proceeds from a cluster of rank $r - 1$ to a cluster of rank r; in this manner, only the already evaluated best stability of each cluster of rank $r - 1$ is used to assign values to the next rank clusters.

For example, for M_2W (sign of charge omitted) we use $W_2 \rightarrow W_3 \rightarrow MW_2 \rightarrow M_2W$; $MW \rightarrow MW_2 \rightarrow M_2W$; $M_2 \rightarrow M_2W$ and $M_2 \rightarrow M_3 \rightarrow M_2W$. However, for example, $MW \rightarrow M_2 \rightarrow M_2W$ is not used, since the first step here connects clusters whose relative stabilities were already assigned, and using the directly measured value for the $MW \rightarrow M_2$ reaction would overemphasize the weight of this measurement in building up the next column.

The n paths reaching a cluster of rank r from the rank $r - 1$ clusters give n values for ΔG_{total} for that cluster. Each of these n values is assigned a random error, which is the propagated error associated with the precursor cluster and of the steps used in that particular path. A weighted least-squares average of these n values for the given cluster is assigned as the chosen value. Note that the weighted averaging allows less influence by values derived from long paths, since these have larger propagated errors.

2. Notes on Terminology. The total number of components in a cluster is often denoted as "cluster size". This may be misleading, however, since clusters with the same number of

monomers may differ greatly in size; and a "smaller cluster" $(CH_3OH)_4$ is larger in physical size thn a "larger cluster" $(H_2O)_6$. Above, the term "rank r" was used to avoid this ambiguity.

In the present paper, mixed clusters are denoted as $(CH_3OH)_m(H_2O)_nH^+$ and $((CH_3OH)_m(H_2O)_n - H)^-$. The notation is somewhat inconvenient, especially for the anions. However, alternative notations would imply structures that are not always predictable. For example, for $(CH_3CN)(H_2O)_3H^+$, the intuitive structure would be $CH_3CNH^+ \cdot 3H_2O$, while ab initio calculations show $H_3O^+ \cdot 2H_2O \cdot CH_3CN$. Therefore, notation such as $CH_3O^- \cdot mCH_3OH \cdot nH_2O$ should be avoided. Another, somewhat more accurate alternative, such as $((CH_3OH)_m(H_2O)_n - H^+)$ to denote the deprotonated anion clusters would also be confusing. A further advantage to the present notation is that it is symmetric for anionic and cationic clusters of similar composition.

A shorthand notation such as $M_mW_n^-$ is used in Figure 5 and Tables III and IV. For example, $M_2W_2^- = [(MeOH)_2(H_2O)_2 - H]^- = MeO^- \cdot MeOH \cdot H_2O$, etc. $M_mW_n^-$ as used here should not be confused with the radical anion $[(CH_3OH)(H_2O)]^{\cdot -}$.

The Effects of Chloro Substitution on the Electronic Structure of ClCr+, ClMn+, and ClFe+ and Their Reactivity with Small Alkanes

M. L. Mandich,* M. L. Steigerwald,* and W. D. Reents, Jr.*

Contribution from AT&T Bell Laboratories, Murray Hill, New Jersey 07974. Received February 10, 1986

Abstract: The exothermic reactions of ClCr+, ClMn+, and ClFe+ with small alkanes in the gas phase have been investigated in the ion trap of a Fourier transform mass spectrometer. ClFe+ is unreactive. In the ClMn+ reactions, the chlorine radical is displaced, yielding Mn+-(alkane) products. ClCr+ activates C–C and C–H bonds of the alkanes leading to ClCr+-(alkene) products resulting from loss of H_2 or CH_4. The reactivity of ClCr+ is particularly unusual since ground-state Cr+ does not react exothermically with small alkanes. A description of the metal-to-chlorine bond has also been obtained with ab initio Hartree–Fock and generalized valence bond calculations. These calculations show that ClMn+ and ClFe+ have a covalent bond between the Cl and the metal which is in the σ space between the two nuclei. An unusual situation occurs in the case of ClCr+ where two bonding configurations are close in energy. One has a covalent σ bond as in ClMn+ and ClFe+. The other has a covalent bond in the π space between the nuclei with the σ space supporting strong donor/acceptor bonding between a doubly occupied Cl orbital and the empty valence s space on the metal. This peculiar bond permits the ClCr+ to act as a diradical species which explains its unexpected reactivity.

Studies of the reactions of coordinatively unsaturated metal ions in the gas phase have revealed rich and unprecedented chemistry at single transition-metal centers. Perhaps the most striking feature of this reactivity is that these metal ions are capable of exothermically activating the relatively inert C–C and C–H bonds of saturated hydrocarbons. This reactivity has been investigated for the atomic metal ions, and extensive information is now available for the first-row transition metals and many of the second-row transition metals.[1-8] Nonetheless, since these metal ions have no ligands, direct comparisons cannot necessarily be made with the large body of knowledge about homogeneous organometallic systems. Therefore, much will be learned about the

differences in reactivity and thermochemistry between the gaseous atomic metal ions and corresponding solution-phase organometallic molecules by examining intermediate prototypes such as partially coordinated metal ions. There have been a few studies of partially ligated metal ions, e.g., several $(C_5H_5)M^+$,[9] MH^+,[10] MD^+,[11] MCH_3^+,[12] and MCO^+[13] ions as well as FeO^+[14] and $TiCl_n^+$.[15] Currently, however, reactivities of the coordinated species are much less well described than for the bare metal ion analogues. In this work, we report the reactions of the series ClCr+, ClMn+, and ClFe+ with small alkanes. The reactivity for ClCr+ is particularly unusual. Whereas Cr+ does not react exothermically with small alkanes, ClCr+ does. This is the first demonstration that addition

(1) Muller, J. *J. Adv. Mass. Spectrum.* **1976**, *68*, 823.
(2) Allison, J.; Freas, R. B.; Ridge, D. P. *J. Am. Chem. Soc.* **1979**, *101*, 1332.
(3) Larson, B. S.; Ridge, D. P. *J. Am. Chem. Soc.* **1984**, *106*, 1912.
(4) Armentrout, P. B.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1980**, *102*, 1736.
(5) Houriet, R.; Halle, L. F.; Beauchamp, J. L. *Organometallics* **1983**, *2*, 1818.
(6) Tolbert, M. A.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 8117.
(7) Byrd, G. D.; Burnier, R. C.; Freiser, B. S. *J. Am. Chem. Soc.* **1982**, *104*, 3565.
(8) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1983**, *105*, 5197.

(9) Beauchamp, J. L.; Stevens, A. E.; Corderman, R. R. *Pure Appl. Chem.* **1979**, *51*, 967.
(10) Halle, L. F.; Klein, F. S.; Beauchamp, J. J. *J. Am. Chem. Soc.* **1984**, *106*, 2543.
(11) Carlin, T. J.; Sallans, L.; Cassady, C. J.; Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1983**, *105*, 6321.
(12) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1984**, *106*, 3891.
(13) Freas, R. B.; Ridge, D. P. *J. Am. Chem. Soc.* **1980**, *102*, 7129.
(14) Jackson, T. C.; Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1984**, *106*, 1252.
(15) Allison, J.; Ridge, D. P. *J. Am. Chem. Soc.* **1977**, *99*, 35.

of a ligand can cause an unreactive atomic metal ion to become reactive toward C–C and C–H activation.[16] The bonding between the chlorine ligand and the metal ions is also examined with use of ab initio calculations. Our calculations show that unusual bonding exists for ClCr$^+$ as compared to ClMn$^+$ and ClFe$^+$. This can account for the unexpected reactivity of ClCr$^+$.

Experimental Section

Method. A Nicolet FT/MS-1000 Fourier transform mass spectrometer was used to obtain experimental data. Typical conditions were the following: magnetic field strength, 2.97 T; cell dimensions, 25.4 × 25.4 × 76.2 mm; electron energy, 70 eV; trapping voltage, 0.5–1.0 V; trapping time, 1 ms to 3 s; number of data points; 32K; mass range, 50–500 amu; pressure of organometallic, $\sim$3 × 10^{-8} Torr; pressure of alkane, $\sim$2 × 10^{-7} Torr. Pressures were measured with a Bayard-Alpert ionization gauge. All compounds were introduced into the mass spectrometer through variable leak valves from an inlet heated to $\sim$50 °C. At 50 °C, the three organometallic precursors (vide infra) had vapor pressures which were sufficient to allow for their direct introduction into the ion cell. Higher temperatures were avoided since decomposition of the organometallics became significant and caused deterioration of the desired ion signals.

The alkanes were commercially available materials and were used without further purification. CpCr(NO)$_2$Cl^{17} and CpFe(CO)$_2$Cl^{18} were synthesized via literature methods; Mn(CO)$_5$Cl was obtained from Pressure Chemical Co. All three organometallic compounds were recrystallized several times to remove water and organic impurities and then subjected to freeze–pump–thaw cycles to remove residual gases.

Ions derived from the alkanes were ejected from the cell by standard double resonance.[19] In addition, the most abundant ion from the alkane was ejected during ion formation to enhance the intensities of the remaining ions.

All reaction pathways observed were checked by ejecting the reactant ion and verifying a decrease in the product ion intensity. The elemental composition of the product ion was verified by accurate mass measurement (within 10 ppm) with sufficient mass resolution ($M/\Delta M > 5000$) to differentiate potentially overlapping masses, e.g., MC$_2$H$_4$$^+$ and MCO$^+$.

The three reactant ions, ClCr$^+$, ClMn$^+$, and ClFe$^+$, were prepared by electron impact from the neutral precursors CpCr(NO)$_2$Cl, Mn(CO)$_5$Cl, and CpFe(CO)$_2$Cl, respectively. An electron impact energy of 70 eV was typically used.

Experiments were performed in order to establish that the observed reactions result from ground-state rather than excited-state reactant ions. Approximately half of the reactions were rerun with use of an electron impact energy of 20 eV. The results at 70 and 20 eV were identical within experimental error. The product intensities were also monitored as a function of time. Kinetic analysis of the time dependence of the ion signals shows that all of the observed reactions are slow and that all product formations can be characterized by using a single pseudo-first-order rate constant. The rate constants for the ClCr$^+$ reactions are all $\sim$6 × 10^{-11} cm^3 molecule^{-1} s^{-1}; the rate constants for the ClMn$^+$ reactions lie in the range of $\sim$5–20 × 10^{-11} cm^3 molecule^{-1} s^{-1}.[20] Both the ClCr$^+$ and ClMn$^+$ populations react throughout the trapping time to form the observed products. In particular, the ClCr$^+$ reactions were monitored for a trapping time of 3 s at which time 75% of the initial ClCr$^+$ population was converted to products. Together, these measurements indicate that the observed chemistry results from ground-state ions rather that a small population of excited-state ClCr$^+$ or ClMn$^+$.

---

(16) There have been cases where addition of a ligand has caused a metal ion to become *more* reactive. For example, FeO$^+$ reacts exothermically with ethane whereas Fe$^+$ does not.[14] Nonetheless, Fe$^+$ does react exothermically with larger alkanes (propane, etc.). There are other examples where a ligand has served to increase reactivity such that a coordinated transition-metal ion will react to yield products with smaller alkanes or a more diverse spectrum of products for a given alkane. The ClCr$^+$ reactions described herein are unique in that *no* reactions of ground-state Cr$^+$ with *any* saturated alkanes have been observed.

(17) Hoyano, J. K.; Legzdins, P.; Maliton, J. T. *Inorg. Synth.* **1980**, *18*, 129.

(18) Piper, T. S.; Cotton, F. A.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1955**, *1*, 165.

(19) Beauchamp, J. L. *Annu. Rev. Phys. Chem.* **1971**, *22*, 527.

(20) These rate constants are determined by using pressures measured with a Bayard-Alpert ionization gauge and then corrected for instrumentation effects and sensitivity to the respective alkanes relative to CH$_4$. (Bartmess, J. E.; Georgiadis, R. M. *Vacuum* **1983**, *33*, 149. Reents, W. D., Jr.; Mujsce, A. M. *Int. J. Mass Spectrom. Ion Phys.* **1984**, *59*, 65. The pressure correction factor obtained by this approach may be off by up to a factor of 3 which would change the absolute value of the cited rate constants but leave the relative values unchanged.
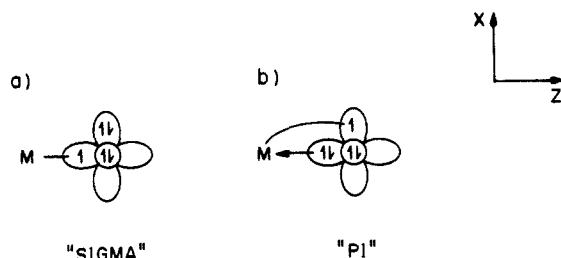

Figure 1. Two possible bonding configurations in ClM$^+$. In each diagram, the Cl atom is depicted as three intersecting p orbitals (x and z are in the plane, y is perpendicular to the page). The doubly occupied 3s orbital of Cl is not represented, nor are the metal orbitals depicted. (a) The "σ" state. In this state the singly occupied Cl orbital is in the σ space and overlaps a σ orbital (s + d + p) on the metal to form a covalent bond. There is a small amount of pπ back-bonding from the remaining doubly occupied orbitals of Cl onto the metal. (b) The "π" state. In this state the singly occupied Cl orbital is in one of the π directions (π_x in the diagram). This orbital overlaps a π_x orbital on the metal to form a covalent bond. The Cl p$_\sigma$ orbital is a strong two-electron donor in this state, and there is a small amount of pπ back-bonding from the remaining doubly occupied p$_y$ orbital on Cl onto the metal.

Table I. Product Distributions for Exothermic Reactions of ClCr$^+$, ClMn$^+$, and ClFe$^+$ with Alkanes^a

alkane	reacting ion	ionic product where neutral lost = Cl$\cdot$	ionic product where neutral lost = H$_2$; C$_m$H$_{2m+2}$
C$_3$H$_8$ (propane)	ClCr$^+$	NR	NR
	ClMn$^+$	MnC$_3$H$_8$$^+$	0
	ClFe$^+$	NR	NR
n-C$_4$H$_{10}$ (butane)	ClCr$^+$	0	ClCrC$_4$H$_8$$^+$
	ClMn$^+$	MnC$_4$H$_{10}$$^+$	0
	ClFe$^+$	NR	NR
i-C$_4$H$_{10}$ (2-methylpropane)	ClCr$^+$	0	ClCrC$_4$H$_8$$^+$
	ClMn$^+$	MnC$_4$H$_{10}$$^+$	0
	ClFe$^+$	NR	NR
neo-C$_5$H$_{12}$ (2,2-dimethylpropane)	ClCr$^+$	0	ClCrC$_4$H$_8$$^+$
	ClMn$^+$	MnC$_5$H$_{12}$$^+$	0
	ClFe$^+$	NR	NR

^{a} Where an ionic product is listed, it is 100% of the observed reaction products; a zero indicates that reactivity is observed but not corresponding to the loss of the particular neutral. "NR" signifies that no reaction at all was observed.

Details of the Electronic Structure Calculations. Electronic structure calculations were performed on ClCr$^+$, ClMn$^+$, ClFe$^+$, and ClV. The goal of these calculations was to determine the ground electronic state of each molecule as well as to begin to locate some of the potentially important excited states. Hartree–Fock and Generalized Valence Bond (GVB)[21] calculational methods were employed. In the GVB calculations, the *covalent* M–Cl bond was described by a pair of singly occupied orbitals (a GVB pair), and the remaining electrons were described in a Hartree–Fock sense. This two-configuration self-consistent field (SCF) calculation is called a GVB(1/2) calculation: one electronic pair is described by two orbitals. These calculations were performed with the California Institute of Technology Molecular Quantum Mechanics program package.[22,23] Valence double-ζ basis sets were used throughout. Effective potentials were used to replace the core electrons on each center.[24-26] In the case of ClCr$^+$, the calculations were repeated with

---

(21) Goddard, W. A., III; Dunning, T. H., Jr.; Hunt, W. J.; Hay, P. J. *Acc. Chem. Res.* **1973**, *6*, 368.

(22) Bair, R. A.; Goddard, W. A. III; Voter, A. F.; Rappe', A. K.; Yaffe, L. G.; Bobrowicz, F. W.; Wadt, W. R.; Hay, P. J.; Hunt, W. J., GVB2P5 program, unpublished.

(23) Bobrowicz, F. W.; Goddard, W. A., III *Method in Theoretical Chemistry*; Plenum: New York, 1977; Vol. 3, p 79.

(24) Goddard, W. A., III; Rappe', A. K. In *Potential Energy Surfaces and Dynamics Calcuations*; Truhlar, D. G., Ed.; Plenum: New York, 1981; pp 661–684.

(25) Rappe', A. K.; Smedley, T. A.; Goddard, W. A., III, *J. Phys. Chem.* **1981**, *85*, 1662.

(26) Rappe's, A. K.; Smedley, T. A.; Goddard, W. A., III *J. Phys. Chem.* **1981**, *85*, 2607.

Table II. Calculated Splittings, Δ, between the "σ" and "π" States (See Figure 1)

species	$\Delta(\text{"}\sigma\text{"}-\text{"}\pi\text{"})$ (kcal/mol)	
	HF	GVB (1/2)
$ClCr^+$	8	12
$ClMn^+$	157	
$ClFe^+$	123	
VCl	2	

Table III. Calculated Bond Lengths

species	state	$R(M-Cl)$ (Å)	
		HF	GVB (1/2)
$ClCr^+$	"σ"	2.262	2.286
	"π"	2.282	2.272
$ClMn^+$	"σ"	2.2^a	2.2^a
	"π"	2.2^a	2.2^a
$ClFe^+$	"σ"	2.228	
	"π"	2.2^a	2.2^a
VCl	"σ"	2.2^a	2.2^a
	"π"	2.2^a	2.2^a

^{a} Indicates value assigned for calculation, no further geometry optimization was performed.
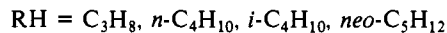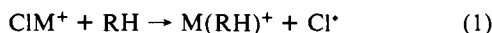
use of a fully ab initio description of the Cr atom. Agreement between the fully ab initio calculations and those using the effective potentials was within 0.01 Å in bond length and 1.2 kcal/mol in state splittings.

The bond lengths were optimized for both states of $ClCr^+$ and the ground state of $ClFe^+$. For the $ClFe^+$ excited state and all states considered for ClV and $ClMn^+$, the bond length was fixed at 2.2 Å. Further optimization was not considered important because of the magnitude of state splittings which were observed at these geometries.

For each ClM^+, two electronic states were considered. The "σ" state has a covalent metal–chlorine bond in the σ space of the molecule (Figure 1a), while the "π" state has a covalent metal–chlorine bond in the π space of the molecule (Figure 1b). In each case, the "σ"/"π" splitting was calculated at the Hartree–Fock level, and in $ClCr^+$ the splitting was calculated at the GVB (1/2) level as well.

Results

Experimental. A summary of the reactions of $ClCr^+$, $ClMn^+$, and $ClFe^+$ with propane, n-butane, isobutane, and neopentane is given in Table I. The first product column in Table I designates the products of those reactions which arise from simple ligand displacement; the alkane exothermically attaches to the metal center followed by loss of the Cl ligand in the form of a Cl atom, reaction 1. Out of the three ClM^+ studied, only $ClMn^+$ displays

$$ClM^+ + RH \rightarrow M(RH)^+ + Cl^\bullet \qquad (1)$$

$$RH = C_3H_8, \ n\text{-}C_4H_{10}, \ i\text{-}C_4H_{10}, \ neo\text{-}C_5H_{12}$$

this type of reactivity. The second product column in Table I designates those products arising from activation of the C–C and/or C–H bonds of the alkane at the metal center followed by loss of neutral H_2 or CH_4. In these reactions, the Cl ligand remains on the metal center as in, for example, reaction 2. This reactivity

$$ClCr^+ + i\text{-}C_4H_{10} \rightarrow ClCrC_4H_8^+ + H_2 \qquad (2)$$

is displayed by only the $ClCr^+$ species. The $ClFe^+$ ion does not react exothermically with any of these four alkanes.

Theoretical. Table II lists the calculated energetic splitting, Δ, between the "σ" and "π" states (Figure 1) for ClV, $ClCr^+$, $ClMn^+$, and $ClFe^+$ at the Hartree–Fock level and for $ClCr^+$ at the GVB (1/2) level of calculation. Only in the cases of $ClCr^+$ and ClV were the two states comparable in total energy. In ClV, the states were virtually identical (see below). The bond lengths resulting from geometry optimization are listed for both states in Table III, except where estimated as noted above.

Discussion

The Nature of the Cl–M⁺ Bond in $ClCr^+$, $ClMn^+$, and $ClFe^+$. Owing to the large electronegativity difference between chlorine and the transition metals, ionic $Cl^- - M^{2+}$ is the simplest picture of the ClM^+ metal-to-chlorine bond. The importance of this ionic

Table IV. Estimated Ionic Bond Dissociation Energies for $M^+ - Cl^-$ and $M^{2+} - Cl^-$ (M = V, Cr, Mn, and Fe)

metal	IP^I (eV)^b	IP^{II} (eV)^c	D_e(ionic) (kcal/mol)^a	
			$M^+ - Cl^-$	$M^{2+} - Cl^-$
V	6.74	14.65	79	
Cr	6.766	16.50	78	4
Mn	7.435	15.64	63	24
Fe	7.870	16.18	52	12

$^a R_0 = 2.2$ Å; see text and Table III. $^b IP^I$ is the energy required for $M \rightarrow M^+ + e^-$.[54] $^c IP^{II}$ is the energy required for $M^+ \rightarrow M^{2+} + e^-$.[54]

description can be assessed energetically according to eq 3. The electrostatic binding between the anion and the cation is given

$$D_e^{ION}(Cl^- - M^{2+}) = (q_A q_C / R_{AC}) = IP^{II}(M) + EA(Cl) \qquad (3)$$

by $q_A q_C / R_{AC}$, where q_A and q_C are the respective ionic charges and R_{AC} is the equilibrium internuclear separation of the ions. $IP^{II}(M)$ is the second ionization potential for M ($M^+ \rightarrow M^{2+} + e^-$), and EA(Cl) is the electron affinity of Cl (3.6 eV). The value of $D_e^{ION}(Cl^- - M^{2+})$ gives a measure of the importance of ionic bonding. If D_e^{ION} is near or below 0, it can be asserted that ionic bonding of the $Cl^- - M^{2+}$ form is unimportant. The estimated values of $D_e^{ION}(Cl^- - M^{2+})$ are shown in Table IV. Included for comparison is a list of estimated values of $D_e^{ION}(Cl^- - M^+)$ for the corresponding *neutral* species.

Several conclusions can be drawn from the estimates in Table IV. First, for the *neutral* ClM species, the ionic limit predicts strong Cl–M bonds. Thus the qualitative description of ClM as $Cl^- - M^+$ is reasonable. Second, with the possible exception of $ClMn^+$, all three ClM^+ species are only weakly bound by pure ionic forces in the order $D_e(Mn^{2+} - Cl^-) > D_e(Fe^{2+} - Cl^-) > D_e(Cr^{2+} - Cl^-)$. This predicted trend is clearly contradicted by the reactions observed for the three ClM^+ species (Table I). Here, the $Cl-Mn^+$ bond is sufficiently weak that the Cl ligand is displaced by small alkanes.[27] In contrast, the $Cl-Fe^+$ and the $Cl-Cr^+$ bonds are impervious to alkane displacement.[28] $ClCr^+$ is observed to undergo more complex reactivity with alkanes but without loss of Cl even in the form of, for example, HCl or CH_3Cl. Clearly a description of these three ClM^+ species which includes only ionic forces is inadequate.

As expected from the discussion above, the results of our theoretical calculations (Table II) indicate that the bonding in neutral VCl is ionic. This is substantiated not only by the Mulliken populations (0.6 electron transferred from V to Cl, indicating a strongly polarized bond) but also by the near degeneracy of the two (d^4) electronic states ("σ" and "π", see Table II) which differ only in the distribution of the four quintet-coupled electrons among the five d orbitals.[29] (Note that a small splitting is also calculated for $ClCr^+$, but the reason differs as will be discussed below.) Analogous results are expected for the neutral ClCr, ClMn, and ClFe species.

(27) An alternative interpretation can be proposed to explain the observed reactivity where Mn^+ binds alkanes *much* more strongly than does Fe^+. Assuming that the $M-CO^+$ bond strengths are roughly equal, this does not appear to be the case from ligand displacement experiments. These show that butanes and larger alkanes displace CO from $FeCO^+$ and that alkanes as small as ethane will displace CO from $MnCO^+$. No alkane, even as large as neopentane, is observed to displace the Cl ligand from $ClFe^+$. (Mandich, M. L.; Reents, W. D., Jr.; Steigerwald, M. L., work in progress.) Also, in the absence of an equilibrium between the two competing ligands, a reaction barrier preventing the attachment of the alkane to the metal center can be invoked. Since ion–induced dipole interactions are expected to favor the formation of an intermediate "loose" complex between the ClM^+ and the alkane (where the magnitude of the attractive forces would not depend greatly on the particular M), this explanation seems unlikely. Once this complex forms, it would be expected to decay via the most exothermic path, i.e., the loss of the most weakly bound ligand which may be either Cl or the alkane.

(28) Note that Cl⁻ displacement may be prevented in the case of $ClCr^+$ by the other competing reactions. This cannot be definitively ruled out; however, the rates of Cl⁻ displacement from $ClMn^+$ are 1–3 times the reaction rates of $ClCr^+$ which suggests that the absence of Cl⁻ displacement from $ClCr^+$ is not due to kinetic factors.

(29) Ballhausen, C. J. *Introduction to Ligand Field Theory*; McGraw-Hill: New York, 1962.

The situation for the corresponding ClM positive ions is quite different; the Cl–M$^+$ bond is best described as covalent. The electronic structure calculations also indicate that the description of the metal-to-chlorine bond is qualitatively similar for ClMn$^+$ and ClFe$^+$, but the bonding is different in ClCr$^+$ (Table II). The bonding in ClMn$^+$ and ClFe$^+$ is best described as the overlap of the singly occupied pσ orbital on Cl with the singly occupied 4s orbital on M$^+$ (Figure 1a). Both Mn$^+$ and Fe$^+$ have 3d^{n}4s^1 ground electronic states. In each case the singly occupied 4s orbital is radially larger than the 3d orbitals and more easily ionized (the ground states of Mn^{2+} and Fe^{2+} are both 3d^n), and the spin-coupling between the 4s electron and the 3d electrons is weak (for Mn$^+$: $\Delta(^7S-^5S) = 1.17$ eV, for Fe$^+$: $\Delta(^6D-^4D) = 1.03$ eV (both values for Δ are averaged over the J states)). These facts indicate why the 4s orbital is the most likely orbital on the metal to bond to the chlorine atom. Overall, this covalent two-electron σ bond is only slightly polar.[30]

The situation for ClCr$^+$ differs from ClMn$^+$ and ClFe$^+$ in that there are two states which are close in energy but quite different in character. One state ("σ") has a covalent bond between a singly occupied pσ orbital on Cl and an orbital on Cr$^+$ which is a hybrid between a 4s and a 3d$_{z^2}$ orbital. The covalent bond in the σ space is supplemented by donor bonding from doubly occupied pπ_x and pπ_y orbitals on the Cl to the Cr. The second state ("π") has a covalent bond between a singly occupied pπ orbital on Cl and a dπ orbital on Cr$^+$. Here, the covalent bond (which is now in the π space; and, owing to the intrinsically smaller π overlap, is expected to be a weak covalent interaction) is supplemented by donor bonding from the doubly occupied pσ orbital and the remaining pπ orbital on Cl to the acidic Cr$^+$. Thus in each state the Cl–Cr$^+$ linkage is a partial triple bond where one bond is covalent (one electron is donated to the bond from each center) and two bonds are of the donor–acceptor type (two lone pairs of electrons are donated from chlorine to chromium). The nearness in energy of the "π" state to the "σ" state appears to be largely due to the high-spin d^5 ground state of Cr$^+$. In order for Cr$^+$ to bond covalently to a ligand, components of higher energy and lower spin state must be incorporated. Covalent σ bonds require more complete spin recoupling than covalent π bonds since σ bonding orbital overlaps are greater than π bonding orbital overlaps. The extent to which covalent bonding dominates in ClCr$^+$ ultimately dictates the extent to which lower spin states on Cr$^+$ must be used at the cost of its sextet d^5 character. We believe that multiple-configuration SCF calculations (which will allow the mixing of configurations, some of which favor the covalent bonding picture and others of which favor the intraatomic high-spin coupling) will show the "π" state to be at least quite close to the "σ" state, if not the ground state itself.

Another interpretation of the results of our calculations is that ClCr$^+$ is best described as Cl$^-$–Cr^{2+} and that the near-degeneracy of the "σ" and "π" states is simply the near-degeneracy of the corresponding ligand-field states, as for VCl. There are three arguments against this alternative view. First, the data in Table IV show that, of the members of the series studied here, chromium is the metal ion least likely to display Cl$^-$–M^{2+} bonding. Yet it is the only metal ion which shows the "σ"/"π" degeneracy in our electronic structure calculation. Second, if a dominant component of the bonding is of the form Cl$^-$–M^{2+}, then ClMn$^+$ should be more strongly bound that either ClCr$^+$ or ClFe$^+$. Our experimental data refute this (Table I). Finally, our self-consistent-field calculations, which probably overestimate the ionic contributions to the wave functions, show only 0.2–0.25 electron transferred from M$^+$ to Cl. This is in marked contrast to the 0.6 electron transferred from V to Cl in neutral VCl.

Comparison of Bonding in MH$^+$ and ClM$^+$. Considering the structural simplicity of the hydrogen atom, it is expected that the electronic structure and bonding in transition-metal hydrides and the corresponding ions is as uncomplicated as the structure and bonding in metal-containing diatomics can be. Experimental and theoretical work in the past few years has shown that even the

Table V. M–H$^+$ Bond Dissociation Energies

species	experiment^a (kcal/mol)	theory (kcal/mol)	M$^+$ ground state config
Cr–H$^+$	27.7[31]	24.3[39], 22.5[37]	3d^5
Mn–H$^+$	51.4[31]	39.6[39]	3d^{5}4s^1
Fe–H$^+$	52.8[31]	47.0[39]	3d^{6}4s^1

^{a}Experimental values cited are from recent measurements; previously derived values are referenced but not enumerated in the table.

simple case of the transition-metal hydride molecules is quite complex. The multitude of low-lying electronic states in metal atoms and ions gives transition-metal chemistry some of its richness, but it also gives rise to potential ambiguity in assessing the electronic structure of metal-containing molecules.

A description of the bond in M–H$^+$ is emerging from the productive interplay of experiment and theory (Table V).[31-39] The following salient points have been noted. (1) The hydrogen atom is not hydridic in the literal sense. There is little electron density transferred from M$^+$ to H. This is not surprising in view of the large second ionization potentials of the metals and the low electron affinity of hydrogen (see previous discussion attendant to eq 3). (2) The hydrogen atom uses its singly occupied 1s orbital to bond to an orbital on the metal which is a hybrid of valence s, valence d, and, to a lesser extent, valence p orbitals. (3) The overlap of the hydrogen 1s orbital and the singly occupied hybrid orbital on the metal leads to a covalent, nonpolar, two-electron bond. Given these facts, it has been possible to correlate experimentally measured values of the MH$^+$ bond strength with estimates (derived from atomic spectroscopy data) for the promotion energy (energy required to prepare a bonding electronic configuration on the metal).[40]

After the M–H$^+$ series, the M–X$^+$ (X = halide) series is expected to be the easiest to describe because, in general, the halides are monovalent like hydrogen. This is to be contrasted with cases such as MO$^+$ and other metal chalcogenides, MN$^+$ and other metal pnictides, and MR$^+$ (where, e.g., R = CH$_3$, CH$_2$, CH, and C). Here, the potential for multiple covalent bonds makes analysis much more complicated.

Our results suggest that even the simple case of metal halides is complicated because the halide can bond to the metal with its singly occupied p orbital to make either a convalent σ bond as in the "σ" state or a covalent π bond as in the "π" state. Therefore, the periodic trends in the Cl–M$^+$ bond strengths are not expected to be the same as for the M–H$^+$ bond strengths. Nor are these bond strengths easily correlated with estimates of the promotion energy as is the case for the M–H$^+$.

One ramification of these results is that caution should be exercised when the formalism of oxidation states and electron counting is used—even qualitatively—to describe the bonding and

(31) Elkind, J. L.; Armentrout, P. B. *Typical Transition Metal Hydride Bond Energies: First and Second Row*, work in progress.

(32) Armentrout, P. B.; Beauchamp, J. L. *Chem. Phys.* **1980**, *50*, 37.

(33) Armentrout, P. B.; Halle, L. F.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 6501.

(34) Mandich, M. L.; Halle, L. F.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 4403.

(35) Halle, L. F.; Klein, F. S.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 2543.

(36) Tolbert, M. A.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 8117.

(37) Alvarado-Swaisgood, A. E.; Allison, J.; Harrison, J. F. *J. Phys. Chem.* **1985**, *89*, 2517.

(38) Alvarado-Swaisgood, A. E.; Harrison, J. F. *J. Phys. Chem.* **1985**, *89*, 5198.

(39) Schilling, J. B.; Goddard, W. A., III; Beauchamp, J. L. *J. Am. Chem. Soc.* **1986**, *108*, 582.

(40) Two important effects to consider when determining the energy required to prepare this bonding configuration (the effective promotion energy) are the valence s/valence d splittings and, within a given orbital occupation, the intraatomic spin-recoupling which is required to allow the electron in the hybrid orbital to couple with the hydrogenic electron to form a covalent bonding pair. For example, in order to make a covalent bond in CrH$^+$, not only must some fraction of d^{4}s^1 character be included in the description of the "bonding" Cr$^+$ at the expense of the d^5 Cr$^+$ ground state but also a significant amount of quartet spin coupling must be included at the expense of the sextet coupling of the Cr$^+$ ground state. The procedures involved in this calculation have been previously described in detail.[34]

(30) Mullikan populations are Cl$^{-0.2}$–Fe$^{+1.2}$ and Cl$^{-0.26}$–Mn$^{+1.26}$.

Scheme I

Scheme II
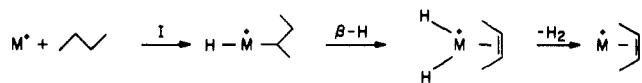
reactivity in these highly acidic, coordinatively unsaturated metal ions. Furthermore, in view of the limited extent of electron transfer from the positive metal ion to even a very electronegative ligand such as chlorine, it is probably erroneous to speak of oxidative additions to these metal ions as being physically oxidative at all. As knowledge of theoretical descriptions combined with experimental measurements of bond strengths of various M^+–L species continues to increase, a greater understanding of these truly unique metal centers will surely be obtained.

Reactivity of $ClCr^+$, $ClMn^+$, and $ClFe^+$ with Small Alkanes. (1) Contrasts with V^+, Cr^+, Mn^+, and Fe^+. The ClM^+ species are vastly different from the corresponding atomic metal cations in their reactivity with small alkanes. For example, whereas Fe^+ reacts exothermically with all alkanes larger than propane to produce an array of products,[8,13,41] $ClFe^+$ is totally unreactive. Even more striking is that whereas Cr^+ displays no reactivity,[41] $ClCr^+$ does react with alkanes larger than propane. In fact the only other instances of exothermic gas-phase Cr^+ reactivity with alkanes involve excited state Cr^+ ions which lie at least 1.5 eV above the ground state.[13,42,43] It is fascinating that the addition of a rather simple ligand to the metal ion has caused the erstwhile inert center to react. As predicated by the discussion of the bonding, $ClCr^+$ displays a different product spectrum from its formally isoelectronic partner, V^+.[44-46] Finally, Mn^{+41} is unreactive. $ClMn^+$ does not appear to activate the alkane C–C or C–H bonds and reacts via simple alkane displacement of the chlorine ligand.

(2) Proposed Reaction Mechanisms. Although many of the details are uncertain or unknown, the currently accepted mechanism for the reaction of gas-phase metal-center cations with saturated alkanes is depicted in Scheme I for the case for C–H activation leading ultimately to dehydrogenation.[2] In the context of this mechanism, the first step (labelled "I") is probably the most critical in determining the reactivity of a particular metal ion. In this step, the C–H bond in the alkane must be cleaved in an exothermic process. This can occur only when the transition metal is then able to form two new strong bonds, one to the hydrogen and another to the alkyl group.[33] Thus, Cr^+ is expected to be unreactive since its high-spin d^5 ground state is unable to form even one ligand bond.[47] Similarly, as our calculations indicate, $ClMn^+$ uses the one energetically "available" electron on Mn^+ to bond to the Cl, leaving the remaining valence electrons in a high-spin d^5 configuration as in Cr^+. Mn^+ itself can form one covalent bond with its unpaired 4s electron, but additional bonds are expected to be weak since they would involve participation of the d^5 electrons. Fe^+ is able to react with alkanes while $ClFe^+$ is not. This suggests that Fe^+ is able to support two strong bonds to covalent ligands, but not three.[48] Note that the formation of covalent bonds is emphasized above as opposed to the usual descriptions involving oxidative additions to the metal center which
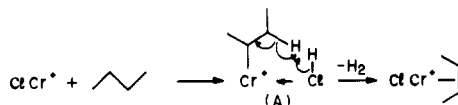
would require ionic bonding between the metal and the ligand. While this does not qualitatively change the mechanism, it appears to be a more accurate picture of the bonding in the various intermediates along the reaction coordinate.

The unusual bonding in $ClCr^+$ affords several mechanisms which are consistent with the observed reactions. The first possibility is that the electrons involved in the Cl–Cr^+ bond do not participate in the reaction and that the remaining d electrons on Cr are available to form the two covalent bonds to start the reaction along the coordinate depicted by the mechanism in Scheme I. Thus, in this limit, $ClCr^+$ has the same number of d electrons as V^+ to form bonds with H and/or alkyl groups. The differences in the reactivity of these two species indicate that they are not equivalent. Overall, V^+ is rather unreactive with alkanes, and small product cross sections are observed. For example, although V^+ is observed to dehydrogenate propane exothermically, the V^+–C_5H_{12} adduct is the major product observed for reaction with neopentane.[45,46] These results indicate that the d^4 electrons on V^+ are sufficiently high spin coupled that the formation of additional bonds to these electrons is energetically unfavorable. A similar situation does not appear to arise for the same d^4 electrons on $ClCr^+$. This may arise because the presence of the π bonding between the $ClCr^+$ modifies the bond strengths of additional ligands.

Another explanation is that the reaction of $ClCr^+$ with alkanes proceeds along an entirely different pathway involving participation of the bonding "π" state. In this alternative mechanism, shown in Scheme II, the initial alkane coordination to the metal center is followed by addition of an alkane C–H bond across the weak $ClCr^+$ π bond to form intermediate A.[49-51] The weakness of this π bond ensures a low barrier for the process. Since the Cr–C bond in A is expected to be quite weak,[31,33] all bonds β to it should be weakened.[52] This facilitates 1,2 elimination of H_2 from A via the pericyclic process shown in Scheme II to generate the observed ionic products. Note that HCl is not lost from A which would leave behind a [H–Cr^+–alkene] product instead of the observed [Cl–Cr^+–alkene] product. The elimination step is very nearly isoenergetic with respect to formation of the bond in either H_2 or HCl (bond strengths are 104 and 103 kcal/mol, respectively). Exclusive loss of H_2 therefore suggests that the Cl–Cr^+ bond is stronger than the Cr^+–H bond. This mechanism appears to be energetically feasible given the thermochemical data that are currently available. Addition of the alkane across the Cl–Cr^+ π bond breaks the weak π bond and the R–H bond ($\sim$95 kcal/mole) and makes an HCl bond ($\sim$103 kcal/mol) plus a Cr^+–R bond ($\sim$37 kcal/mol).[53] Another attractive feature of this mechanism is that it does not require extensive spin recoupling of the remaining d^4 core electrons on Cr^+ along the reaction pathway. The d electron on Cr^+ which bonds to the alkyl group has already been

(41) Halle, L. F.; Armentrout, P. B.; Beauchamp, J. L. *Organometallics* **1982**, *1*, 963.

(42) Halle, L. F.; Armentrout, P. B.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 962.

(43) Reents, W. D., Jr.; Strobel, F.; Freas, R. B., III; Wronka, J.; Ridge, D. P. *J. Phys. Chem.* **1985**, *89*, 5666.

(44) Kappes, M. M.; Staley, R. H., unpublished results.

(45) Aristov, N.; Armentrout, P. B. *J. Am. Chem. Soc.*, in press.

(46) Aristov, N.; Armentrout, P. B., work in progress.

(47) Single bond energies of Cr^+ to H and CH_3 have been measured and are in accordance with the predicted energetic cost of breaking up the half-filled d^5 shell.[33]

(48) The observed exothermic reactivity of FeD^+ with alkanes larger than ethane[11] requires an alternative mechanism to that outlined, e.g., in Scheme I. The L–Fe^+ species (e.g., H–Fe^+) may access a four-centered transition state[49] which can proceed to final products when the bond strength of R–Fe^+ exceeds that of L–Fe^+. This explanation is supported by the results of ion beam studies of the reactions of FeH^+.[10]

(49) Steigerwald, M. L.; Goddard, W. A., III *J. Am. Chem. Soc.* **1984**, *106*, 308.

(50) Upton, T. H.; Rappe', A. K. *J. Am. Chem. Soc.* **1985**, *107*, 1206.

(51) Similar "super radical" behavior may be present for other LM^+ where there is π bonding. For example, a similar mechanism has been proposed for the reactions of FeO^+ which displays an even greater reactivity with alkanes than does Fe^+ itself.[14] $ClFe^+$ does not display similar reactivity which is consistent with our calculations, indicating negligible contribution from π bonding.

(52) It is expected that the Cr–C bond in intermediate A, which should be similar to that in $CrCH_3^+$,[31,33] is weak enough that it looks like an alkyl radical coordinated to an $(HCl)Cr^+$ ion. In this limit the labilization of the bonds β to the bonding carbon is seen as the weaking of bonds β to a radical center. See, for example: Benson, S. W. *Thermochemical Kinetics*: Wiley Interscience: New York, 1976; p 72.

(53) This is only a crude estimate based upon the bond energy known for Cr^+–CH_3.[33]

(54) Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, J. T. *J. Phys. Chem. Ref. Data* **1977**, *6*, Suppl. 1.

spin decoupled from the d^4 core electrons to make the $ClCr^+$ bond. This allows the CrR^+ bond to form without further loss of intraatomic exchange energy. This is in contrast to the mechanism in Scheme I which requires the high-spin d^4 electrons on Cr^+ to decouple in order to form two additional bonds (at the cost of exchange energy) and then recouple following the loss of H_2.

Conclusions

1. The exothermic reactions of $ClCr^+$, $ClMn^+$, and $ClFe^+$ with small alkanes in the gas phase have been measured. $ClFe^+$ is unreactive. The Cl in $ClMn^+$ is displaced by alkanes larger than ethane. $ClCr^+$ activates C–C and C–H bonds of the alkanes leading to $ClCr^+$–alkene products resulting from loss of H_2 or CH_4.

2. The reactivity of $ClCr^+$ is remarkable because Cr^+ is unreactive. This is the first example of chemical activation of an unreactive transition-metal ion in the gas phase.

3. Electronic structure calculations were performed to obtain a description of the bonding in $ClCr^+$, $ClMn^+$, and $ClFe^+$. (a) These calculations indicate that the singly occupied Cl p orbital overlaps the singly occupied metal s orbital to form a covalent

σ bond in $ClMn^+$ and $ClFe^+$. (b) The calculations also indicate that there are two states which are low in energy in $ClCr^+$. One contains a covalent σ bond similar to those in $ClMn^+$ and $ClFe^+$. The other contains not a covalent σ bond but rather a covalent π bond. This finding underscores the complexities of the bonding which is possible for these highly acidic, coordinatively unsaturated transition metal ions.

4. Chemical activation of Cr^+ by the chlorine ligand can be explained by the unusual $Cl–Cr^+$ bond. Addition of a C–H bond *directly* across the covalent bond is proposed as a low-energy reaction pathway for the reaction with alkanes. Addition of the same C–H bond to the chromium atomic ion is known to be so high in energy that it is not observed exothermically.

Dialkoxyethylidene and η²-1,2-Dialkoxyethylene Iron Compounds as C₂ Templates for Generating Acetaldehyde and a Glycolaldehyde Ether

Edward J. Crawford, Thomas W. Bodnar, and Alan R. Cutler*

Contribution from the Department of Chemistry, Rensselaer Polytechnic Institute, Troy, New York 12181. Received November 14, 1985. Revised Manuscript Received July 5, 1986

Abstract: Full details on the preparation and characterization of the α-ethoxy-β-methoxyethylidene Fp **5**, on its irreversible isomerization to the η²-1,2-methoxyethoxyethylene Fp salt **6**, and on its reduction to the α-ethoxy-β-methoxyethyl Fp **17** are presented. Other examples of *cis*-1,2-dialkoxyethylene Fp salts also are synthesized. The dimethoxy example **11** upon hydrolysis gives the α-methoxyformylmethyl Fp complex **14**, whereas reducing it gives the α,β-dimethoxyethyl complex **18**. Both spectroscopically characterized α,β-dialkoxyethyl complexes afford η²-vinyl ether Fp compounds **19** (R = CH_3) and **20** (R = CH_2CH_3) upon treating with $Ph_3C^+PF_6^-$. β-Methoxide abstraction from **18** predominates. Hydrolysis of **19** then gives $FpCH_2CHO$ **15**, which after treating with acid and iodide yields acetaldehyde. The α-methoxyformylmethyl **14**, in turn, gives methoxyacetaldehyde. Thus, coordinated ligand reactions are presented that use the methoxyacetyl ligand on $FpCOCH_2OCH_3$ (**4**) as a C_2 template in selectively incorporating both of these skeletal carbon centers into either acetaldehyde or methoxyacetaldehyde.

Hydroxyacetyl organometallic complexes $MCOCH_2OH$ (**1**) have been suggested as intermediates in the synthesis of C_2 (and possibly larger) oxygenated organic molecules from synthesis gas (CO–H_2 mixtures) and homogeneous transition-metal catalysts.[1] These complexes are believed to hydrogenate their acyl ligands (eq 1) and to generate α,β-dihydroxyethyl complexes **3**. The alkyl **3**, in principle, produces ethylene glycol, or it repeats the sequence (eq 1) and extends the chain.[2] The glycolaldehyde intermediate

(1)
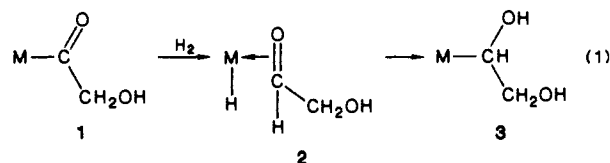
2 envisaged[3] also could serve as a branching point in the overall mechanism (and hence product distribution), since reducing **2**

(1) Hydroxyacetyl intermediates **1** could arise through carbonylating hydroxymethyl complexes MCH_2OH, which are assumed to be present in steady-state amounts as the reduction product of ligated CO. Reviews on homogeneous analogues of Fischer–Tropsch Chemistry: Dombek, B. D. *Adv. Catal.* **1983**, *32*, 325. Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 117. Sneedon, R. P. A. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Ed.; Pergamon Press: New York, 1982; Chapter 50.2. Blackborow, J. R.; Daroda, R. J.; Wilkinson, G. *Coord. Chem. Rev.* **1982**, *43*, 17. Gladysz, J. A. *Adv. Organomet. Chem.* **1982**, *20*, 1. Frohning, C. D. In *New Syntheses with Carbon Monoxide*; Falbe, J., Ed.; Springer-Verlag: Berlin and New York, 1980, Chapter 4. Eisenberg, R.; Hendrickson, D. E. *Adv. Catal.* **1979**, *28*, 79. Muetterties, E. L.; Stein, J. *Chem. Rev.* **1979**, *79*, 479. Masters, C. *Adv. Organomet. Chem.* **1979**, *17*, 61.

(2) This mechanism is often discussed in the context of procuring ethylene glycol from synthesis gas by using homogeneous catalysts: (a) Pruett, R. L. *Ann. N.Y. Acad. Sci.* **1977**, *295*, 239. Pruett, R. L. *Science (Washington, DC)* **1981**, *211*, 11. (b) Dombek, B. D. *J. Am. Chem. Soc.* **1979**, *101*, 6466. (c) Dombek, B. D. *Ibid.* **1980**, *102*, 6855. Dombek, B. D. *J. Organomet. Chem.* **1983**, *250*, 467. Dombek, B. D. *Ann. N.Y. Acad. Sci.* **1983**, *415*, 176. (d) Feder, H. M.; Rathke, J. W. *Ann. N.Y. Acad. Sci.* **1980**, *333*, 45. (e) Fahey, D. R. *J. Am. Chem. Soc.* **1981**, *103*, 136. (f) Keim, W.; Berger, M.; Schlupp, J. *J. Catal.* **1980**, *61*, 359. Keim, W.; Berger, M.; Eisenbeis, A.; Kadelka, J.; Schulpp, J. *J. Mol. Catal.* **1981**, *13*, 95. (g) Knifton, J. F. *J. Am. Chem. Soc.* **1981**, *103*, 3959. Knifton, J. F. *J. Mol. Catal.* **1985**, *30*, 281. (h) Vaughn, G. D.; Gladysz, J. A. *Organometallics* **1984**, *3*, 1596.