligand may prove to be a fairly general type of reaction^{8-10,28} in organometallic chemistry. In addition, the regiochemistry of the silvl migration product has been shown to be dependent on the steric bulk of substituents already present on the cyclopentadienyl ring. The demonstration of ring metalation of 15 with LDA opens a new area of chemistry of ring-substituted derivatives of the CpFe(CO)₂R system.

Experimental Section

All reactions, filtrations, and chromatographies were carried out in a dry nitrogen atmosphere by using oven-dried glassware. Organic solvents were dried by using standard procedures and were degassed immediately prior to use. The chlorosilanes were obtained from Petrarch and distilled prior to use. Bis[dicarbonyl(methylcyclopentadienyl)iron] was obtained from Strem Chemical, Inc., and was used without further purification. Bis-(dicarbonylcyclopentadienyl)iron,²³ (trimethylsilyl)cyclopentadiene,²⁴ CpFe(CO)₂SiMe₃,² CpFe(CO)₂SiMe₂Ph,¹⁴ CpFe- $(CO)_2Me$,²⁵ and trityl fluoroborate²⁶ were prepared by following reported procedures. (Dimethylphenylsilyl)cyclopentadiene was prepared by using a modification of a reported procedure²⁷ (NaCp used instead of CpMgBr). Florisil used for chromatographic separations was 100-200 mesh. Melting points were measured on a Thomas-Hoover Unimelt apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer 237B spectrometer using NaCl solution cells. Proton NMR spectra were obtained on either a Varian EM360 or a Perkin-Elmer R-12B spectrometer. Mass spectra (70 eV) were recorded on a DuPont DP-1 mass spectrometer. Elemental analyses were performed by Micanal, Tucson, AZ.

CpFe(CO)₂SiMe₂n-Pr (1c). A solution containing 0.02 mol of CpFe(CO)₂Na in 100 mL of THF was prepared by the standard method and cooled to 0 °C. Chlorodimethylpropylsilane (3.1 mL, 0.02 mol) was added all at once by syringe. The reaction mixture was stirred overnight while coming to ambient temperature. Solvent was removed from the mixture under reduced pressure, and the dark orange residue was extracted with 3×100 mL of petroleum ether. The extracts were filtered through a mixture of sand and Celite, and the solvent was removed by vacuum transfer. Distillation of the residue afforded pure 1b (3.83 g, 69%): bp 124-127 °C (1 mm); mp 37-38.5 °C; IR (CHCl₃) 1992, 1937 cm⁻¹; ¹H NMR (CS₂) δ 4.68 (s, Cp), 1.63–0.60 (m, CH₂CH₂CH₃), 0.36 (s, CH₃). Anal. Calcd for C₁₂H₁₈FeO₂Si: C, 51.81; H, 6.52. Found: C, 51.71; H, 6.52.

General Preparation of $(RMe_2SiCp)Fe(CO)_2R'$ by Silyl Group Migration. The preparations of 2d and 4a described here illustrate the general procedure used for the compounds shown in Scheme I.

A solution of 1a (1.02 g, 4.1 mmol) in 30 mL of THF at -78°C was treated with 2.04 mL of a 2 M solution of n-butyllithium in hexane (4.1 mmol). The mixture changed from yellow to orange in color. After being stirred for 30 min at -78 °C, the mixture was treated with benzyl chloride (0.46 mL, 4.1 mmol) and stirred for 2 h at 0 °C. Solvent was removed from the mixture under reduced pressure, and the residue was loaded onto a Florisil column. Petroleum ether eluted a yellow band containing 2d. Solvent was removed under reduced pressure and the residue crystallized. A second chromatography of this material on Florisil yielded an analytically pure sample of 2d (0.99 g, 71%): mp 37.5-39 °C; IR (CH₂Cl₂) 2004, 1951 cm⁻¹; ¹H NMR (CS₂) δ 6.98 (b s, Ph), 4.57 (b s, Cp), 2.58 (s, CH₂), 0.24 (s, SiMe₃); MS, m/e 340, 312, 284, 269, 193. Anal. Calcd for C₁₇H₂₀FeO₂Si: C, 60.01; H, 5.92. Found: C, 60.57; H, 6.11.

A solution of 1c (1.11g, 4 mmol) in 20 mL of THF at -78 °C was treated with 2.1 mL of a 2 M solution of n-butyllithium in hexane (4.2 mmol). The reaction mixture quickly turned a deep orange color. After being stirred for 1.5 h at -78 °C, the mixture was treated with CH₃I (3.7 mL, 6 mmol) and stirred for 1 h while coming to 0 °C. Solvent was removed under reduced pressure. and the yellow oily residue was chromatographed on Florisil. Petroleum ether eluted a bright yellow band. Solvent was removed under vacuum leaving 4a as a yellow oil (1.09 g, 93%): IR (CHCl₃) 1996, 1945 cm⁻¹; ¹H NMR (CS₂) δ 4.76 (m, Cp), 1.80–0.53 (m, Ch₂CH₂CH₃), 0.28 (s, Si(CH₃)₂), 0.16 (s, FeCH₃).

The properties of compounds 2a, 2b, and 2c have been reported in ref 7.

(DMPSCp)Fe(CO)₂Et (3b). The compound was isolated as a yellow oil in 74% yield: IR (CH₂Cl₂) 1995, 1937 cm⁻¹; ¹H NMR $(CS_2) \delta$ 7.41 (m, Ph), 4.77 (m, Cp), 1.68–1.04 (m, CH₂CH₃), 0.59 (s, CH₃); MS, m/e 312, 284, 256, 255.

(n-PrMe₂SiCp)Fe(CO)₂Et (4b). The compound was isolated as a yellow oil in 81% yield: IR (CHCl₃) 1995, 1940 cm⁻¹; ¹H NMR (CS₂) δ 4.73 (m, Cp), 1.77-0.53 (complex, CH₂CH₃ and CH₂CH₂CH₃), 0.25 (s, CH₃).

Bis[dicarbonyl[(trimethylsilyl)cyclopentadienyl]iron] (5a). (Trimethylsilyl)cyclopentadiene (5.5 g, 0.04 mol) was dissolved in 35 mL of toluene in a flask fitted with a reflux condenser. Iron pentacarbonyl (7.8 g, 0.04 mol) was added, and the mixture was heated at reflux for 24 h. Toluene and unreacted iron pentacarbonyl were removed by simple distillation, and the residue was chromatographed on Florisil. Petroleum ether eluted a yellow band (1,1'-bis(trimethylsilyl)ferrocene), and petroleum ether/ether (95:5) eluted the product as a reddish violet band. Removal of the solvent under reduced pressure afforded 6.4 g (54%) of dark violet crystals: mp 102-104 °C (lit.^{13b} mp 107 °C); ¹H NMR $(CDCl_3) \delta 4.89 (t, Cp), 4.49 (t, Cp), 0.36 (s, SiMe_3).$

Bis[dicarbonyl[(dimethylphenylsilyl)cyclopentadienyl)]iron] (5b). A mixture of (dimethylphenylsilyl)cyclopentadiene (1.74 g, 8.7 mmol), iron pentacarbonyl (1.70 g, 8.7 mmol), and 30 mL of toluene was heated under reflux for 26 h. The mixture was reduced to about one-fourth of its volume by simple distillation of toluene, and the residue was chromatographed on Florisil. Pentane eluted a yellow band, and CH₂Cl₂ eluted the product as a dark red band. Removal of the solvent under reduced pressure afforded 2.25 g (41%) of dark red crystals: mp 140–144°; ¹H NMR (CDCl₃) δ 7.42 (m, Ph), 4.92 (t, Cp), 4.54 (t, Cp), 0.69 (s, SiMe₂). Anal. Calcd for $C_{30}H_{30}Fe_2O_4Si_2$: C, 57.89; H, 4.86. Found: C, 57.22; H, 4.85.

 $(TMSCp)Fe(CO)_2(\eta^1-CH_2CH=CH_2)$ (2e). An amalgam was prepared in a three-neck flask fitted with an overhead stirrer by adding sodium (1.0 g, 43 mmol) in small pieces to 6 mL of mercury. THF (75 mL) was added followed by 5a (2.49 g, 5 mmol). The mixture was stirred vigorously for 2 h. The yellow-orange solution containing $(TMSCp)Fe(CO_2)Na$ was transferred by cannula to a clean flask and cooled to 0 °C. Allyl chloride (1.22 mL, 15 mmol) was added by syringe, and the mixture quickly turned a greenish brown color. After the mixture was stirred for 2 h at 0 °C, the solvent was removed under reduced pressure. The residue was extracted with 4×35 mL of petroleum ether, and the extracts were combined and filtered through a mixture of sand and Celite. After concentration under reduced pressure the residue was chromatographed on Florisil. Petroleum ether eluted 2e as a yellow band. Solvent was removed under vacuum leaving 2e as a yellow oil (2.0 g, 69%): IR (CHCl₃) 1995, 1940 cm⁻¹; ¹H NMR

⁽²³⁾ King, R. B. "Organometallic Syntheses"; Academic Press: New York, 1965; Vol. 1, p 114.
(24) Kraihanzel, C. S.; Losee, M. L. J. Am. Chem. Soc. 1968, 90, 4701.
(25) Piper, T. S.; Wilkinson, G. J. Inorg. Nucl. Chem. 1956, 3, 104.
(26) Dauben, H. J.; Honnen, L. R.; Harmon, K. M. J. Org. Chem. 1960, 05 1449.

^{25, 1442} (27) Kira, M.; Watanabe, M.; Sakurai, H. J. Am. Chem. Soc. 1977, 99, 7780

⁽²⁸⁾ Heah, P. C.; Gladysz, J. A. J. Am. Chem. Soc. 1984, 106, 7636.

 $(CS_2) \delta$ 5.95 (ddt, =CH), 4.96-4.33 (m, =CH₂) 4.70 (br s, Cp), 2.09 (d, CH₂), 0.28 (s, SiMe₃).

(TMSCp)Fe(CO)₂TMS (2g). A solution of (TMSCp)Fe-(CO)₂Na (43 mmol) in 225 mL of THF was prepared as described above from 10.7 g (21.5 mmol) of 5a and treated with chlorotrimethylsilane (6.35 mL, 50 mmol). After a workup similar to that described above, the crude reaction product was chromatographed on Florisil. Petroleum ether eluted 2g as a yellow band. Solvent was removed under vacuum leaving 2g as an amber oil which crystallized on refrigeration (7.30 g, 53%): IR (CHCl₃) 1989, 1929 cm⁻¹; ¹H NMR (CS₂) δ 4.66 (m, Cp), 0.43 (s, Fe–SiMe₃), 0.34 (s, SiMe₃); MS, m/e 322, 307, 294, 266, 251, 249. Anal. Calcd for C₁₃H₂₂FeO₂Si₂: C, 48.44; H, 6.88. Found: C, 48.18; H, 6.89.

(TMSCp)Fe(CO)₂(η^2 -CH₂=CHCH₃)PF₆ (6a). Complex 2e (1.18 g, 4.07 mmol) was dissolved in a mixture of 30 mL of THF and 30 mL of ether, and 0.55 mL (4.05 mmol) of 65% aqueous HPF₆ was added by syringe. A yellow solid began to form immediately, and 40 mL of ether was added to the mixture. The solid was collected by filtration, washed with ether, and dried under vacuum. Recrystallization from CH₂Cl₂/ether afforded 6a as a bright yellow solid (0.76 g, 43%): IR (CH₂Cl₂) 2070, 2031 cm⁻¹; ¹H NMR (C₃D₆O) δ 5.99 (t, Cp), 5.87 (t, Cp), 5.63–4.98 (m, =CH), 4.04 (d, J = 8 Hz, cis =CH), 3.64 (d, J = 14.5 Hz, trans =CH), 1.92 (d, J = 6 Hz, CH₃). Anal. Calcd for C₁₃H₁₉FeO₂SiPF₆: C, 35.80; H, 4.39. Found: C, 35.90; H, 4.43.

(TMSCp)Fe(CO)₂(π^2 -CH₂=C(CH₃)₂)PF₆(6b). A solution containing (TMSCp)Fe(CO)₂Na (10 mmol) in THF was prepared as described for the preparation of 2e. After being cooled to 0 °C, the solution was treated with 3-chloro-2-methylpropene (1.48 mL, 15 mmol) and stirred for 2 h. Addition of 1.36 mL (10 mmol) of 65% aqueous HPF₆ at 0 °C caused an orange solid to precipitate. The solid was collected by filtration, washed with ether, and dried under vacuum. Recrystallization from CH₂Cl₂/ether afforded **6b** as an orange solid (3.11 g, 69%): IR (CH₂Cl₂) 2061, 2019 cm⁻¹; ¹H NMR (C₃D₆O) δ 5.95 (s, Cp), 4.03 (s, =CH₂), 1.99 (s, CH₃), 0.45 (s, SiMe₃). Anal. Calcd for C₁₄H₂₁FeO₂SiPF₆: C, 37.55; H, 4.70. Found: C, 37.24; H, 4.84.

(DMPSCp)Fe(CO)₂TMS (7). A THF solution containing 9 mmol of (DMPSCp)Fe(CO)₂Na was prepared as described previously from 5b (2.82 g, 4.5 mmol). The solution was treated with chlorotrimethylsilane (1.14 mL, 9 mmol) and stirred for 2 h. After a workup similar to that for 2g, the crude product was chromatographed on Florisil. Petroleum ether eluted 7 as a yellow band. Solvent was removed under vacuum leaving 7 as an amber oil which crystallized on refrigeration (2.21 g, 64%): IR (CHCl₃) 1993, 1937 cm⁻¹; ¹H NMR (CS₂) δ 7.49 (m, Ph), 4.65 (br s, Cp), 0.71 (s, SiMe₂), 0.44 (s, SiMe₃); MS, m/e 384, 369, 356, 328, 313, 255.

(MeCp)Fe(CO)₂TMS (8). A solution of $(MeCp)Fe(CO)_2Na$ (10 mmol) in 150 mL of THF was prepared in the standard fashion. Chlorotrimethylsilane (1.2 mL, 9.5 mmol) was added, and the mixture was stirred for 4 h. Workup as before gave a crude product which was chromatographed on Florisil. Petroleum ether eluted 8 as a light yellow band. Continued elution with petroleum ether/ether (98:2) afforded a small amount of material identified as 1,1'-dimethylferrocene. The yield of 8 was 1.43 g (57%): IR (CHCl₃) 1992, 1938 cm⁻¹, ¹H NMR (CS₂) δ 4.68 (t, Cp), 4.44 (t, Cp), 2.02 (s, CH₃), 0.43 (s, SiMe₃); MS, m/e 249, 236, 208, 193.

 $(MeCpTMS)Fe(CO)_2(\eta^2-C_2H_4)BF_4$ (9). A solution of 8 (1.23) g, 4.7 mmol) in THF at -78 °C was treated with n-BuLi (3.9 mL of a 1.3 M solution in hexane, 5.1 mmol). After being stirred for 4 h at -78 °C, the mixture was treated with ethyl bromide (0.35 mL, 4.7 mmol) and stored overnight in a freezer at -10 °C. Solvent was removed under reduced pressure, and the residue was chromatographed on Florisil. Petroleum ether eluted a yellow band from which solvent was removed under reduced pressure affording (MeCpTMS)Fe(CO)₂Et as an amber oil (0.87 g, 64%): IR (CH_2Cl_2) 1984, 1926 cm⁻¹; MS, m/e 292, 264, 236, 208, 207. The ¹H NMR spectrum of this material was complex, and the presence of two TMS group resonances at δ 0.31 and 0.26 indicated two isomers. The remaining material (0.78 g, 2.7 mmol) was dissolved in 20 mL of CH₂Cl₂ and treated with tritvl fluoroborate (0.88 g, 2.7 mmol). After 3 h the cationic complex was precipitated by slow addition of ether and collected by filtration. The crude product was recrystallized from acetone/ether, collected, and dried under vacuum to afford 9 as yellow crystals (0.74 g, 73%): IR-

(CH₂Cl₂) 2078, 2039 cm⁻¹; ¹H NMR (CD₃NO₂) δ 5.48 (m, Cp), 3.72 (s, vinyl), 2.12 (s, CH₃ of 1,2 isomer), 2.03 (s, CH₃ of 1,3 isomer), 0.46 (s, TMS of 1,2 isomer), 0.41 (s, TMS of 1,3 isomer). Anal. Calcd for C₁₃H₁₉FeO₂SiBF₄: C, 41.30; H, 5.07. Found: C, 41.14; H, 5.19.

 $(1,3-(TMS)_2Cp)Fe(CO)_2(\eta^2-C_2H_4)BF_4$ (10). A solution of 2g (1.15 g, 3.6 mmol) in THF at -78 °C was treated with n-BuLi (2.1 mL of a 1.8 M solution in hexane, 3.8 mmol). After being stirred for 6 h at -78 °C, the mixture was warmed to 0 °C and treated with 0.4 mL of ethyl bromide (5.4 mmol). Solvent was removed under reduced pressure after the mixture had stirred for 3.5 h at 0 °C, and the residue was chromatographed on Florisil. Petroleum ether eluted a yellow band from which solvent was removed under reduced pressure affording (1,3-(TMS)₂Cp)Fe-(CO)₂Et as a yellow oil (1.09 g, 88%): IR (CH₂Cl₂) 1988, 1935 cm^{-1} ; ¹H NMR (CS₂) δ 4.78 (d, 2 H, Cp), 4.69 (t, 1 H, Cp), 1.68–1.04 $(m, CH_2CH_3), 0.33 (s, TMS); MS, m/e 322 (M^+ - CO), 294, 266,$ 265. The ethyl complex (0.9 g, 2.6 mmol) was dissolved in 25 mL of CH₂Cl₂ at 0 °C and treated with trityl fluoroborate (0.86 g, 2.6 mmol). After the mixture was stirred for 1.5 h at 0 °C, ether was added slowly to the mixture causing the cationic complex to precipitate. The crude product was collected and recrystallized from CH_2Cl_2 /ether affording 10 as yellow crystals (0.85 g, 76%): IR $(CH_2\tilde{C}l_2)$ 2071, 2037 cm⁻¹; ¹H NMR $(C_3D_6O) \delta$ 5.97 (d, 2 H, Cp), 5.89 (t, 1 H, Cp), 3.94 (s, vinyl), 0.48 (s, TMS). Anal. Calcd for C₁₅H₂₅FeO₂Si₂BF₄: C, 41.30; H, 5.78. Found: C, 41.36; H, 5.73

(1-DMPS-3-TMSCp)Fe(CO)₂Et (11). This compound was prepared in 78% yield from 2 mmol of 7 in a manner similar to that described above for the preparation of (1,3-(TMS)₂Cp)Fe-(CO)₂Et: IR (CH₂Cl₂) 1993, 1937 cm⁻¹; ¹H NMR (CS₂) δ 7.77 (m, Ph), 4.83 (d, 2 H, Cp), 4.67 (t, 1 H, Cp), 1.69–1.05 (m, CH₂CH₃), 0.76 (s, SiMe₂), 0.38 (s, TMS); MS, m/e 412, 384, 356, 328, 327. Treatment of this material with trityl fluoroborate yielded 12 as shown by changes in the carbonyl region of the IR spectrum, but the product could not be obtained in crystalline form.

(DMPSCp)Fe(CO)₂(η^2 -C₂H₄)BF₄ (14a). A solution of 0.57 g of 3a (1.7 mmol) in 25 mL CH₂Cl₂ maintained at 0 °C was treated with trityl fluoroborate (0.55 g, 1.7 mmol). After 1.5 h ether was added slowly to precipitate the product which was collected by filtration and dried under vacuum. Recrystallization from CH₂Cl₂/ether afforded 14a as yellow crystals (0.47 g, 66%): IR (CH₂Cl₂) 2081, 2042 cm⁻¹; ¹H NMR (C₃D₆O) δ 7.58 (m, Ph), 5.96 (s, Cp), 3.86 (s, vinyl), 0.70 (s, SiMe₂). Anal. Calcd for C₁₇H₁₉FeO₂SiBF₄: C, 47.92; H, 4.49. Found: C, 47.67; H, 4.51.

(*n*-PrSiMe₂Cp)Fe(CO)₂(η^2 -C₂H₄)BF₄ (14b). This compound was prepared from 4b (2.2 mmol) as described above for 14a. Recrystallization from CH₂Cl₂/ether afforded 14b as a pale yellow solid (0.71 g, 82%): IR (CH₂Cl₂) 2073, 2036 cm⁻¹; ¹H NMR (C₃D₆O) δ 5.97 (s, Cp), 3.95 (s, vinyl), 1.73–0.68 (m, CH₂CH₂CH₃), 0.47 (s, SiMe₂). Anal. Calcd for C₁₄H₂₁FeO₂SiBF₄: C, 42.89; H, 5.40. Found: C. 42.76; H, 5.34.

Preparation of 2a from 15. A solution of 0.5 g (2.6 mmol) of 15 in 20 mL of THF at -30 °C was added by cannula to a -30 °C solution of 2.73 mmol of lithium diisopropylamide in 10 mL of THF. After being stirred for 3 h at -30 °C, the mixture was treated with chlorotrimethylsilane (0.28 g, 2.6 mmol). This mixture was stirred for 2 h at -30 °C, and the solvent was removed under reduced pressure. The residue was chromatographed on Florisil, and 2a was eluted as a golden yellow band with pentane. Removal of solvent under reduced pressure left 0.36 g of a yellow oil (52%). The spectroscopic properties of this material match exactly those of 2a prepared by silyl group migration or by methylation (TMSCp)Fe(CO)₂Na.

Preparation of 3a from 15. Compound **3a** was prepared in 97% yield from 15 and chlorodimethylphenylsilane following the same procedure as that outlined for the preparation of **2a**: IR (CHCl₃) 1995, 1940 cm⁻¹; ¹H NMR (CS₂) δ 7.37 (br s, Ph), 4.77 (m, Cp), 0.62 (s, SiMe₂), 0.17 (s, FeCH₃).

Crossover Reactions. A solution of 0.5 equiv of 8 (2.6 mmol) and 0.5 equiv. of 1b (2.6 mmol) in 75 mL of THF at -78 °C was treated with 1.2 equiv of a solution of *n*-BuLi in hexane. This mixture was stirred at -78 °C for 4 h and then warmed to 0 °C during 1 h. Ethyl bromide (6.2 mmol) was added, and the mixture was stirred for 2 h at 0 °C. Workup as described above for the silyl migration reactions gave a crude product which was chromatographed on Florisil. Elution with petroleum ether yielded two fractions. Evaporation of solvent left two yellow oils identified on the basis of spectroscopic properties as 3b and (MeCpTMS)Fe(CO)₂Et. Careful mass spectral analysis of these materials showed no measurable quantities of the possible intermolecular products (Scheme IV), one of which (2b) had been previously analyzed by mass spectroscopy. Similar results were obtained when the experiment was repeated with 2.5 mmol of each starting material in 20 mL of THF.

A solution of (Me₃SiCp)Fe(CO)₂DMPS and 7 (2 mmol) in 20 mL of THF were treated as described in the previous paragraph. A single product was isolated after workup and chromatography, and it was identified as 11 on the basis of spectroscopic data. Mass spectral analysis gave no indication of intermolecular products (Scheme IV). The experiment was repeated by using 1 mmol of each starting material in 100 mL of THF, and a single product identified as 11 was obtained.

Acknowledgment. This research was supported in part by the Office of Research, California State University, Long Beach.

Registry No. 1a, 31811-63-9; 1b, 41680-29-9; 1c, 97279-47-5; 2a, 80611-30-9; 2d, 97279-55-5; 2e, 97279-72-6; 2g, 97279-74-8; 3a, 97279-56-6; 3b, 97279-57-7; 4a, 97279-58-8; 4b, 97279-59-9; 5a, 12570-83-1; 5b, 97279-48-6; 6a, 97279-61-3; 6b, 97279-63-5; 7, 97279-64-6; 8, 74102-43-5; 9 (1,2-isomer), 97279-50-0; 9 (1,3-isomer), 97279-54-4; 10, 97279-66-8; 11, 97279-67-9; 12, 97279-77-1; 14a, 97279-69-1; 14b, 97279-71-5; 15, 12080-06-7; TMSCp, 25134-15-0; DMPSCp, 64743-26-6; CpFe(CO)₂Na, 12152-20-4; Fe(CO)₅, 13463-40-6; (TMSCp)Fe(CO)₂Na, 97279-73-7; (DMPSCp)Fe-(CO)₂Na, 97279-75-9; (MeCp)Fe(CO)₂Na, 97279-76-0; (1,2-MeCpTMS)Fe(CO)₂Et, 97279-52-2; (1,3-MeCpTMS)Fe(CO)₂Et, 97279-51-1; (1,3-(TMS)₂Cp)Fe(CO)₂Et, 97293-80-6; (TMSCp)-Fe(CO)₂DMPS, 97279-78-2; (TMSCp)₂Fe, 12189-86-5; (MeCp)₂Fe, 1291-47-0; ClSiMe₃, 75-77-4; EtBr, 74-96-4; ClSiMe₂Ph, 768-33-2; chlorodimethylpropylsilane, 17477-29-1; benzyl chloride, 100-44-7; allyl chloride, 107-05-1; 3-chloro-2-methylpropene, 563-47-3; trityl fluoroborate, 341-02-6.

Halide-Assisted Dealkylation of Alkylcobalamins by Iodine. **Kinetics and Mechanism**

Yueh-Tai Fanchiang

Department of Chemistry, Kent State University, Kent, Ohio 44242

Received October 29, 1984

The reactions of iodine with methylcobalamin and ethylcobalamin in aqueous solution have been examined. Stoichiometry and product analyses show the iodine cleavage of Co–C bond of CH_3 - B_{12} proceeds via the reaction CH_3 - $B_{12} + I_2 + X^- + H_2O \rightarrow H_2O$ - $B_{12}^+ + CH_3X + 2I^-$. Thus the demethylation of CH_3 - B_{12} by I₂ performed in the presence of $CI^-(1.0 \text{ M})$ produces CH_3CI instead of CH_3I . This stoichiometry, coupled with the kinetic data, strongly supports a mechanism involving an electron transfer from $R-B_{12}$ to I_2 to generate $R-B_{12}^+$ cation radical. The transient radical undergoes a nucleophilically induced heterolytic cleavage to yield B_{12r} and RX. In methanol solution, the absorption spectrum of a stable charge-transfer complex is observed immediately upon mixing iodine and CH_3 - B_{12} . Detailed mechanism for the iodine cleavage of Co-C bonds is discussed.

Introduction

Methylcobalamin (CH_3-B_{12}) is involved in several biological processes, including the methionine synthesis,¹ the formation of methane,² the synthesis of acetate from carbon dioxide,³ and the biomethylation of heavy metals such as mercury⁴ and arsenic.⁵ In the enzymatic reactions the corrinoid cofactor serves alternately as an acceptor and as a donor for the methyl group. Thus an essential feature in our understanding of the methylcobalamin-dependent biochemical reactions is the formation and cleavage of the cobalt-carbon bond. The Co-C cleavage by an electrophile such as Hg(II), which generally leads to the methylation of the attacking electrophile, has long been considered as a direct displacement of the cobalt atom by attack at the α -carbon.⁶ Our recent work on the alkylcobalamin alkylation of Pt(II)/Pt(IV) couples,7 diaquocobinamide,8 tetracyanoethylene,⁹ and a reinvestigation of Hg(II)^{10,11} have, however, raised the question of an alternative route, i.e., the single-electron-transfer (SET) methyl-transfer mechanism. In these studies, the kinetic data were found to be more consistent with the electron-transfer mechanism than with the direct mechanism.⁷⁻¹⁰ The kinetic studies however, are not conclusive for the distinguishableness between these two mechanisms. Furthermore, the kinetic and mechanistic data of the methylation of electrophiles are often complicated by the rapid interaction of the electrophile with 5,6-dimethylbenzimidazole base of the alkylcobalamin. Therefore it is important to investigate the alkyl-transfer reactions between alkylcobalamins and

0276-7333/85/2304-1515\$01.50/0 © 1985 American Chemical Society

⁽¹⁾ Taylor, R. T. In "B₁₂"; Dolphin, D., Ed.; Wiley: New York, 1982; Vol. 2, p 307.

⁽²⁾ Poston, J. M.; Stadtman, T. C. In "Cobalamin, Biochemistry and Pathophysiology"; Babior, B. H., Ed.; Wiley: New York, 1975; p 111.
(3) Ljungdhal, L. G.; Wood, H. G. In "B₁₂"; Dolphin, D., Ed.; Wiley:

New York, 1982; Vol. 2, p 165. (4) Wood, J. M.; Kennedy, F. S.; Rosen, C. G. Nature (London) 1968,

^{220, 173}

⁽⁵⁾ McBride, B. C.; Wolfe, R. S. Biochemistry 1971, 10, 4312.
(6) (a) Wood, J. M. Science (Washington, D.C.) 1974, 183, 1049. (b) Ridley, W. P.; Dizikes, L. J.; Wood, J. M. Science (Washington, D.C.) 1977, 197, 329. (c) Wood, J. M. In "B₁₂"; Dolphin, D.; Ed.; Wiley: New York, 1982; Vol. 2, p 151. (d) Thayer, J. S.; Brinckman, F. E. Adv. Organomet. Chem. 1982, 20, 313.

^{(7) (}a) Anges, G.; Bendle, S.; Hill, H. A. O.; Williams, F. R.; Williams, (1) (a) Anges, G., Dendle, S., Hui, H. A. O., Winanis, F. H., Winanis, F. K., Winanis, Y. H., Winanis, Y. L. Bioinorg. Chem. Soc. D 1971, 850.
 (b) Taylor, R. T.; Hanna, M. L. Bioinorg. Chem. 1976, 6, 281.
 (c) Fanchiang, Y.-T.; Ridley, W. P.; Wood, J. M. J. Am. Chem. Soc. 1979, 101, 1442.
 (d) Fanchiang, Y.-T.; Pignatello, J. J.; Wood, J. M. Organometallics 1983, 2, 1748.
 (e) Fanchiang, Y.-T.; Pignatello, J. J.; Wood, J. M. Organometallics 1983, 2, 1752. (f) Fan-(a) Fanchiang, Y.-T.; Bratt, G. T.; Hogenkamp, H. P. C. Proc. Natl. Acad. Sci. U.S.A. 1984, 81, 2698.
(b) Fanchiang, Y.-T.; Chem. Soc., Chem. Commun. 1982, 1369.
(c) Fanchiang, Y.-T. J. Chem. Soc., Chem. Commun. 1982, 1369.
(c) Fanchiang, Y.-T. J. Chem. Soc., Chem. Commun. 1982, 1369.

 ⁽¹⁰⁾ Fanchiang, Y.-T. *Inorg. Chem.* 1984, 23, 3428.
 (11) (a) DeSimone, R. E.; Penley, M. W.; Charbonneau, L.; Smith, S.

G.; Wood, J. M.; Hill, H. A. O.; Pratt, J. M.; Ridsdale, S.; Williams, R. J. P. Biochim. Biophys. Acta 1973, 304, 851. (b) Chu, V. C. W.; Gruenwedal, D. W. Bioinorg. Chem. 1977, 7, 169. (c) Craig, P. J.; Morton, S. F. J. Organomet. Chem. 1978, 145, 79.