proton resonances to hydrogen nucleii in atoms substituted equatorially or axially at boron atoms B(2) and B(5).

Experimental Section

Preparations. I and II were obtained by methods cited previously.[1,2] Alternatively, preparation (II) was made by a sequence of reactions starting with B_5H_9 instead of $CH_3B_5H_8$, then using $(BH_2CH_3)_2$ instead of diborane(6).[11] Extraordinary care is required to purify these rather unstable substances. The preferred process is fractional codistillation[12] followed by passage through a short (0.5-cm diameter × 6 cm long) column packed with 20% mineral oil on firebrick. This column was scrupulously dried by several hours conditioning with diborane. The function of the column was to "smooth out" the dissymmetrically distributed output from fractional codistillation.[11]

The isomeric methylpentaboranes(9),[13] diborane(6),[14] monomethyldiborane(6),[10a,14] 1,2-dimethyldiborane(6),[15] pentaborane(11),[16] and perdeuteriopentaborane(11)[3] were prepared as described in the references.

NMR. Unless otherwise stated all isotopic species were at natural abundance. Early observations of ^{11}B NMR on preparation I were made at 80 MHz on a spectrometer built at the University of California, Los Angeles. ^1H NMR spectra of the hydrogen nucleii in the methyl groups of preparation I were determined at 60 MHz by using a Varian HA-60 spectrometer with a V4343 temperature-control attachment. All measurements were made on neat samples.

Other NMR measurements were made at 64.2 MHz for ^{11}B and 200.1 MHz for ^1H on a Bruker CXP 200 and on a Bruker WM-500 spectrometer set at 160.437 MHz for ^{11}B and at 500.137 MHz for ^1H. For these measurements the samples were dissolved in deuteriochloroform, which had been treated with 4A molecular sieves. The concentrations were approximately 0.04 mole fraction. Temperatures were maintained from −60 °C to 15 °C with standard Bruker controllers. Boron trifluoride diethyl etherate in $DCCl_3$ was used as the external standard for ^{11}B, and the residual protons in $DCCl_3$ were used as the internal reference for ^1H with $\delta(Me_4Si) = 0$. Values of chemical shift upfield from the references are given the negative sign; downfield values are positive.

Data Processing. Chemical shifts and coupling constants were determined graphically from the analog charts recorded by the NMR spectrometers. Curves produced by the Bruker-WM500 were integrated by the device incorporated in the machine. Members of the pseudodoublets arising from the methyl group as observed at 60 MHz and at 500 MHz were compared by using the Dupont curve resolver. The ratios of area were considered to be the equilibrium constants. The inductive effects of substituting a methyl group for a hydrogen atom on the boron atom framework were calculated from

$$\Delta\delta(A(S)) = \delta(A(S))_i - \delta(A(S))_0$$

where S is the location of atom A (B or H), i is a methylated species, 2-methyl or 3-methyl, and the zero subscript denotes the corresponding value for pentaborane(11).

The data in Table IV were fitted to linear relation by using least-squares computation[17] to give the equations in Table V.

Acknowledgment. R.C.P.H. had support for his studies under NSF Grant GP 28928X. Thanks are due to Professor F. A. L. Anet for use of his in-house-constructed NMR spectrometer operating at 80 MHz for ^{11}B, to Craig Bradley for operating the machine, and to Professor M. F. Hawthorne for arranging our visit. Appreciation is due to the Murdock Charitable Trust for funds to purchase the Bruker WM 500 NMR spectrometer and to Dr. Gary Drobny for assistance in operating the machine.

Registry No. 2-$CH_3B_5H_{10}$, 88574-97-4; 3-$CH_3B_5H_{10}$, 68051-06-9.

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[11] Sloat, D. E. Ph.D. Dissertation, University of Washington, 1981; *Diss. Abstr. Int., B* **1982**, *42*, 2366.

[12] Cady, G. H.; Siegworth, D. P. *Anal. Chem.* **1959**, *31*, 618.

[13] Onak, T. P.; Gerhart, F. J. *Inorg. Chem.* **1962**, *1*, 742. Ryschkewitsch, G. E.; Harris, S. W.; Mezey, E. J.; Sisler, Harry H.; Weilmuenster, E. A.; Garrett, A. B. *Ibid.* **1962**, *1*, 742.

[14] Buttlar, R. O. Ph.D. Dissertation, Indiana University, 1963; *Diss. Abstr.* **1963**, *23*, 4101.

[15] Deever, W. R. Ph.D. Dissertation, University of Washington, 1968; *Diss. Abstr.* B **1968**, *29*, 918.

[16] Klein, M. J.; Harrison, B. D.; Solomon, I. J. *J. Am. Chem. Soc.* **1958**, *80*, 4149. See also ref 3.

[17] Taylor, John R. "An Introduction to Error Analysis"; University Science Books: Mill Valley, CA, 1982.

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Synthesis and Reactions of Substituted Alkyl Trifluoromethyl Ethers

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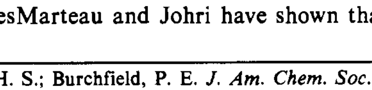
Received August 2, 1985

Trifluoromethyl hypochlorite has been reacted with $RCH{=}CH_2$ (R = $SO_2CH{=}CH_2$, $(CH_3O)_3Si$, Cl_3Si, $(CH_3)_3Si$) to form isomeric mixtures of the trifluoromethyl ethers. With SbF_3, $CF_3OCH_2CH(SiCl_3)Cl$ gave $CF_3OCH_2CH(SiF_3)Cl$, and when $CF_3OCH[Si(CH_3)_3]CH_2Cl$ was thermolyzed, the vinyl ether $CF_3OCH{=}CH_2$ resulted. The addition product of CF_3OCl with $Cl_2C{=}CHCl$ was dehydrochlorinated to $CF_3OCCl{=}CCl_2$, which when chlorinated gave $CF_3OCCl_2CCl_3$. The latter could not be obtained by direct reaction of CF_3OCl with tetrachloroethylene. Dechlorination of the $CF_3OCl/Cl_2C{=}CF_2$ addition products (**6a**) gave $CF_3OCCl{=}CF_2$, which formed a bis(trifluoromethyl) ether (**6c**/**d**) with CF_3OCl. The latter when dechlorinated gave $(CF_3O)_2C{=}CF_2$ (**6e**). 1,1,1-Trifluoropropene with CF_3OCl gave a 60% yield of the Markovnikov-type addition **8a**, which when reacted with KOH formed *cis*-$CF_3CH{=}CClH$ as a result of the loss of $[CF_3OH]$. The former with CF_3OCl produced $CF_3OCH(CF_3)CHCl_2$. The yields of trifluoromethyl ethers formed by reaction of $CH_3OC(O)CH{=}CH_2$, $CH_3C(O)CH{=}CH_2$, and $HC(O)CH{=}CH_2$ with CF_3OCl decreased from 65 to 5%.

Introduction

Fluoroalkyl ethers have high synthetic value as monomers for polymerizations as well as for their useful physical properties.[1] However, the preparation of alkyl trifluoromethyl ethers is difficult, and only a few synthetic routes are known. The standard method, the addition of alcohols to olefins, fails because of CF_3OH is unstable except at low temperature, and the yields and variety of compounds generated by electrochemical fluorination or halogen-exchange reactions are very small.[2,3] Aldrich and Sheppard prepared alkyl trifluoromethyl ethers by treating fluoroformates with sulfur tetrafluoride but their method is limited only to stabilized starting material.[4]

A more extensive approach is the addition of trifluoromethyl hypohalites to olefins[5]



Recently DesMarteau and Johri have shown that the CF_3OF

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[1] Lovelace, A. M.; Rausch, D. A.; Postelnek, W. "Aliphatic Fluorine Compounds"; Reinhold: New York, 1958; pp 155 ff.

[2] Simons, J. H. U.S. Patent 2 500 388, 1950; *Chem. Abstr.* **1950**, *44*, 5236B.

[3] Booth, H. S.; Burchfield, P. E. *J. Am. Chem. Soc.* **1935**, *57*, 2070.

[4] Aldrich, P. E.; Sheppard, W. A. *J. Org. Chem.* **1964**, *29*, 11.

[5] Shreeve, J. M. *Adv. Inorg. Chem. Radiochem.* **1983**, *26*, 1190.

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Table I. Isomeric Yields Correlated to Electronegativities of Silicon Substituents X

	X		
	CH_3	OCH_3	Cl
% a	52	60	87
% b	48	40	13
$X_E{}^a$	2.63	2.68	3.0

[a] For X_E values see ref 9.

addition is more consistent with a radical mechanism while the reactions of the corresponding hypochlorite obey the rule of Markovnikov and yield fewer isomers.[6]

However, with a few exceptions, only additions of CF_3OCl to simple olefins have been reported.[6,7] Attracted by the high yields of these syntheses, we have investigated a more extensive series of reactions with olefins bonded to more or less reactive substituents. Our results show that trifluoromethyl hypochlorite is a useful reagent for the synthesis of substituted alkyl trifluoromethyl ethers. Several reactions of the prepared compounds demonstrate the extraordinary stability of the ether bridge once the carbon–oxygen bond is formed.

Results and Discussion

Addition Reaction of Trifluoromethyl Hypochlorite to Substituted Olefins. It has been reported that trifluoromethyl hypofluorite reacts very violently with ethylene and other simple olefins.[8] We found that the addition of trifluoromethyl hypochlorite even to substituted highly reactive olefins proceeds very smoothly at low temperature (−116 °C). Several series of experiments in different solvents gave similar results in general. Only in the case of addition to acrylic compounds did a dilutant decrease the extent of side reactions slightly.

The regioselectivity of the CF_3OCl addition to substituted vinyl systems seems to be more consistent with a concerted ionic mechanism rather than a radical mechanism. According to the modified Markovnikov rule, the positive chlorine is bonded to the more electron-rich carbon of the olefin depending on the nature of the substituent linked to the vinylic system. This may be demonstrated by the results of the reactions with vinyl silanes.

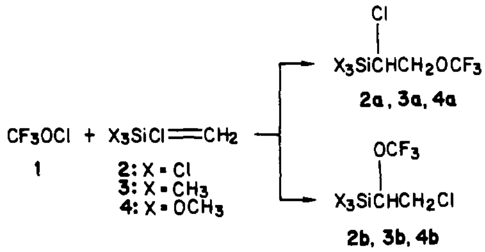
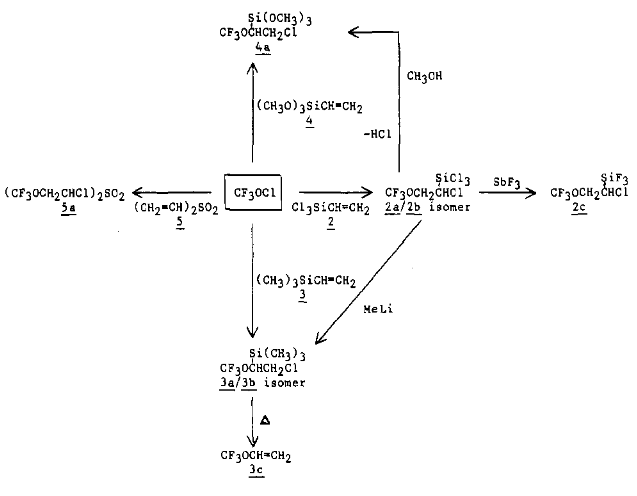


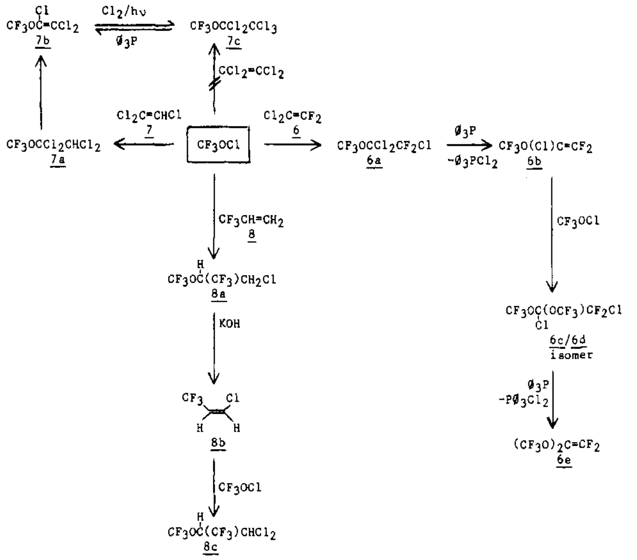
Table I shows the amounts of isomers based on the integration of the ^{19}F NMR spectra correlated to the group electronegativities of the substituents bonded to silicon.

These results are consistent with a previous report dealing with the electron-withdrawing effect caused by the occupation of the d orbitals of silicon on the electrophilic addition of hydrogen iodide to vinyl silanes.[10,11] The greater tendency toward formation of a preferred isomer as shown in Table I may be considered as an indication of the increase of strength of the pπ–dπ bond between the silicon and the α-carbon atom of the olefin relative to the electronegativity of the other substituents bonded to silicon. Similar effects due to the resonance structures $X{-}CH{=}CH_2 \rightleftarrows {}^-X{=}CH{-}{}^+CH_2$ are found in the reactions of CF_3OCl with vinyl sulfones and acrylic compounds.

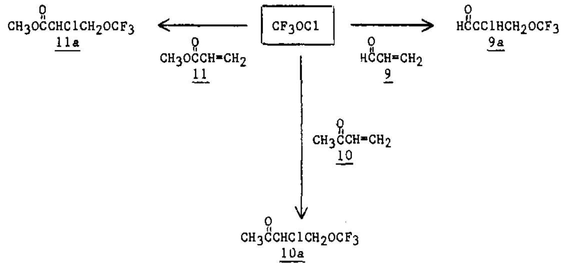
Scheme I



Scheme II



Scheme III



A second argument for an ionic addition mechanism is that only small amounts of side products result from a radical chlorofluorination or chlorination in general. DesMarteau and Johri reported similar byproducts in their reactions with simple olefins.[6] We agree with their suggestion that these impurities are generated by traces of chlorine monofluoride and chlorine in the starting hypochlorite as the amount of chlorofluoroalkane varies in similar experiments with different preparations of CF_3OCl. Surprisingly, we were not successful in adding CF_3OCl to tetrachloroethylene, 2,3-dichlorohexafluorobut-2-ene and 2,3-dichlorohexafluorocyclopent-2-ene, although the reaction of the hypochlorite with tetrafluoroethylene has been reported.[7] However, no reaction with perfluorobut-2-ene and perfluorobut-2-yne was observed. Similarly, we found no interaction with perfluorocyclopentene and perfluorocyclobutene.

On the other hand, we obtained (trifluoromethoxy)pentachloroethane (7c) (Scheme II), the expected addition product of CF_3OCl and tetrachloroethylene, easily by chlorination of (tri-

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(6) Johri, K. K.; DesMarteau, D. D. *J. Org. Chem.* **1983**, *48*, 242.
(7) Anderson, L. R.; Young, D. E.; Gould, D. E.; Juurik-Hogan, R.; Nuechterlein, D.; Fox, W. B. *J. Org. Chem.* **1970**, *35*, 3730.
(8) Porter, R. S.; Cady, G. H. *J. Am. Chem. Soc.* **1957**, *79*, 5625.
(9) Wells, P. R. In "*Prog. Phys. Org. Chem.*" **1968**, *6*, 111 ff.
(10) Larsson, E. *Chalmers Tek. Högsk. Handl.* **1951**, *115*, 25.
(11) Sidgwick, N. V. "Electronic Theory of Valence"; Oxford University Press; London, 1921; p 157.

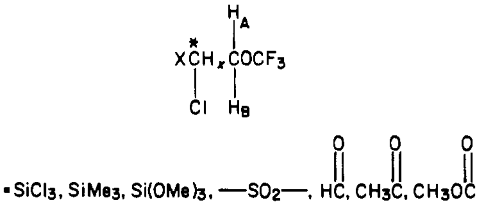
fluoromethoxy)trichloroethene (**7b**). **7c** was stable at room temperature and showed no degradation over several weeks. A comparison of the nonreactive olefins showed some similarities. They all have a highly symmetrical structure and are substituted either by chlorine or a fluoroalkyl group. This suggests that steric effects as well as the high symmetry of the nonpolarized double bond hinder the ionic addition. Unusual amounts of byproducts were obtained in the addition experiments with acrylic compounds. While acrylonitrile did not form a trifluoro ether, the yields of the reactions with methyl acrylate (**11**) (Scheme III), methyl vinyl ketone (**10**) and acrolein (**9**) decreased from 65 to 5%. In all reaction mixtures, large amounts of carbonyl fluoride and hydrogen fluoride, which were probably formed in a reaction of CF_3OCl with hydrogen chloride generated as an intermediate, were found. The IR spectra of the side products, e.g. in the reaction with acrolein, indicated that an acid chloride was formed. Similar results have been reported concerning a degradation of acrylic compounds in the reaction with elemental chlorine.[12]

Reactions of the Synthesized Trifluoromethyl Ethers. The chemical properties of various substituted trifluoromethyl ethers have received little attention. It has been reported that trifluoromethanol itself is only stable up to −60 °C,[13] but in contrast, 1-(trifluoromethoxy)-2-chlorotetrafluoroethane showed no degradation at 400 °C even in the presence of potassium hydroxide.[7] Our reactions of several trifluoromethyl ethers with several kinds of substrates showed that the trifluoromethoxy group once bonded to a carbon atom gives a much stronger bond than a comparable chlorine–carbon bond. However, it is interesting to note that in the dehydrohalogenation reaction of 1,1,1-trifluoro-2-(trifluoromethoxy)-3-chloropropane (**8a**), the major product formed in 75% yield was 1-(trifluoromethyl)-2-chloroethane (**8b**). Elimination of [$HOCF_3$] has been observed by Sheppard and Aldrich[4] when 1-(trifluoromethoxy)-2-chloroethane was treated with a base. Although no specific explanation was given, the authors suggested that acidity of the protons α to the trifluoromethoxy group may be the rate-controlling factor. Addition of trifluoromethyl hypochlorite to cis-1,1,1-trifluoro-3-chloropropene (**8b**) obeys the Markovnikov rule, giving **8c** as the major product. We found no degradation or loss of the trifluoromethoxy group in the dehydrohalogenation reaction of 1-(trifluoromethoxy)-1,1-dichloro-2,2-dichloroethane (**7a**). The newly synthesized vinyl ethers exhibit olefinic behavior and may be considered to be new starting materials for the preparation of saturated fluoro ethers.

The chlorination of **7b** to (trifluoromethoxy)pentachloroethane (**7c**) has already been mentioned in this paper. Just as with tetrachloroethylene, **7b** does not react with CF_3OCl, probably for the reasons already discussed above. Appel and Schöler reported the dechlorination of hexachloroethane to tetrachloroethylene with several phosphines.[14] Our attempt to dechlorinate **7c** with triphenylphosphine gave **7b** in nearly quantitative yields, and no interaction of the trifluoromethoxy group with the dechlorinating agent was found. Furthermore, we observed no loss of the CF_3O group in a series of reactions of 1-chloro-1-(trichlorosilyl)-2-(trifluoromethoxy)ethane (**2a**) (Scheme I) with various substrates. The addition of methanol to **2a** resulted in a vigorous reaction, and hydrogen chloride was evolved. The product was identical with **4a**. At low temperature, methyllithium converted **2a** into **3b**. The halogen-exchange reaction using antimony trifluoride yielded the corresponding (trifluorosilyl)ethyl trifluoromethyl ether **2c**.[15] If the isomer mixture **3a/b** was heated to above 100 °C, elimination of trimethylchlorosilane occurred and trifluoromethyl vinyl ether **3c** was formed.[7] As expected, the isomer with chlorine and trimethylsilyl group geminally bonded was stable and was recovered. These results indicate the strength of the ether bond compared to the much weaker carbon–chlorine bond. There was no indication of trimethylfluorosilane or trimethylsilyl trifluoromethyl ether formation.

The identification of the new trifluoromethyl ethers and their reaction products was based on ^1H and ^{19}F NMR, mass, and infrared spectra. In some cases, elemental analyses were performed for additional proof. In the IR spectra, the typical very strong absorption bands of the trifluoromethoxy group in the region from 1180 to 1280 cm^{-1} are found in all new compounds. The relative amounts of the isomers were calculated from the ^{19}F NMR spectra. According to the literature, the chemical shift of the CF_3O group is a distinctive indicator for the substituents bound to the same carbon atom.[7] Our results fit very well with the values given, and these values were used for the identification of the isomers. We obtained additional information about the orientation from the mass spectra, e.g., in the mass spectrum of **2a**, an intense fragment of *m/e* 181 due to the $Cl_3Si\text{–}^{+}CH\text{–}Cl$ cation with the typical pattern of a four-chlorine-containing group can be found. An additional chemical proof concerning the orientation is, of course, the results of the reactions with the (trichlorosilyl)ethyl trifluoromethyl ether.

The ^1H NMR spectra of the products generated by the reactions of CF_3OCl with the simple vinylic compounds gave ABX systems for the protons bonded to the α and β carbon due to the presence of an asymmetric carbon atom



$$X\overset{*}{\underset{Cl}{C}}H_x\overset{H_A}{\underset{H_B}{C}}OCF_3$$

$$X = SiCl_3,\ SiMe_3,\ Si(OMe)_3,\ \text{—}SO_2\text{—},\ H\overset{O}{\overset{\|}{C}},\ CH_3\overset{O}{\overset{\|}{C}},\ CH_3O\overset{O}{\overset{\|}{C}}$$

However, we were not able to analyze the signal systems in all cases because of additional signals arising from the isomer. Usually we found no coupling between the fluorine atoms of the trifluoromethoxy group and the protons bonded to the α-carbon. Only $CF_3OCH{=}CH_2$ (**3c**) showed coupling between fluorine and all protons in the olefinic system, probably caused by an interaction with the double bond. In addition, it is of interest to note that the compound $(CF_3O)_2C{=}CF_2$ (**6e**) showed coupling between fluorines on the methoxy groups and the fluorines on the β-carbon, $J_{OCF_3\text{-}F} = 2.24$ Hz.

Fluorinated ethers, such as 1-(trifluoromethoxy)-1,1-dichloro-2,2-difluoro-2-chloroethane (**6a**) (Scheme II) undergo dechlorination readily to give vinyl ethers (**6b**) in quantitative yield. Subsequent addition of trifluoromethyl hypochlorite, gave the polyfluoro ethers **6c**/**d**. Dechlorination gave 1,1-bis(trifluoromethoxy)-2,2-difluoroethene, (**6e**). Since product **6e** was contaminated with several impurities, it was separated by GC/MS and gave a molecular ion and other characteristic peaks.

Some of the perfluorinated ethers prepared may have some industrial applications; however, the presence of chlorine in such ethers may prove to diminish this usefulness. Dechlorination followed by subsequent addition of trifluoromethyl hypochlorite to the olefins will yield ethers of lower chlorine content. These ethers should be about as polar as their chlorine analogues since the electronegativity of the trifluoromethoxy group is similar to that of chlorine.

Experimental Section

Materials. Trifluoromethyl hypochlorite was prepared according to the literature method.[16,17] The olefins C_2Cl_4, $CHCl{=}CCl_2$, $Me_3SiCH{=}CH_2$, $Cl_3SiCH{=}CH_2$, $(MeO)_3SiCH{=}CH_2$, and $SO_2(CH{=}CH_2)_2$ (Aldrich) and $Cl_2C{=}CF_2$ and $CF_3CH{=}CH_2$ (PCR) were used as received. $CH_3OC(O)CH{=}CH_2$, $CH_3C(O)CH{=}CH_2$, and $HC(O)\text{-}CH{=}CH_2$ from Aldrich were distilled before use.

General Procedures. Gases and volatile materials were handled in a conventional Pyrex glass vacuum system equipped with a Heise-Bourdon tube gauge. Products were isolated by trap-to-trap distillation through a four-trap system. Infrared spectra were recorded with a Perkin-Elmer 599B spectrometer either by using a 10-cm cell equipped with KBr

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(12) Bayer, O. *Angew. Chem.* **1949**, *61*, 239.
(13) Seppelt, K. *Angew. Chem.* **1977**, *89*, 325.
(14) Appel, R.; Geisler, K.; Schöler, H. *Chem. Ber.* **1977**, *110*, 376.
(15) Boolle, H. S.; Martin, W. F. *J. Am. Chem. Soc.* **1946**, *68*, 2655.
(16) Gould, D. E.; Anderson, L. R.; Young, D.; Fox, W. B. *J. Am. Chem. Soc.* **1969**, *91*, 1310.
(17) Schack, C. J.; Mayer, W. *J. Am. Chem. Soc.* **1969**, *91*, 2902.

windows or as a liquid film between two KBr plates. ^{19}F, ^{1}H, and ^{31}P NMR spectra were obtained on a JEOL FX90Q spectrometer by using $CFCl_3$, Me_4Si, and H_3PO_4 as internal standards. Mass spectra were taken with a Hitachi Perkin-Elmer RMU-6E or a VG 7070HS mass spectrometer at an ionization potential of 17 eV. Elemental analyses were performed by Beller Mikroanalytisches Laboratorium, Göttingen, West Germany.

Reactions of CF_3OCl with Olefins. The addition reactions were carried out initially in the same manner. A 250-mL Pyrex round-bottomed flask equipped with a ₮19/22 inner joint and a Kontes-Teflon valve was charged with 10 mmol of olefin. The flask was attached to the vacuum line, cooled to −196 °C, and evacuated. Then, 11 mmol of CF_3OCl was condensed into the vessel, which was transferred immediately to an ethanol/liquid N_2 slush bath (−116 °C) and allowed to warm to 25 °C overnight. The volatile materials were separated by trap-to-trap distillation, and the involatile liquid residues were distilled under vacuum with a microdistillation apparatus.

Dehydrochlorination Reaction. A 100-mL round-bottomed flask equipped with a standard taper inner joint and a Kontes Teflon valve was charged with an excess of powdered potassium hydroxide. After the vessel was evacuated and cooled to −196 °C, the ether was added and the mixture was warmed slowly to 0 °C by placing the vessel in an ice bath. The vinyl ethers produced are usually sufficiently volatile to be collected by using trap-to-trap distillation.

Dechlorination Reaction Using Triphenylphosphine.[14] A procedure similar to that used for the dehydrochlorination reactions was followed. Dry THF was used and the reaction vessel was stirred well for 3 h at −20 °C before the volatile compounds were distilled.

(a) Reaction of CF_3OCl with $Cl_3SiCH{=}CH_2$ (**2**) gave $CF_3OCH_2CHClSiCl_3$ (**2a**) and $CF_3OCH(SiCl_3)CH_2Cl$ (**2b**). The isomers were isolated by distillation (90% yield); bp 55 °C (15 torr). Spectral data are as follows. ^{19}F NMR: ϕ −60.5 (s), −58.03 (s). ^{1}H NMR ($CF_3OCH_AH_BCH_XClSiCl_3$): δ_A 4.06, δ_B 3.99, δ_X 3.55; $J_{AX} = 3.2$ Hz, $J_{BX} = 5.6$ Hz, $J_{AB} = 11$ Hz. Infrared (capillary film): 1275 vs, 1245 vs, 1220 s, 1175 vs, 1055 m, 1035 m, 995 m, 885 m, 800 w, 780 m, 655 m, 625 vs, 610 vs, 495 m cm^{-1}. MS (17 eV) mass (fragment), relative intensity): 280 (M^+), 2; 244 (M^+ −HCl), 8; 195 ($M^+ - OCF_3$), 15; 181 ($M^+ - CH_2OCF_3$), 15; 147 ($M^+ - SiCl_3$), 65; 133 ($SiCl_3^+$), 100; 112 ($M^+ - SiCl_4$), 95; 99 ($CH_2OCF_3^+$), 100; 69 (CF_3^+), 100. Correct chlorine isotope ratios are observed.

Anal. Calcd for $C_3H_3Cl_4F_3OSi$: 12.85; H, 1.06. Found: C, 12.81; H, 1.14.

(b) Reaction of CF_3OCl with $(CH_3)_2SiCH{=}CH_2$ (**3**) gave an isomeric mixture of $(CH_3)_3SiCHClCH_2(OCF_3)$ (**3a**) and $(CH_3)_3SiCH(OCF_3)CH_2Cl$ (**3b**), which was isolated in a trap at −35 °C by trap-to-trap distillation (total yield 90%). Spectral data are as follows. ^{19}F NMR: ϕ −61.27 (s), −58.6 (s) for each isomer. ^{1}H NMR ($CF_3OCH_AH_BCH_XClSi(CH_3)_3$): δ_A 4.28, δ_B 4.15, δ_X 3.41, δ_{CH_3} 0.18; $J_{AB} = 10.8$ Hz, $J_{AX} = 4.8$ Hz, $J_{BX} = 8.8$ Hz. ^{1}H NMR ($(CH_3)_3SiCH(OCF_3)CH_2Cl$): δ_{CH_3} 0.18, δ_{CH_2} 3.76 (d), δ_{CH} 4.14 (t); $J = 4$ Hz. Infrared (capillary film): 2980 s, 2950 m, 1400 m, 1270 vs, 1220 vs, 1160–1130 vs, 1070 s, 1020 m, 920 s, 860 vs, 840 vs, 780 m, 760 s, 730 w, 700 s, 690 m, 630 s, cm^{-1}. MS (17 eV) (mass (fragment), relative intensity): 220 (M^+), 1; 147 ($M^+ - (CH_3)_3Si$), 80; 121 ($M^+ - CH_2OCF_3$), 20; 108 ($(CH_3)_3SiCl^+$), 100; 85 (CF_3O^+), 80; 73 ($(CH_3)_3Si^+$), 100; 69 (CF_3^+), 100.

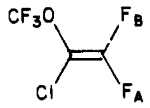
Anal. Calcd. for $C_6H_{12}ClF_3OSi$: C, 32.72; H, 5.44. Found: C, 32.77; H, 5.53.

(c) Reaction of CF_3OCl with $(CH_3O)_3SiCH{=}CH_2$ (**4**) gave an isomeric mixture of $(CH_3O)_3SiCH(OCF_3)CH_2Cl$ (**4a**) and $(CH_3O)_3SiCHClCH_2OCF_3$ (**4b**), which isolated by trap-to-trap distillation in a trap at −20 °C. Spectral data are as follows. ^{19}F NMR: for **4a**, ϕ −60.64; for **4b**, ϕ −59.07. ^{1}H NMR: for **4a**, δ 3.65; for **4b**, δ 3.52. The protons bonded to the α- and β-carbons appear as broad multiplets from δ 4.15–4.5 and δ 3.35–3.60. Infrared (capillary film): 2990 m, 2980 s, 2920 m, 1460 m, 1290, 1100 vs, 1030 s, 980 m, 940 s, 910 vs, 890 s, 830 m and 720 w, cm^{-1}.

(d) Reaction of CF_3OCl with $SO_2(CH{=}CH_2)_2$ (**5**) gave $SO_2(CH_X(OCF_3)CH_AH_BCl)_2$ (**5a**). Compound **5a** was distilled, after the volatile compounds were removed, in a microdistillation apparatus (bp 61 °C (10^{-3} torr); 57%). Spectral data are as follows. ^{19}F NMR: ϕ −60.57. ^{1}H NMR: δ_A 5.16, δ_B 5.02, δ_X 3.19; $J_{AB} = 14.5$ Hz, $J_{AX} = 10.8$ Hz, $J_{BX} = 9.52$ Hz. Infrared (capillary film): 2980 m, 1450 w, 1390 s, 1320 vs, 1260 vs, 1210 vs, 1160–1140 vs, 1090 vs, 1070 s, 1030 s, 980 s, 950 m, 890 m, 780 s, 740 m, 730 w, 660 s cm^{-1}. MS (CI) (mass (fragment), relative intensity): 274 ($MH^+ - OCF_3$), 1; 212 ($MH^+ - CHClCH_2OCF_3$), 2; 161 ($SO_2CHCH_2Cl_2^+$), 3; 146 ($CHClCHOCF_3^+$), 28; 99 ($CH_2OCF_3^+$), 13; 69 (CF_3^+), 56; 64 (SO_2), 14.

(e) Reaction of CF_3OCl with $F_2C{=}CCl_2$ (**6**) gave $CF_3OCCl_2CF_2Cl$ (**6a**) free from its isomer, and **6a** was isolated in a trap at −60 °C (60%). NMR and IR spectral data agree with the literature.[6]

(f) Dechlorination of $CF_3OCCl_2CF_2Cl$ (**6a**) gave **6b**



in 90% yield. Compound **6b** was isolated by a trap-to-trap distillation in a trap at −98 °C. Spectral data are as follows. ^{19}F NMR: ϕ_{CF_3O} −59.65 (d), ϕ_A −99.15 (q of d), ϕ_B −99.62 (d); $J_{CF_3O-F_A} = 4.1$ Hz, $J_{AB} = 38.6$ Hz, $J_{CF_3O-F_B} < 0.6$ Hz. Infrared (gas phase): 1768 vs, 1335 vs, 1280 s, 1220–1180 (br), 1040 vs, 900 m, 820 w, 755 vs, 700 m, 610 w, 540 w, 530 w, 490 s cm^{-1}.

(g) Reaction of CF_3OCl with **6b** gave the mixture of isomers $CF_3OCCl(OCF_3)CF_2{}^{A}Cl$ (**6c**) and $CF_3{}^{A}OCCl_2CF_2{}^{C}(OCF_3{}^{B})$ (**6d**) that were isolated by trap-to-trap distillation in a trap at −58 °C. The spectral data are as follows. ^{19}F NMR for **6c**: ϕ_{OCF_3} −51.0 (t), ϕ_A −64.1 (h); $J_{OCF_3-F_A} = 3.41$ Hz. ^{19}F NMR for **6d**: ϕ_{OCF_3A} −51.3 (s), ϕ_{OCF_3B} −52.0 (t), ϕ_C −84.1 (q); $J_{OCF_3BF_C} = 8.97$ Hz. Infrared (gas phase): 1390 w, sh, 1310–1080 br, s, 970 m, 880 s, 845 s, 820 s, 800 s, 770 s, 660 s, 625 s, 535 w, 490 s cm^{-1}. MS (17 eV) (mass (fragment), relative intensity): 267 ($M^+ - Cl$), 6; 217 ($M^+ - CF_2Cl$), 3; 135 ($M^+ - C(OCF_3)Cl_2$), 17; 69 (CF_3^+), 100. Appropriate chlorine isotope ratios were observed.

(h) Dechlorination of isomers **6c** and **6d** gave $(CF_3O)_2C{=}CF_2$ (**6e**), which stopped in a trap at −96 °C. Compound **6e** was found to be contaminated with ether **6d**. Spectral data are as follows. ^{19}F NMR: ϕ_{CF_3} −59.48 (t), ϕ_F −103.32 (h); $J_{CF_3-F} = 2.24$ Hz. Infrared (gas phase): 1800 w, 1765 s, 1335 s, 1300–1150 br, s, 1100 sh, 1050 s, 930 m, 900 m, 750 s, 670 m, 490 s cm^{-1}. GC/MS (17 eV) (mass (fragment), relative intensity): 232 (M^+), 8; 213 ($M^+ - F$), 51; 147 ($CF_3OC_2F_2^+$), 28; 69 (CF_3^+), 100.

(i) Reaction of CF_3OCl with $Cl_2C{=}CHCl$ (**7**) gave $CF_3OCCl_2CHCl_2$ (**7a**), which was distilled at atmospheric pressure (bp 120 °C (712 torr)). Spectral data are as follows. ^{19}F NMR: ϕ −54.6 (s). ^{1}H NMR: δ 5.89 (s). Infrared (capillary film); 1265 vs, 1220 vs, 1190 vs, 1140 m, 1100 m, 1030 m, 970 w, 910 w, 880 w, 850 s, 825 s, 790 s, 740 s, 650 m, 580 m, 510 w cm^{-1}.

Anal. Calcd for $C_3HF_3Cl_4O$: C, 14.29; H, 0.39. Found: C, 14.66; H, 0.49.

(j) Dehydrochlorination of **7a** gave $CF_3OCCl{=}CCl_2$ (**7b**), which was isolated in a trap at −55 °C (82% yield). Spectral data are as follows. ^{19}F NMR: ϕ −57.74 (s). Infrared (gas phase): 1620 m, 1270 vs, 1230–1170 vs, 1090 s, 990 s, 920 s, 890 vs, 845 vs, 780 m cm^{-1}. A molecular ion is observed at 214. Correct chlorine isotope ratios are observed.

(k) Reaction of $CF_3OCCl{=}CCl_2$ with Cl_2 gave $CF_3OCCl_2CCl_3$ (**7c**), which was isolated in trap at −20 °C. Spectral data are as follows. ^{19}F NMR: ϕ −53.86 (s). Infrared (gas phase): 1270 vs, 1260 vs, 1210 vs, 1150 s, 880 m, 830 w, 770 vs, 750 vs, 720 m cm^{-1}. In the mass spectrum a peak is observed at mass 249 ($M^+ - Cl$). Appropriate chlorine isotope ratios were observed.

(l) Reaction of CF_3OCl and $CF_3CH{=}CH_2$ (**8**) gave the product $CF_3{}^{A}OCH(CF_3{}^{B})CH_2Cl$ (**8a**), which was isolated in a trap at −60 °C (70% yield). The ^{19}F NMR indicates the presence of a small amount of the anti-Markovnikov isomer. Spectral data for **8a** are as follows. ^{19}F NMR: ϕ_A −61.16 (s), ϕ_B −72.45 (d). ^{1}H NMR: δ 4.30 (m), 4.25 (m); $J_{CF_3-H} = 5.14$ Hz. Infrared (gas phase): 2890 w, 1470 w, 1400 sh, w, 1370 m, 1245–1190 vs, 1060 vs, 1030 vs, 900 w, 850 s, 750 m, 700 m, 610 s, 540 m, 520 w, 475 m cm^{-1}. MS (17 eV) (mass (fragment) relative intensity): 167 ($CF_3CHOCF_3^+$), 1; 130 ($CF_3CCH_2Cl^+$), 51; 98 (CF_3OCH^+), 100; 94 (CF_3CCH^+), 4; 69 (CF_3^+), 91.

(m) Dehydrohalogenation of **8a** gave *cis*-$CF_3CH_B{=}CClH_A$ (**8b**), which was isolated in a trap at −120 °C. Spectral data are as follows. ^{19}F NMR: ϕ −68.85 (d of d). ^{1}H NMR: δ_A 6.07 (m), δ_B 5.79 (m); $J_{CF_3-H_A} = 1.47$ Hz, $J_{CF_3-H_B} = 0.85$ Hz, $J_{H_A-H_B} = 2.81$ Hz. Infrared (gas phase): 1645 m, 1440 w, 1385 s, 1325 sh, w, 1295 s, 1270 sh, w, 1180 vs, 1100 vs, 930 s, 850 s, 740 s, 595 m, 525 s cm^{-1}. MS (17 eV) (mass (fragment), relative intensity): 130 (M^+), 70; 111 ($M^+ - F$), 20; 94 ($M^+ - HCl$), 100; 85 (CF_3O^+), 7; 69 (CF_3^+), 94.

(n) Reaction of CF_3OCl and **8b** gave $CF_3OCH(CF_3)CHCl_2$ (**8c**), which was isolated in trap at −60 °C. Spectral data are as follows. ^{19}F NMR: ϕ_A −61.57, ϕ_{OCF_3} −77.43. ^{1}H NMR: δ 4.90, 4.89. Infrared (gas phase): 2980 w, 1400 m, 1315–1175 s, br, 1110 w, 955 w, 925 w, 860 w, 830 m, 800 m, 730 m, 620 w, sh, 600 w, 525 m cm^{-1}. MS (17 eV) (mass (fragment), relative intensity): 214 ($M^+ - HCl$), 3; 166 ($C(OCF_3(CF_3^+)$), 16; 163 ($CF_3CCCl_2^+$), 26; 98 (CF_3OCH^+), 100; 85 (CF_3O^+), 7; 69 (CF_3^+), 94.

(o) Reaction of CF_3OCl with $HC(O)CH{=}CH_2$ (**9**) gave an isomeric mixture of $H^{A}C(O)CH^{B}ClCH_2{}^{C}OCF_3$ (**9a**) and $H^{A'}C(O)CH^{B'}(OCF_3)CH_2{}^{C'}Cl$ (**9b**), which was isolated in a trap at −40 °C. The product was redistilled, giving a yield of 5%. Spectral data are as follows. ^{19}F NMR: ϕ −61.5, −58.8. ^1H NMR: δ_A 9.62 and $\delta_{A'}$ 9.52 (aldehydic proton of the isomers), $\delta_{B,B'}$ 4.7–5.6 (broad multiplet), $\delta_{C,C'}$ 3.5–4.5 (broad multiplet; δ_B:δ_C integration gives a 1:2 ratio. Infrared (gas phase): 2970 m, 1740 s, 1280 vs, 1240 vs, 1175 vs, 930 m, 735 s cm^{-1}.

(p) Reaction of CF_3OCl with $CH_3C(O)CH{=}CH_2$ (**10**) gave the product $CH_3C(O)CHClCH_2OCF_3$ (**10a**), which was isolated in a trap at −40 °C (55%). Spectral data are as follows. ^{19}F NMR: ϕ −60.58. ^1H NMR: δ_{CH_3} 2.37 (s), δ_{CH} 4.68 (t), δ_{CH_2} 4.32 (d); $J_{CH-CH_2} = 4.1$. Hz. Infrared (gas phase): 1735 s, 1360 m, 1280 vs, 1240 vs, 1220 vs, 1170 vs, 1030 m cm^{-1}. MS (17 eV) (mass (fragment), relative intensity) 190 (M^+), 45; 155 ($M^+ - Cl$), 10; 112 ($M^+ - CH_3C(O)Cl$), 100; 105 ($M^+ - OCF_3$), 18; 43 ($CH_3C(O)^+$), 100.

(q) Reaction of CF_3OCl with $CH_3OC(O)CH{=}CH_2$ (**11**) gave $CH_3OC(O)CHClCH_2OCF_3$ (**11a**), which was collected in a trap at −35 °C (65%). Spectral data are as follows. ^{19}F NMR: ϕ −60.6 (s). ^1H NMR: δ_{OCH_3} 2.38 (s), 2.8–to 3.4 (broad multiplet; protons on α- and β-carbons). Infrared (gas phase): 2980 w, 1770 vs, 1430 w, 1340 s, 1290 vs, 1280 vs, 1250 s, 1200 s, 1180 vs, 1080 m, 850 w cm^{-1}. MS (17 eV) (mass (fragment), relative intensity): 206 (M^+), 3; 175 ($M^+ - OCH_3$), 80; 170 ($M^+ - HCl$), 100; 162.5 ($M^+ - CO_2$), 90; 121 ($M^+ - OCF_3$), 20.

Acknowledgment is expressed to the donors of the Petroleum Research Fund, administered by the American Chemical Society, to the AFOSR (82-0247), to the National Science Foundation (Grant CHE-8404974), and to the Merix Corp. for support of this research.

Registry No. **1**, 22082-78-6; **2**, 75-94-5; **2a**, 99728-02-6; **2b**, 99728-03-7; **2c**, 99728-04-8; **3**, 754-05-2; **3a**, 99728-05-9; **3b**, 99728-06-0; **3c**, 1645-89-2; **4**, 2768-02-7; **4a**, 99728-07-1; **4b**, 99728-08-2; **5**, 77-77-0; **5a**, 99748-40-0; **6**, 79-35-6; **6a**, 84011-22-3; **6b**, 99728-09-3; **6c**, 99728-10-6; **6d**, 99728-11-7; **6e**, 45122-12-1; **7**, 79-01-6; **7a**, 99728-12-8; **7b**, 99728-13-9; **7c**, 99728-14-0; **8**, 677-21-4; **8a**, 99728-15-1; **8b**, 99728-16-2; **8c**, 99728-17-3; **9**, 107-02-8; **9a**, 99728-18-4; **9b**, 99728-19-5; **10**, 78-94-4; **10a**, 99728-20-8; **11**, 96-33-3; **11a**, 99728-21-9.

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Kinetics and Mechanism of the Substitution Reactions of the Pentacyanoaquoruthenate(II) Ion with Nitrogen Heterocycles in Aqueous Media

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Received July 24, 1985

The kinetics of the substitution reactions of the $Ru(CN)_5OH_2^{3-}$ ion with a series of nitrogen heterocycle ligands were studied in aqueous media. The rate constants for the formation of $Ru(CN)_5L^{(3-n)-}$ are sensitive to the charge on the incoming ligand L^{n+}. The kinetic and activation parameters are consistent with an ion-pair dissociative mechanism, with a rate constant of 10 ± 5 s^{-1} (25.0 °C, μ = 0.10 M) for water exchange on $Ru(CN)_5OH_2^{3-}$. This value is 30 times lower than that for $Fe(CN)_5OH_2^{3-}$ but larger than that for cationic complexes such as $Ru(OH_2)_6^{2+}$ or $Ru(NH_3)_5OH_2^{2+}$. The differences in substitution lability are discussed in terms of electronic effects on the M–OH_2 bond interactions. At higher acidities (pH <5) the substitution rates for $Ru(CN)_5OH_2^{3-}$ decrease substantially as the protonation of a cyanide ligand yields a more substitution-inert $(HNC)Ru(CN)_4OH_2^{2-}$ ion (pK_a = 2.24 ± 0.10).

Introduction

In the past dozen years the chemistry of substituted pentacyanoferrate(II) complexes, $Fe(CN)_5L^{3-}$, has been the subject of numerous kinetic and spectroscopic investigations.[1-10] It has been demonstrated that the complexation reactions of $Fe(CN)_5OH_2^{3-}$ with a variety of ligands L and the dissociation reactions of $Fe(CN)_5L^{3-}$, in the presence of excess L′, follow a dissociative mechanism of ligand substitution. In addition an extensive correlation has been established between the spectroscopic properties of $Fe(CN)_5L^{3-}$ and $Ru(NH_3)_5L^{2+}$ complexes, both low-spin d^6 systems.

Although the synthesis of the analogous $Ru(CN)_5OH_2^{3-}$ ion was first reported some time ago,[11] it is only recently that this species has been utilized in the preparation of substituted pentacyanoruthenate(II) complexes with aromatic nitrogen heterocyles.[12] Unlike the $Fe(CN)_5OH_2^{3-}$ ion, the kinetics and mechanism of substitution reactions of $Ru(CN)_5OH_2^{3-}$ have yet to be reported. While the $Ru(OH_2)_6^{2+}$ ion is much more inert to substitution[13] than the $Fe(OH_2)_6^{2+}$ ion,[14] resulting from a difference in their spin configurations, the rates of substitution for the low-spin $Ru(CN)_5OH_2^{3-}$ and $Fe(CN)_5OH_2^{3-}$ complexes are expected to be of similar magnitude.

Table I. UV–Visible Band Maxima and Molar Absorptivity Coefficients for Substituted Pentacyanoruthenate(II) Complexes, $Ru(CN)_5L^{(3-n)-}$, in Aqueous Solution

ligand	λ_{max}, nm	$10^{-3}\epsilon$, M^{-1} cm^{-1}
H_2O	308	1.64
pyridine	317	5.02
isonicotinate	351	5.00
4,4′-bipyridine	368	8.80
pyrazine	370	5.04
1-(4-pyridyl)pyridinium	393	5.04
2,3-pyrazinedicarboxylate	418	2.52
N-methylpyrazinium	522	6.84

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(1) Toma, H. E.; Malin, J. M. *Inorg. Chem.* **1973**, *12*, 1039, 2080.
(2) Shepherd, R. E. *J. Am. Chem. Soc.* **1976**, *98*, 3329.
(3) Sullivan, T. R.; Stranks, D. R.; Burgess, J.; Haines, R. I. *J. Chem. Soc., Dalton Trans.* **1977**, 1460.
(4) Malin, J. M.; Ryan, D. A.; O'Halloran, T. V. *J. Am. Chem. Soc.* **1978**, *100*, 2097.
(5) Katz, N. E.; Blesa, M. A.; Olabe, J. A.; Aymonino, P. J. *Inorg. Chim. Acta* 1978, *27*, L65; *J. Chem. Soc., Dalton Trans.* **1978**, 1603.
(6) Szecsy, A. P. Miller, S. S.; Haim, A. *Inorg. Chim. Acta* **1978**, *28*, 189.
(7) Toma, H. E.; Martins, J. M.; Giesbrecht, E. *J. Chem. Soc., Dalton Trans.* **1978**, 1610.
(8) Macartney, D. H.; McAuley, A. *Inorg. Chem.* **1981**, *20*, 748.
(9) Macartney, D. H.; McAuley, A. *J. Chem. Soc., Dalton Trans.*, **1981**, 1780.
(10) Toma, H. E.; Batista, A. A.; Gray, H. B. *J. Am. Chem. Soc.* **1982**, *104*, 7509.
(11) Legros, J. *C. R. Hebd. Seances Acad. Sci.* **1959**, *248*, 1339.
(12) Johnson, C. R.; Shepherd, R. E. *Inorg. Chem.* **1983**, *22*, 1117, 2439.
(13) Bernhard, P.; Helm, L.; Rapaport, I.; Ludi, A.; Merbach, A. E. *J. Chem. Soc., Chem. Commun.* **1984**, 302.
(14) Swift, T. J.; Connick, R. E. *J. Chem. Phys.* **1962**, *37*, 307.

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