Table II

RCF^{A}F^{B}NClF	J_{AB}, Hz	Δ_{AB}/J_{AB}
ClCF$_2$NClF^a	128	2.0
CF$_3$CF$_2$NClF^b	201	4.6
C$_2$F$_5$CF$_2$NClF^b	204	4.9
CCl$_3$CF$_2$NClF^b	182	9.8
FClNCF$_2$CF$_2$NClF (A)^b	195	5.0
FClNCF$_2$CF$_2$NClF (B)^b	195	3.5

^{a} Reference 4. ^{b} This work.

tion.[14] The application of this reaction to a variety of >C=N– derivatives will be reported separately.[8]

All the RNClF derivatives obtained in this work are stable, colorless liquids at 22 °C. None have shown any tendency to explode, although caution is advised in handling these materials. In NMR studies, CCl$_3$CF$_2$NClF did not decompose at 100 °C in CCl$_4$, and (CF$_2$NClF)$_2$ was stable in CFCl$_3$ at 60 °C, the highest temperature used. The stability of ClCF$_2$NClF was examined in some detail, since previous reports indicated the compound eliminated Cl$_2$ at 25 °C.[4] We found that pure ClCF$_2$NClF is stable at 25 °C in glass or fluorine-passivated stainless-steel and that the compound is unaffected by ordinary room light. At 100 °C in Pyrex, the compound was recovered quantitatively after 1 day. The previously observed instability must therefore have been due to impurities. This is consistent with long-reaction-time studies done with ClCN/ClF/F$_2$, where the yield decreased markedly after standing 1 day as compared to a 4-h reaction time.

The ^{19}F NMR spectra of RCF$_2$NClF provide additional evidence for the high barriers to inversion observed in fluorinated amines.[4,15] The asymmetric nitrogen atom causes the two methylene fluorines to be diastereotopic, as long as the rate of inversion at nitrogen is slow on the NMR time scale. As was previously observed for ClCF$_2$NClF and (CF$_3$)$_2$CFN-ClF, this gives rise to ABX-type spin systems with a large geminal F–F coupling.[4] As long as there are two fluorine atoms on the α-carbon, the inversion barrier will be quite high in perhalogenated systems.[16]

In previous work with (CF$_3$)$_2$CFNClF, equivalence of the CF$_3$ groups was observed at 60 °C, whereas ClCF$_2$NClF did not exhibit coalescence up to 100 °C.[4] In this work, CCl$_3$C-F$_2$NClF was heated to 100 °C in CCl$_4$, where the two methylene fluorines were still separated by 1750 Hz and had moved only 20 Hz toward the center as compared to the 29 °C spectrum. In (CF$_2$NClF)$_2$ the NMR spectrum shows the presence of two diastereomers which we have labeled A and B. They are not formed in equal amounts, which is reasonable considering that the compound is probably formed by the stepwise fluorination of the intermediate (CF$_2$NCl$_2$)$_2$. The NMR for the two diastereomers can be considered that of two AA′BB′XX′ spin systems. Not all the coupling constants could be evaluated, and the values given in the Experimental Section are only approximate except for J_{AB} and $J_{A'B'}$, which could be easily determined from the experimental spectra. Heating this sample to 60 °C caused the CF$_2$ multiplets of isomer A to move 22 Hz to the center while the change in isomer B was only 5 Hz. For comparison, the Δ_{AB}/J_{AB} values for the known perhaloamines of the type RCF^{A}F^{B}NClF are given in Table II.

Summary

In summary a wide variety of *N*-chloro-*N*-fluoroperhaloalkylamines can now be prepared in excellent yield. The chlorofluorination reaction can probably be used with nearly any perhalogenated cyano derivative. These new amines are expected to have an interesting reaction chemistry via the reactivity of the N–Cl bond, and they are the precursors to the high-yield synthesis of *N*-fluorimines and *N*-fluoramines.[6,8]

(14) There are many reports on the reaction of F$_2$ with unsaturated carbon–nitrogen compounds^2 using flow systems and/or metal fluoride catalysts.

(15) Griffith, D. L.; Roberts, J. D. *J. Am. Chem. Soc.* **1965**, *87*, 4089. Johnson, F. A.; Haney, L.; Stevens, T. E. *J. Org. Chem.* **1967**, *32*, 466.

(16) In CH$_3$CF$_2$NClF, the ^{19}F NMR of the CF$_2$ group is a basic quartet with some additional splitting. The CF$_2$ group does not exhibit the expected ABXM$_3$ second-order pattern, implying that the inversion rate at nitrogen is fast at ~30 °C or that the chemical shifts are accidentally degenerate.

Circumnavigation of Uranylhexafluoroacetylacetonate by Lewis Bases

G. M. KRAMER,* M. B. DINES, R. KASTRUP, M. T. MELCHIOR, and E. T. MAAS, Jr.

The chelated uranylhexafluoroacetylacetonate ion forms adducts with Lewis bases which are fluxional when studied by ^{19}F NMR. The compounds have a pentagonal-bipyramidal geometry in which the base occupies one site in the equatorial ring. The kinetic parameters suggest that the equilibrating process is one in which the base migrates to a complementary site on the other side of the uranyl ion via intermediate capped octahedral structures.

The tetrahydrofuran adduct of uranylhexafluoroacetylacetonate, **1**, has recently been described.[1] An X-ray crystal structure determination revealed a linear UO$_2^{2+}$ ion surrounded equatorially by a pentagonal array of the five oxygen atoms

contributed by the pair of bidentate anions and the tetrahydrofuran molecule. In this configuration there are CF$_3$ and carbonyl groups both near and remote from the THF molecule, and NMR studies might be expected to display a magnetic inequality between them. At ambient temperatures in nonpolar solvents, however, both ^{19}F and ^{13}C NMR studies indicate single sharp resonances for the CF$_3$ and carbonyl groups.

(1) G. M. Kramer, M. B. Dines, R. B. Hall, A. Kaldor, A. R. Jacobsen and J. C. Scanlon, *Inorg. Chem.*, **19**, 1340 (1980).
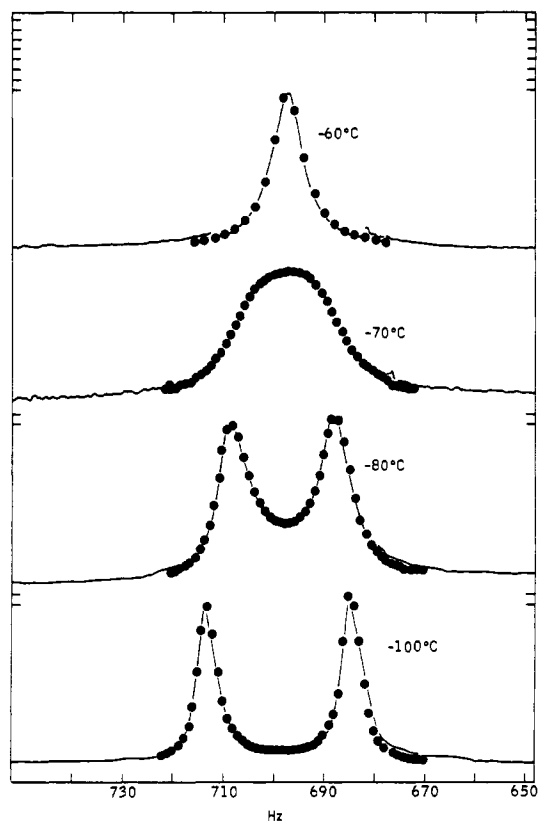
Figure 1. ^{19}F NMR spectra of $UO_2[(CF_3CO)_2CH]_2 \cdot THF$. The ^{19}F spectra were obtained on a Varian XL-100 spectrometer at 94.1 MHz with a 0.04 M solution of the uranyl complex.

This disparity has been resolved by low-temperature magnetic resonance studies which show the THF adduct to be a fluxional molecule. The data strongly suggest that the process is intramolecular. The THF adduct is representative of the behavior of a homologous series of compounds in which the Lewis base is varied.

Experimental Section

Fluorine-19 nuclear magnetic resonance is the principal tool which was applied to the problem of determining the reasons for the apparent magnetic equivalence of the CF_3 groups. Initial low-temperature studies in $DCCl_3$ and CD_2Cl_2 were unsuccessful in resolving the singlet into its components due either to insolubility of the uranyl complex or to solvent freezing. These difficulties were eliminated by using a three-component mixture of 90% CD_2Cl_2 and 10% of an 80:20 blend of methycyclohexane and isopentane as the solvent. In this solution concentrations of 0.04 M can readily be maintained to below -100 °C.

NMR data were obtained on a Varian XL-100 spectrophotometer. The kinetic parameters were calculated by using a Fortran program on the assumption of a two-site-exchange process.[2] The experimental spectra are compared with a set of calculated spectra for the THF complex in Figure 1.

Results and Discussion

The ^{19}F NMR spectrum of **1** exhibits a coalescence temperature of about -70 °C and is well resolved at -100 °C into two singlets separated by 0.30 ppm. The center of the singlets is 74 ppm upfield of $FCCl_3$, used as an internal reference.

The problem to be addressed first is whether the coalescence is due to an intramolecular rearrangement or is brought about by a dissociation–displacement mechanism. The intramolecular path we favor could be viewed as the THF precessing

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(2)   The Fortran program used was obtained from L. Jackman at Penn State. It was the program DNRAXI: "Calculation of Rates from D NMR Line Shapes for a Two-Site AX Exchange Case with Unequal Populations and Lifetimes."

Table I. Fluxional Process Parameters

UO_2-$[(CF_3CO)_2$-$CH]_2 \cdot$ THF, M	E_a, kcal/ mol	$\Delta S^{\ddagger}$, eu	k(calcd), s^{-1} -50 °C	0 °C	30 °C
0.002	4.2 ± 2.0	-28.8	450	2500	5500
0.040	4.4 ± 1.5	-30.5	122	750	1670

about an octahedral distribution of oxygen atoms surrounding the uranium atom:

$x = THF$
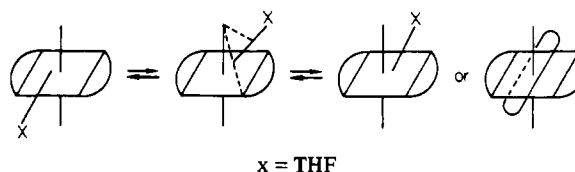
It should be noted that the X-ray structure of the crystal shows both chelating rings are bent in the same direction from the pentagonal plane of the oxygen atoms. If the rings are still bent in solution, the base migration will presumably occur over the less congested side of the molecule. Another possible intramolecular path is one in which the hexafluoroacetylacetonate groups rotate, either through a concerted path or by momentarily opening the chelation ring and swinging the anion 180° about the remaining U–O bond before reestablishing the ring. The result of this rearrangement is to interchange the positions of the CF_3 groups with respect to the neutral base.

Alternatively, equilibration might be induced by the dissociation process of eq 1 and 2. In fact, ^1H NMR data have

$$\qquad (1)$$

$$\qquad (2)$$
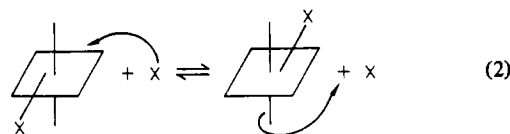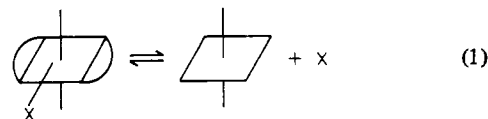
shown that when excess THF is added to solutions of **1**, fast exchange does occur as evidenced by an averaging of the chemical shift of the methylene protons. Thus a miniscule amount of free THF might lead to the observed ^{19}F equilibrations. A process involving a rate-determining dissociation of THF is therefore a real possibility. Less likely would be a rate-determining bimolecular encounter of two THF complexes because the transition state of such a process would appear to have severe barriers to the proper juxtaposition of the reacting moieties.

These possibilities can be weighed on the basis of a kinetic analysis of the equilibrating process. The activation energy and activation entropy of 0.04 and 0.002 M solutions of **1** are listed in Table I. There is a small difference in the first-order rate constants which decrease slightly at the higher concentration. This is attributed to experimental error. The fact that the reaction is first order excludes a bimolecular rate-determining step. First-order rate constants would, however, be consistent with either an intramolecular rearrangement or a slow dissociation followed by fast displacement. These might be distinguished on the basis of the expected activation entropies, since a dissociative path would normally have a small or positive activation entropy. Only an intramolecular process would appear to be consistent with the observed $\Delta S^{\ddagger}$ of -30 eu.

While these considerations appear to eliminate an intermolecular path, large negative entropies of activation have

occasionally been found in concerted reactions in which a solvent or solute molecule enters the bonding sphere of a reactant simultaneously with the elimination a leaving group. These reactions may exhibit pseudo-first-order behavior, and hence additional information about the fluxional uranyl process is desirable.[3]

Strong evidence for an intramolecular process was obtained from studies of an equimolar mixture of the THF and TMP adducts.[4] At −100 °C both complexes are frozen and the spectra consist of the overlap of slightly shifted pairs of peaks. On warming of the complexes, the THF pair collapses to a singlet, but the TMP pair remains "frozen" on the NMR time scale to above −10 °C. Thus one observes the resolved phosphate spectrum over a fairly broad range of temperature while the THF adduct rearranges rapidly. The unique coalescence of the peaks of the uranyl–THF complex in the mixture rules out bimolecular displacement reactions involving the attack of free THF or TMP on the complexes because, if this was a major factor, both complexes should have coalesced as they did when in solution by themselves.

Since the coalescence temperatures of the THF and TMP adducts separately are −70 and −60 °C, the preceding experiment raises the interesting question of why the TMP complex remains "frozen" to much higher temperatures in the mixture. A possible explanation is that the equimolar mixture exists as a 1:1 complex of the uranyl–THF and uranyl–TMP adducts. Since TMP is more basic than THF, it is reasonable to suppose that the uranyl–TMP adduct is relatively more nucleophilic and that the 1:1 complex is primarily stabilized by ion–dipole interactions between the U^{6+} center of the uranyl–THF adduct and the electron density on the uranyl oxygen atoms of the TMP adduct:
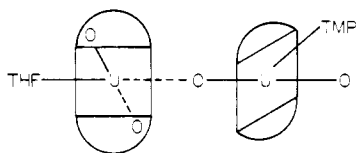
If the bound THF molecule and the uranyl–TMP adduct would now migrate about the uranyl ion to which both are bound, the F NMR spectrum of the latter will coalesce readily while that of the bound uranyl–TMP adduct will not.

Since, as mentioned above, the chelating rings on both uranyl components are probably bent from the pentagonal plane of the bipyramidal pentagon in their equilibrium configurations, the simultaneous coordination of THF and the uranyl–TMP adduct probably imposes severe steric constraints on the structure of the 1:1 complex. It is likely that both of these ligands will be forced to the opposite side of the plane from that occupied by the chelating rings. The ligand mobility would presumably take place on the hemisphere to which they are directed.

Returning to the question of intermolecular vs. intramolecular rearrangements for the uranyl–THF complex itself, the preceding discussion suggests that the molecule is rearranging by the latter path. Whether the path involves migration of the base or rotation of the anionic ligands will be considered next.

Table II contains kinetic information for the methanol, dimethyl sulfoxide, trimethyl phosphate, pyridine N-oxide, triethylphosphine oxide and hexamethylphosphoramide complexes. It also contains data for the trimethyl phosphate adduct in the presence of excess THF and for Et_3PO and HMPA adducts in a 50:50 mixture of benzene and toluene.

Table II. Fluxional Rearrangement Parameters of Uranylhexafluoroacetylacetonate Chelates

	E_a, kcal/ mol	$\Delta S^{\ddagger}$, eu	k, s^{-1}		
ligand[a]			−50 °C	0 °C	30 °C
In CD_2Cl_2, Methylcyclohexene and Isopentane					
MeOH	6.2 ± 2.0	−20.8	280	3600	11000
THF (0.04 M)	4.4 ± 1.5	−30.5	122	750	1670
THF (0.01 M)	4.4 ± 1.7	−28.1	390	2400	5300
THF (0.002 M)	4.2 ± 2.0	−28.8	450	2500	5500
Me_2SO	6.3 ± 2.0	−17.4	1200	16000	51000
TMP	4.4 ± 1.5	−30.1	140	880	2000
pyNO	4.0 ± 1.3	−28.7	720	3800	7800
Et_3PO	7.9 ± 1.0	−28.8	0.16	4.2	18
HMPA	11.0 ± 1.5	−19.8	0.014	1.3	9.9
In 50:50 Mixture of Benzene and Toluene					
Et_3PO	7.8 ± 1.5	−23.0	3.1	77	320
HMPA	11.3 ± 2.0	−10.4	0.67	70	550

[a] The ligands are THF = tetrahydrofuran, Me_2SO = dimethyl sulfoxide, TMP = trimethyl phosphate, pyNO = pyridine N-oxide, Et_3PO = triethylphosphine oxide, and HMPA = hexamethylphosphoramide.

From equilibrium measurements to be reported elsewhere[5] the Lewis bases increase their bonding to $UO_2[(CF_3CO)_2CH]_2$ in the order MeOH ≤ THF < Me_2SO < TMP < pyNO < Et_3PO < HMPA. All the complexes rearrange with relatively low activation energies and relatively high negative activation entropies. It is interesting to note that the HMPA complex has the highest E_a and smallest $\Delta S^{\ddagger}$ and that these values are solvent dependent. In the aromatic solvent the smaller $\Delta S^{\ddagger}$ indicates that the ground state is more tightly organized than in the more polar methylene chloride solvent.

The rate of the fluxional process decreases markedly as the size and basicity of the Lewis base increase. Size is more important than basicity however in slowing the process so that at 30 °C the equilibrating frequency is 10 Hz with HMPA and about 5000 Hz with THF. The slow fluxional motion of the HMPA adduct is thought to be due to steric interactions between the methyl groups of the base and the trifluoromethyl groups of the anion.

A choice between base migration or anion rotation can now be made by considering the possible effect of changing the size of the base upon the rate of these processes. Increasing its size will introduce nonbonding repulsions into the complex and thus destabilize the ground state. In the migration of the Lewis base these repulsions must become more severe, and hence the transition state ought to be more difficult to reach so that the reaction would be expected to slow down.

The rotation of the anion or opening of the chelating ring on the other hand would tend to reduce the nonbonding interactions with the large base. This should tend to reduce the free energy of activation and result in a rate enhancement.

The fact that the fluxionality slows down as steric requirements increase argues for the migration of the base. The picture of these compounds that emerges is therefore one in which the nucleophile migrates over a restricted potential energy surface from one side of the uranyl ion to the other. Halfway through the migration the structure is a capped octahedron, but whether this is the transition state or possibly a stable intermediate is uncertain at this time. Preliminary ³¹P NMR studies of the HMPA complex suggest that a stable intermediate is produced in this case, but its structure and generalizations to be drawn are still tentative. The probable role of anionic rearrangement in the fluxional behavior of these

(3) (a) H. P. Bennetto and E. F. Caldin, *J. Chem. Soc. A*, 2198 (1971); (b) D. G. Bickley and N. Serpone, *Inorg. Chem.*, **13**, 2908 (1974).
(4) J. H. Levy and A. B. Waugh, *J. Chem. Soc., Dalton Trans.*, **17**, 1628 (1977).

(5) G. M. Kramer, M. B. Dines, and E. T. Maas, Jr., *Inorg. Chem.*, in press.

uranyl compounds is considered to be small but is being studied in a continuing investigation.

The compounds used in this work were prepared via the same procedures used for the tetrahydrofuran adduct. They were crystalline compounds which were purified by sublimation and afforded H NMR spectra and elemental analyses indi-

cative of the monobasic adducts.

Contribution from the Institut für Anorganische Chemie, Universität Würzburg, Würzburg, West Germany

Carbonyl Monoolefin Derivatives of the Group 6 Transition Metals. 2.[1] Kinetics of Olefin Displacement

W. A. SCHENK* and H. MÜLLER

The monoolefin complexes *cis*-$M(CO)_4L$(olefin) (M = Cr, Mo, W; L = PR_3) react with triisopropyl phosphite to form *cis*-$M(CO)_4[P(O(i\text{-}Pr))_3]$ derivatives. The reactions are first order in substrate and zero order in entering ligand with the rates increasing with changes in the metal W ≪ Mo ≪ Cr, changes in the coligand L $PEt_3 < P(i\text{-}Pr)Ph_2 < P(i\text{-}Pr)_2Ph < PPh_3 < P(i\text{-}Pr)_3$, and changes in the olefinic ligand maleic anhydride ≪ dimethyl fumarate < bis(trimethylsilyl) fumarate < dimethyl maleate < ethylene. A dissociative mechanism is proposed involving the rupture of the metal–olefin bond as the rate-determining step.

Introduction

During the last decade homogeneous catalysis has become a field of intense interest to both organic and organometallic chemists. Many important reactions involving olefins, e.g., isomerization, double-bond migration, hydrogenation, and hydroformylation, are efficiently catalyzed by organic derivatives of the heavier group 8 transition metals ruthenium through platinum.[2] In view of the limited availability of these elements it would be desirable to design catalysts based on the more abundant earlier transition metals such as molybdenum or tungsten.

All transition-metal-catalyzed olefin reactions involve the formation and rupture of a metal–olefin bond at some stage of the catalytic cycle. It is, therefore, of prime importance to know how the lability of the metal–olefin bond in transition-metal complexes $ML_mL'_n$(olefin) depends on the nature of the metal and the coligands L and L' as well as on the substituents at the double bond. As a first step we have investigated the kinetics of olefin displacement in compounds of the type *cis*-$M(CO)_4L$(olefin), where M = Cr, Mo, or W, L = tertiary phosphine, and olefin = maleic anhydride (ma), dimethyl maleate (dmm), dimethyl fumarate (dmf), and bis(trimethylsilyl) fumarate (btf). Although a number of monoolefin derivatives of the group 6 metals are known to date,[3] their reactivity has not yet been investigated in detail.

Table I. Rate Constants for the Reaction $M(CO)_4L$(olefin) + $P(O(i\text{-}Pr))_3 \rightarrow M(CO)_4L[P(O(i\text{-}Pr))_3]$ + Olefin in Dichloroethane Solution at 25 °C

M	L	olefin[a]	$[P(O(i\text{-}Pr))_3]$, M	$10^4 k$, s^{-1}
Cr	PEt$_3$	ma	0.20	53
Mo	PEt$_3$	ma	0.10	0.26
			0.20	0.25
	Pi-Pr$_3$	ma	0.10	80
W	Pi-Pr$_3$	ma	0.33	<0.1
	PEt$_3$	dmf	0.40	0.24
	Pi-Pr$_3$	dmf	0.20	55
			0.33	55
			1.24	52
	Pi-Pr$_2$Ph	dmf	0.33	13
			0.66	14
	Pi-PrPh$_2$	dmf	0.19	3.5
			0.33	3.7
	PPh$_3$	dmf	0.20	31
			1.00	31
	Pi-Pr$_3$	btf	1.00	120
	Pi-Pr$_3$	dmm	0.40	1700

[a] ma = maleic anhydride, dmf = dimethyl fumarate, btf = bis(trimethylsilyl) fumarate, dmm = dimethyl maleate.

Experimental Section

Materials. 1,2-Dichloroethane was dried over P_4O_{10} and distilled under nitrogen. Triisopropyl phosphite was distilled at reduced pressure prior to use. The olefin derivatives of chromium, molybdenum, and tungsten were prepared as described previously.[1]

Kinetic Measurements. All reactions with rate constants exceeding 10^{-3} s^{-1} (i.e., $t_{1/2}$ < 10 min) were followed by using stopped-flow techniques. Freshly prepared solutions of both reactants in 1,2-dichloroethane were injected via a mixing chamber into a CaF_2 IR cell. The cell was mounted in a close-fitting steel block kept at 25 °C by means of a closed-cycle water thermostat. Optical path lengths of 0.1 or 1.0 mm were employed depending on the concentration of the starting material. A matched cell containing the pure solvent was placed in the reference beam of the spectrometer (Perkin-Elmer 283). Reactions were monitored by following the decrease of absorption of the starting olefin complex at the high-energy carbonyl peak at ~2050 cm^{-1} with the instrument operating in time drive mode. Spectra of the solutions were run after 10 half-lives; complete conversion to the expected cis tetracarbonyl phosphine phosphite complex was observed in all cases.

The slower reactions were carried out in the conventional way in Schlenk tubes under nitrogen. The tubes were wrapped in aluminum foil and stored in a thermostated water bath. Samples were withdrawn

(1) Part 1: Schenk, W. A.; Müller, H. *Z. Anorg. Allg. Chem.,* in press.
(2) Henrici-Olive, G.; Olive, S. "Coordination and Catalysis"; Verlag Chemie: Weinheim, 1977.
(3) (a) Fischer, E. O.; Kuzel, P. *Z. Naturforsch., B: Anorg. Chem., Org. Chem., Biochem., Biophys., Biol.* **1961,** *16B,* 475. (b) Fischer, E. O.; Fichtel, K. *Chem. Ber.* **1961,** *94,* 1200. (c) Stolz, I. W.; Dobson, G. R.; Sheline, R. K. *Inorg. Chem.* **1963,** *2,* 1264. (d) Strohmeier, W.; Hellmann, H. *Chem. Ber.* **1965,** *98,* 1598. (e) Guttenberger, F.; Strohmeier, W. *Ibid.* **1967,** *100,* 2807. (f) Angelici, R. J.; Busetto, L. *Inorg. Chem.* **1968,** *7,* 1935. (g) Herberhold, M. *Angew. Chem.* **1968,** *80,* 314; *Angew. Chem., Int. Ed. Engl.* **1968,** *7,* 305. (h) Herberhold, M.; Jablonski, C. R. *J. Organomet. Chem.* **1968,** *14,* 457. (i) Herberhold, M.; Jablonski, C. R. *Inorg. Chim. Acta* **1973,** *7,* 241. (j) Wrighton, M.; Hammond, G. S.; Gray, H. B. *J. Am. Chem. Soc.* **1971,** *93,* 6048. (k) Nasielski, J.; Denisoff, O. *J. Organomet. Chem.* **1974,** *81,* 385. (l) Nasielski, J.; Denisoff, O. *Ibid.* **1975,** *102,* 65. (m) Schaper, H.; Behrens, H. *Ibid.* **1976,** *113,* 377. (n) Byrne, J. W.; Blaser, H. V.; Osborn, J. A. *J. Am. Chem. Soc.* **1975,** *97,* 3871. (o) Kreiter, C. G.; Strack, H. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1975,** *30B,* 748. (p) Koemm, U.; Kreiter, C. G.; Strack, H. *J. Organomet. Chem.* **1978,** *148,* 179.