

of AgPF_6 (14.2 mg) in CH_3OH (10.5 mL) with $[\text{AuCl}(\text{PPh}_3)]$ (27.8 mg) in acetone (4 mL). The solvent volume was reduced under vacuum, and the product was precipitated with ether (25 mL), washed with pentane (20 mL) at 0 °C, and dried under high vacuum. Anal. Calcd for $\text{C}_{30}\text{H}_{29}\text{AuF}_6\text{N}_2\text{P}_2$: C, 36.6; H, 3.0; N, 2.9. Found: C, 36.3; H, 2.75; N, 2.7%. NMR (-60 °C): ^1H , δ 1.28 [s, $^2J(\text{PtH}) = 68$ Hz, MePt]; ^{31}P , δ 3.9 [s, $^2J(\text{PtP}) = 1250$ Hz, PAuPt].

Reactions of Complex 3a. To a solution of **3a** (6 mg) in acetone (4 mL) was added KCl (2 mg) in water (1 mL). The solvents were evaporated under vacuum and the products identified by NMR: $[\text{PtMe}_2(\text{bpy})]$, ^1H , δ 0.95 [s, $^2J(\text{PtH}) = 86$ Hz, PtMe]; $[\text{AuCl}(\text{PPh}_3)]$, ^{31}P , δ 26.6 [s, PAu]. The reaction of **3a** with PPh_3 to give $[\text{PtMe}_2(\text{bpy})]$ and $[\text{Au}(\text{PPh}_3)_2]\text{NO}_3$ [^{31}P , δ 37.6 (PAu)] was carried out in a similar way.

$[\text{PtMe}_2(\text{bpy})(\text{AgPPh}_3)]\text{BF}_4$ (3d). To a solution of $[\text{PtMe}_2(\text{bpy})]$ (8.0 mg, 0.021 mmol) in acetone- d_6 (0.5 mL) at -70 °C was added slowly a solution of Ph_3P (6.0 mg, 0.023 mmol) and AgBF_4 (4.5 mg, 0.023 mmol) in acetone- d_6 (0.05 mL). A color change from red to yellow was observed. NMR in acetone- d_6 : ^1H (-70 °C), δ 1.13 [d, 6 H, $^2J(\text{PtH}) = 75$, $^3J(\text{AgH}) = 2$ Hz, PtMe]; ^{31}P (-80 °C), δ -0.5 [d \times 2, $^1J(^{107}\text{AgP}) = 606$, $^1J(^{109}\text{AgP}) = 676$ Hz]; ^{195}Pt (-80 °C), δ 475 [d, br, $^1J(\text{AgPt}) = 680$ Hz, average of $^1J(^{107}\text{AgPt})$ and $^1J(^{109}\text{AgPt})$].

When the above solution was allowed to warm to room temperature, a silver mirror was deposited. The solution then contained *fac*- $[\text{PtMe}_3(\text{PPh}_3)(\text{bpy})]^+$ [NMR: ^1H , δ 1.37 [d, $^3J(\text{PH}) = 8$, $^2J(\text{PtH}) = 68$ Hz, MePt trans to bpy], 0.53 [d, $^3J(\text{PH}) = 7.5$, $^2J(\text{PtH}) = 60$ Hz, MePt trans to P]; ^{31}P , δ -8.5 [s, $^1J(\text{PtP}) = 1045$ Hz, PtP] and $[\text{PtMe}(\text{PPh}_3)(\text{bpy})]^+$ [NMR: ^1H , δ 0.80 [d, $^3J(\text{PH}) = 3.5$ Hz, $^2J(\text{PtH}) = 71.5$ Hz, MePt]; ^{31}P , δ 15.0 [s, $^1J(\text{PtP}) = 4340$ Hz, PtP]].

$[\text{PtMe}_2(\text{bpy})]$ with $[\text{AuCl}(\text{SMe}_2)]$. To a solution of $[\text{PtMe}_2(\text{bpy})]$ (8.6 mg, 0.023 mmol) in CD_2Cl_2 (0.3 mL) at -70 °C was added a solution of $[\text{AuCl}(\text{SMe}_2)]$ (8.7 mg, 0.029 mmol) in CD_2Cl_2 (0.3 mL). The ^1H NMR spectrum at -40 °C showed that no reaction had occurred. At -10 °C, a gold mirror was formed and the solution contained equimolar amounts of $[\text{PtClMe}_3(\text{bpy})]$ and $[\text{PtClMe}(\text{bpy})]$, identified by their NMR spectra by comparison with authentic samples. The same products were formed in acetone- d_6 solvent. A similar reaction with excess CuCl in acetone at room temperature gave the same products and copper metal, but in CH_2Cl_2 the known isomers of $[\text{PtMe}_2\text{Cl}(\text{CH}_2\text{Cl})(\text{bpy})]$ and some $[\text{PtMe}_2\text{Cl}_2(\text{bpy})]$ were also formed. Again no PtCu-bonded intermediates were detected.

$[\text{PtMe}_2(\text{bpy})]_2\text{Ag}^+\text{BF}_4^-$ (4). To a solution of $[\text{PtMe}_2(\text{bpy})]$ (71

mg, 0.186 mmol) in acetone (10 mL) at -70 °C was added AgBF_4 (18.4 mg, 0.094 mmol) in acetone (5 mL). A red precipitate formed immediately. After 15 min the solvent was removed and the precipitate was washed with acetone/ether (10 mL, 1:1) at -70 °C and then with ether at 20 °C and dried under vacuum: yield 74 mg; mp 145-152 °C dec. Anal. Calcd for $\text{C}_{24}\text{H}_{28}\text{AgBF}_4\text{N}_4\text{Pt}_2$: C, 30.1; H, 2.95; N, 5.85. Found: C, 30.2; H, 3.2; N, 5.9. NMR in acetone- d_6 : ^1H (-80 °C) δ 0.86 [d, 6 H, $^2J(\text{PtH}) = 65$, $^3J(\text{AgH}) = 4$ Hz, MePt], 7.6-8.6 (m, 8 H, bpy); ^{195}Pt (-80 °C), δ 439 (s, v br, Pt).

Methyl Scrambling Reactions. Two solutions, each containing $[\text{PtMe}_2(\text{bpy})]$ (5.4 mg) and $[\text{Pt}(\text{CD}_3)_2(\text{bpy})]$ (5.4 mg) in CH_2Cl_2 (10 mL), were prepared. To one solution was added AgBF_4 (1.0 mg) in acetone (2 mL) at -78 °C, and the mixture was stirred for 5 min at -78 °C. A solution of NaCl in acetone was added, leading to precipitation of AgCl . The solution was warmed to room temperature, evaporated to dryness, and extracted with CH_2Cl_2 (10 mL) and the CH_2Cl_2 removed to give the product, shown by MS to contain $[\text{PtMe}_2(\text{bpy})]$, $[\text{PtMe}(\text{CD}_3)(\text{bpy})]$, and $[\text{Pt}(\text{CD}_3)_2(\text{bpy})]$ (see text). The second solution, without AgBF_4 , was treated in the same way to serve as a reference.

A solution containing $[\text{Pt}(\text{CD}_3)_2(\text{bpy})]$ (2.7 mg) and $[\text{PtMe}_2(1,10\text{-phenanthroline})]$ (2.6 mg) in acetone- d_6 was prepared. After 2 h the ^1H NMR spectrum gave δ 1.11 [s, $^2J(\text{PtH}) = 85$ Hz] due to $[\text{PtMe}_2(\text{phen})]$ but no resonance at δ 0.95 due to $[\text{PtMe}_2(\text{bpy})]$. Next, AgBF_4 (15 μL , 4×10^{-2} M in acetone) was added, and the NMR spectrum was recorded immediately. A resonance due to CH_3 groups of $[\text{PtMe}_2(\text{bpy})]$ was observed at δ 0.95 [s, $^2J(\text{PtH}) = 86$ Hz], demonstrating methyl for CD_3 scrambling. The experiment shows only the presence of CH_3Pt groups and does not distinguish between $[\text{PtMe}_2(\text{bpy})]$ and $[\text{PtMe}(\text{CD}_3)(\text{bpy})]$.

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Registry No. 1, 52594-52-2; **3a**, 115828-94-9; **3b**, 115936-51-1; **3c**, 115936-52-2; **3d**, 115828-96-1; 4, 115828-98-3; $[\text{Au}(\text{NO}_3)(\text{PPh}_3)]$, 14897-32-6; $[\text{Au}(\text{BF}_4)(\text{PPh}_3)]$, 67215-70-7; $[\text{Au}(\text{PF}_6)(\text{PPh}_3)]$, 83214-85-1; AgPF_6 , 26042-63-7; $[\text{AuCl}(\text{PPh}_3)]$, 14243-64-2; AgBF_4 , 14104-20-2; *fac*- $[\text{PtMe}_3(\text{PPh}_3)(\text{bpy})]^+$, 47756-86-5; $[\text{AuCl}(\text{SMe}_2)]$, 29892-37-3; $[\text{PtClMe}_3(\text{bpy})]$, 38194-03-5; $[\text{PtClMe}(\text{bpy})]$, 50726-77-7; $[\text{PtMe}_2\text{Cl}(\text{CH}_2\text{Cl})(\text{bpy})]$, 115936-53-3; $[\text{PtMe}_2\text{Cl}_2(\text{bpy})]$, 64507-94-4; $[\text{Pt}(\text{CD}_3)_2(\text{bpy})]$, 115828-99-4; $[\text{PtMe}(\text{CD}_3)(\text{bpy})]$, 115829-00-0; $[\text{PtMe}_2(1,10\text{-phenanthroline})]$, 52594-55-5; Au, 7440-57-5; Ag, 7440-22-4; Pt, 7440-06-4; $[\text{Au}(\text{PPh}_3)_2]\text{NO}_3$, 14853-96-4.

Gas-Phase Chemistry of First-Row Transition-Metal- and Metal-Containing Ions with Alkyl Cyanides

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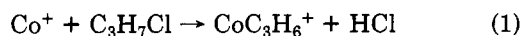
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The gas-phase ion/molecule reactions of first-row transition-metal ions with a series of alkyl cyanides is discussed, with the focus on the chemistry of Co^+ . As the length of the alkyl chain of the nitrile increases, cleavage of C-C bonds far from the functional group is observed, which supports an initial "end-on" interaction with the -CN group. When a single ligand is attached to the metal, the resulting chemistry appears to be very different from that observed for the bare metal ion. The steric nature of the ligand effects is discussed. The observed ion/molecule reactions yield similar results to those suggested by collisional activation studies of transition-metal ion/alkyl cyanide complexes.

I. Introduction

For almost 15 years, reports have appeared in the literature concerning the rich chemistry that transition-metal ions exhibit with organic molecules in the gas phase.¹ Such studies are beginning to provide fundamental insights

into the structure/function relationships of organometallic chemistry. For the prototypical reaction²



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Table I. Reactions of Co⁺ and CoCO⁺ with Alkyl Cyanides

	n								
	1	2	3	(3i)	4	5	6	7	8
Co ⁺ + C _n H _{2n+1} CN	→ CoHCN ⁺ + C ₃ H ₆			0.20					
	→ CoC ₃ H ₆ ⁺ + HCN			0.07					
	→ CoC _n H _{2n+1} CN ⁺	1.0	0.35	0.73	0.26	0.18	0.21	0.22	0.09
	→ CoC _n H _{2n-1} CN ⁺ + H ₂				0.41	0.32	0.11	0.14	0.04
	→ CoC _{n-1} H _{2n-1} CN ⁺ + CH ₂						0.10		
	→ CoC _{n-1} H _{2n-3} CN ⁺ + CH ₄								0.02
	→ CoC _{n-2} H _{2n-3} CN ⁺ + C ₂ H ₄			0.60	0.11	0.38	0.17	0.06	0.05
	→ CoC _{n-2} H _{2n-5} CN ⁺ + C ₂ H ₆						0.07	0.10	0.12
	→ CoC _{n-3} H _{2n-5} CN ⁺ + C ₃ H ₆				0.22		0.34	0.21	0.14
	→ CoC _{n-3} H _{2n-7} CN ⁺ + C ₃ H ₈							0.14	0.18
	→ CoC _{n-4} H _{2n-7} CN ⁺ + C ₄ H ₈					0.12		0.13	0.24
	→ CoC _{n-5} H _{2n-9} CN ⁺ + C ₅ H ₁₀								0.12
	→ CoC _{n-1} H _{2n-2} ⁺ + CH ₃ CN			0.05					
	→ CoCOC _n H _{2n+1} CN ⁺	0.24	0.43	0.85	0.19	0.12		0.13	0.10
CoCO ⁺ + C _n H _{2n+1} CN	→ CoC _n H _{2n+1} CN ⁺ + CO	0.76	0.57	0.15	0.81	0.88	1.0	0.64	0.68
	→ CoC _n H _{2n-1} CN ⁺ + CO + H ₂							0.18	0.22
	→ CoC _{n-1} H _{2n-3} CN ⁺ + CO + CH ₄								0.23
	→ CoC _{n-2} H _{2n-3} CN ⁺ + CO + C ₂ H ₄								0.07
	→ CoC _{n-2} H _{2n-5} CN ⁺ + CO + C ₂ H ₆							0.05	0.16
									0.11

the proposed mechanism for formation of the observed products² involves a sequence of events. A metal insertion into the C-Cl bond is followed by a β-H shift to form the (C₃H₆)Co⁺(HCl) intermediate. This then dissociates in a competitive ligand loss step³⁻⁵ to yield the observed products.

As larger molecules were studied, an additional mechanistic step received attention—the complexation step in which the metal ion and the molecule form an adduct before the “chemistry” (bond cleavage and bond formation) begins. If this initial complex is sufficiently long-lived, preferred geometries of the complex may be an important factor in determining the final product distributions—by determining which bonds in the molecule the metal ion can access.

We have discussed the chain-length effects in the reactions of Co⁺ with alcohols and alkyl halides.⁶ It appears that, if Co⁺ first complexes with the polar group and the chain is sufficiently long, parts of the molecule that are “remote” to the functional group can come into close proximity with the metal ion via 5- and 6-membered rings. These geometries allow for the attack of C-C and C-H bonds far from the functional group. This approach has also been successful in explaining the collisional activation (CA) spectra of Fe⁺(A) complexes, where A is an alkyne⁷ or nitrile,^{8a-d} and may even explain the preference with which transition-metal ions appear to attack skeletal bonds in saturated hydrocarbons.⁹

Consider this first step of reaction 1 in which Co⁺ and propyl chloride form a complex. One might envisage two extremes concerning the interactions that would dominate in determining which geometries would be most favored. One extreme is an electrostatic interaction. If the Co⁺/C₃H₇Cl interaction is dominated by electrostatics, characteristics of the molecule such as its dipole moment, charge distribution, and polarizability would control the situation. The other extreme would require a quantum-

Table II. Some Thermochemical Considerations (kcal/mol)

	X		
	Cl	OH	CN
D(CH ₃ -X) ¹⁵	82	91	117
ΔH(C ₂ H ₅ X → C ₂ H ₄ + HX) ¹⁵	17	11	33
Proton Affinities (PA) of Some Relevant Compounds ²⁴			
L	PA(L), kcal/mol	L	PA(L), kcal/mol
H ₂	101.3	CO	141.9
CH ₄	132.0	HCN	171.4
C ₂ H ₄	162.6	CH ₃ CN	188.4

mechanical description of the complex. This would be the case if dative interactions (Co⁺←:ClR) were dominant. We have recently reported that the metal-ligand bonding in ionic species such as ScCO⁺ and CrCO⁺ is predominantly electrostatic in nature.¹⁰ This has also been suggested^{11,12} for NiCO⁺ and CuCO⁺. One would certainly expect a Dewar-Chatto type bonding scheme in *these* systems, and it does appear to occur in species such as Ni⁰CO.¹¹ However, when the metal is charged, the total bond energy is dominated by the ion-dipole, ion-quadrupole, ion-octopole, and ion-induced dipole interactions. Because of this, we are pursuing electrostatic models for these initially formed metal ion/organic molecule complexes.^{9,13}

In light of the chain-length effects observed for the reactions of metal ions (M⁺) with alcohols, alkyl halides, and alkanes,⁶ one might expect other functional groups to behave differently in their “directing ability” to parts of the molecule far from the functional group. One group of interest is the cyano group, -CN. This work is the first report on bimolecular ion/molecule reactions of transition-metal ions with alkyl cyanides; however, Schwarz et al. have reported a number of experiments in which collisional activation (CA) was performed on complexes generated from ion/molecule reactions involving transition-metal-containing ions and alkyl cyanides.^{8a-d} In their first report,^{8a} a mixture of Fe(CO)₅ and a nitrile, C_nH_{2n+1}CN (n = 1-6), was introduced into the ion source of a mass spectrometer and subjected to electron impact.

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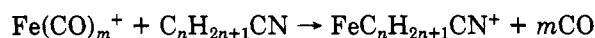
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Table III. Reactions of M⁺ and ML⁺ with C₆H₁₃CN

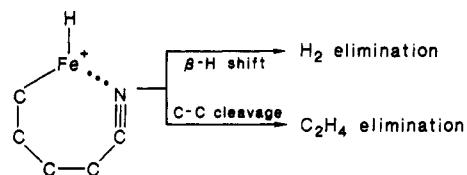
Reactions of M ⁺ with C ₆ H ₁₃ CN		M ⁺				
M ⁺ + C ₆ H ₁₃ CN →	Fe ⁺	Co ⁺	Ni ⁺	Mn ⁺	Cr ⁺	
MC ₆ H ₁₃ CN ⁺	0.08	0.21	0.10	0.80	1.0	
MC ₆ H ₁₁ CN ⁺ + H ₂	0.21	0.11	0.15	0.20		
MC ₆ H ₉ CN ⁺ + 2H ₂	0.11					
MC ₅ H ₁₁ CN ⁺ + CH ₂		0.10				
MC ₄ H ₉ CN ⁺ + C ₂ H ₄	0.38	0.17	0.29			
MC ₄ H ₇ CN ⁺ + C ₂ H ₆		0.07	0.19			
MC ₃ H ₇ CN ⁺ + C ₃ H ₆	0.11	0.34	0.27			
MC ₅ H ₈ ⁺ + CH ₃ CN + H ₂ and/or MC ₃ H ₆ CN ⁺ + C ₃ H ₇	0.11					

Reactions of ML ⁺ with C ₆ H ₁₃ CN		ML ⁺				
ML ⁺ + C ₆ H ₁₃ CN →	FeCO ⁺	CoCO ⁺	NiCO ⁺	NiPF ₃ ⁺	MnCO ⁺	CrCO ⁺
MLC ₆ H ₁₃ CN ⁺		0.13				
MC ₆ H ₁₃ CN ⁺ + L	0.35	0.64	0.33	1.0	1.0	1.0
MC ₆ H ₁₁ CN ⁺ + H ₂ + L	0.65	0.18	0.15			
MC ₄ H ₉ CN ⁺ + C ₂ H ₄ + L			0.39			
MC ₄ H ₇ CN ⁺ + C ₂ H ₆ + L		0.05				
MC ₃ H ₇ CN ⁺ + C ₃ H ₆ + L			0.13			

In their instrument (of "BEB" design), ions with the composition [FeC_nH_{2n+1}CN]⁺ were selected for the collisional activation study. Such ions are formed by ligand-displacement reactions such as



(where $m = 0, 1$ as seen in Tables I and III). These ions undergo 8-kV collisions with helium, and a mass spectrum of the fragment ions thus formed is obtained. Their discussion focused on two dominant processes, in which the selected ion (M⁺), once collisionally activated, forms two species, (M-H₂)⁺ and (M-C₂H₄)⁺. In addition to loss of H₂ and ethylene, loss of other species (e.g., C₂H₅) occurred to yield minor CA products. It was proposed that the ions under study were complexes of Fe⁺ with the intact nitrile and that the metal ion initially complexes with the functional group in an "end-on" fashion. Since labeling studies suggested that H₂ and C₂H₄ elimination occurs from the same part of the alkyl chain, it was proposed that the losses of these two neutrals occur as competing processes, through a common intermediate of the type:



A second paper,^{8b} which highlights the use of fast atom bombardment (FAB) to generate ions such as Fe⁺ from an FeSO₄ target, showed that CA of analogous ions from larger nitriles leads to the loss of C_{3,4}-containing neutrals to a greater extent than loss of ethylene. This was discussed in a subsequent paper,^{8c} in which loss of H₂, alkenes, and alkanes for larger nitriles is noted. For larger nitriles, loss of ethylene and hydrogen could *not* be considered as occurring via a common intermediate, since their origins appear to be different parts of the alkyl chain. Analogous experiments with other metal ions suggest that Co⁺ has a "shorter reach", as reflected in alkane and alkene losses—the results for Co⁺ were more consistent with a conventional metal insertion into C-C bonds/ β -H shift mechanism, while insertion into C-H bonds was presented as the first step in the chemistry of Fe⁺.

Two possible explanations were cited regarding the "shorter reach" observation for Co⁺ chemistry (relative to

Fe⁺). One possibility is that the M⁺-NCR bond length is shorter for M = Co⁺ than for M = Fe⁺. This would affect the intermediate ring sizes that would be accessible. (This explanation correlates with our results¹⁰ on MCO⁺ ions. The bond length order $r(\text{Fe}^+-\text{CO}) > r(\text{Co}^+-\text{CO})$ reflects the fact that the ligand can get closer to Co⁺ because it is smaller than Fe⁺. In general, first-row transition-metal ions such as Co⁺, Ni⁺, and Cr⁺ can get closer to a ligand than can Fe⁺ because the former have only 3d electrons in their valence shell, while Fe⁺ has a 4s electron. The 4s orbital is more spatially extended than the 3d orbitals, resulting in size differences as a function of electronic configuration.) A second possibility may be related to back-bonding, which would affect the rigidity/geometry about the C-C-N...M⁺ portion of the initially formed intermediate. The role of the metal's donor/acceptor ability was pursued further.^{8d} The possible distortion of the N-C-C bond to angles less than 180° due to a change in hybridization that would follow d _{π} - π^* back-bonding was suggested. Results with a third transition-metal ion, Ni⁺, were similar to those presented for Co⁺, leading to the proposal that back-bonding is least important for Fe⁺ of the three metals studied. The back-bonding aspect may be related to metal-ligand bond lengths; those metals that can approach the molecule more closely may provide a situation in which improved orbital overlap for back-bonding occurs.

We present here the products of bimolecular ion/molecule reactions for a variety of transition-metal ions with a series of nitriles. Reactions for several ligated metal ions are also reported. These results provide additional insights into the chemistry of metal centers with polar organic molecules containing one of the more complex ligands of organic chemistry.

II. Experimental Section

All experiments were performed on an ion cyclotron resonance (ICR) mass spectrometer that has been described elsewhere.¹⁴ The instrument is of conventional design and was used in the "drift mode". All samples were degassed by multiple freeze-pump-thaw cycles and were used without further purification.

Metal ions were made by electron impact on the corresponding metal carbonyls. Co(CO)₃NO was used to form Co⁺ and CoCO⁺. Ni(PF₃)₄ was used to generate NiPF₃⁺. The data presented here were derived from ICR spectra obtained by using 1:1 mixtures

(metal compound/organic) at pressures up to 1.0×10^{-5} Torr. From these, ion/molecule reaction products were identified and their precursors determined by using ion cyclotron double-resonance methods. It should be noted that there are ion/molecule reaction products for which unique elemental compositions cannot be assigned. However, we believe that the reactions as listed in Tables I and III represent the chemistry that is occurring; they are self-consistent. Future plans of labeling experiments should provide further information on these complex systems.

III. Results and Discussion

Table I shows the ion/molecule reaction products observed from bimolecular reactions of Co^+ with $\text{C}_n\text{H}_{2n+1}\text{CN}$, for $n = 1-8$ and with isobutyronitrile. Branching ratios indicating the product distributions are shown. A number of observations can be made on these data.

1. Co^+ apparently does not insert into the R-CN bond, except in the case of isobutyronitrile. It is not surprising that this bond would not be attacked as easily as C-OH and C-Cl bonds, since it is the strongest of these bonds.¹⁵ Also, more energy is required to eliminate HCN from RCN than is required to eliminate, e.g., HCl from RCl, as suggested in Table II. Insertion into the C-CN bond in the branched nitrile may be favored since, in contrast to its straight-chain analogue, the branched compound should have a slightly lower C-CN bond energy.¹⁶ Also, the insertion intermediate is expected to be somewhat more stable when the C_3H_7 on the metal is a secondary propyl group.

2. In these reactions for $\text{C}_n\text{H}_{2n+1}\text{CN}$, the chemistry obviously changes as n increases. Dihydrogen elimination (following insertion into C-H bonds) does not occur for $n < 4$; as n varies from 4 to 8, the importance of the H_2 elimination pathway decreases.

3. Attack of the terminal C-C bond is rarely observed and is only a minor product for the largest nitrile studied here.

4. Many of the reaction products appear to be typical for mechanisms in which insertion into C-H and C-C bonds occurs. Insertion into various C-C bonds may lead to an intermediate of the type $\text{R}'\text{-Co}^+\text{-R}''\text{CN}$, where both R' and $\text{R}''\text{CN}$ possess β -H atoms that can shift—thus elimination of ethylene or ethane, propene, or propane, etc. is observed. We can interpret the data based on the metal insertion/ β -H shift mechanism; however, the chemistry could certainly be more complex. We cannot, for example, distinguish between loss of ethane and loss of {ethylene + H_2 }. The patterns of losses of C_nH_{2n} vs $\text{C}_n\text{H}_{2n+2}$ we believe are consistent with a simple mechanism in which the $\text{C}_n\text{H}_{2n+2}$ may be lost as an intact alkane. This has been proposed by Schwarz^{8c} for the chemistry involving Co^+ , while loss of $\text{C}_n\text{H}_{2n+2}$ from Fe^+ reactions may in fact be $\{\text{C}_n\text{H}_{2n} + \text{H}_2\}$ loss.

5. The reactions as listed follow the proton affinity rule,³ consistent with retention of the more strongly bound ligand(s). Proton affinities for molecules representative of those types of species involved in the reactions are given in Table II.

Table III shows, for contrast, the reaction products for a number of other metal ions with a selected cyanide,

(15) Thermodynamic information taken/derived from data in: (a) Franklin, J. L.; Dillard, J. G.; Rosenstock, H. M.; Herron, J. T.; Draxl, K.; Field, F. H. *Natl. Stand. Ref. Data Ser. (U.S., Natl. Bur. Stand.)* 1969, 26. (b) Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, J. T. *J. Phys. Chem. Ref. Data* 1977, 6, Suppl. 1.

(16) Thermochemical data in ref 15a shows this to be the general case, while the difference is not large. If $\Delta D = \{D(\text{i-C}_3\text{H}_7\text{-X}) - D(\text{n-C}_3\text{H}_7\text{-X})\}$, the difference in C-X bond energies, typical values for ΔD are -2 kcal/mol for $\text{X} = \text{OH}$, -4.1 kcal/mol for $\text{X} = \text{NH}_2$, and -3.8 kcal/mol for $\text{X} = \text{NO}_2$.

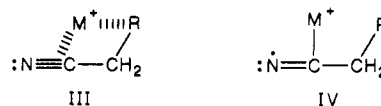
$\text{C}_6\text{H}_{13}\text{CN}$. As is typically observed, the Fe^+ , Co^+ , and Ni^+ ions each form a variety of products, many of which are common to all three metals. In terms of attack of the skeletal bonds, it is interesting to note that ethylene loss dominates for Fe^+ , propene loss dominates for Co^+ , and the two processes occur with approximately equal probabilities for Ni^+ . In contrast to these three metals, Mn^+ and Cr^+ are much less reactive and do not appear to attack C-C bonds.

The $\text{M}^+(\text{RCN})$ Complex. The reactions reported here are best put into perspective by comparison with those observed for other polar organic compounds. First, a few comments are in order on the initial interaction between a transition-metal ion and an alkyl cyanide. Schwarz et al.^{8a} have discussed the side-on (I) and end-on coordination (II) possibilities for the CN group and suggest that the



chemistry is consistent with an end-on description of the complex. (A similar geometry has been proposed for protonated molecules such as protonated HCN.¹⁷) This same conclusion is reached if one considers the $\text{M}^+\text{-RCN}$ complex to be electrostatically bound. If the molecular polarizability is described by the approximate bond-polarizability model, the $\text{C} \equiv \text{N}$ bond is more than twice as polarizable along the bond axis, as it is perpendicular to the internuclear axis.¹⁸ Thus, a greater ion-induced dipole interaction energy would result in the end-on configuration. The charge distribution in an RCN molecule would also favor an end-on complex,¹⁹ since the dipole moments of nitriles are large¹⁹ (e.g., dipole moment of $\text{CH}_3\text{CN} = 3.92$ D), with the nitrogen at the negative end of the dipole. Thus, it appears that the most stable configuration of a transition-metal-ion/alkyl cyanide complex would possess a linear geometry about the C-C-N- M^+ atoms (based on consideration of features of the functional group alone). This suggests another factor that prevents M^+ insertion into the C-CN bond—inaccessibility due to geometric restrictions.

For small nitriles such as acetonitrile, one may expect the end-on geometry (II) to dominate. However, for larger alkyl groups, the substantial polarizability of R may make the geometry shown in III favored, bringing the metal ion to a position where it can form smaller ringed intermediates, not unlike those proposed for saturated polar compounds.^{6,13}



A second possibility is that, upon complexation, sufficient energy is released to essentially promote the nitrile to a triplet state—converting the triple bond to a double bond, with the concurrent formation of an M-C or M-N σ -bond yielding a structure such as IV, again drastically changing the geometric relationship of the metal to the rest of the molecule. We note that, for the HCN molecule, the first triplet state ($^3\text{A}''$) is 4 eV above the ground state.²⁰

(17) See, for example: (a) DeFrees, D. J.; McLean, A. D. *J. Am. Chem. Soc.* 1985, 107, 4350. (b) Pearson, P. K.; Schaefer, H. F., III *Astrophys. J.* 1974, 192, 33.

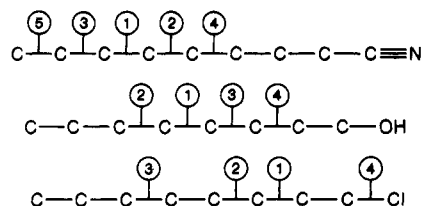
(18) Denbigh, K. G. *Trans. Faraday Soc.* 1940, 36, 936.

(19) Pople, J. A.; Gordon, M. *J. Am. Chem. Soc.* 1967, 89, 4253.

(20) Ditchfield, R.; DelBene, J.; Pople, J. A. *J. Am. Chem. Soc.* 1972, 94, 4806.

If this is typical for alkyl cyanides, the singlet-triplet gap may be prohibitively large for this mechanism to be operative.

The Chemistry of M^+ . To discuss the implications of the possible interaction geometries about the nitrile group, it is useful to consider the skeletal bonds that are attacked and the order of preference for which insertion appears to occur, on the basis of the final product distributions. We have presented previously the approach used to determine the order of preference for insertion,⁶ which is shown here for the $C_8H_{17}X$ compounds ($X = CN, OH, Cl$) for the Co^+ ion. A bond labeled ① is that bond which, upon insertion, leads to the largest fraction of the observed products. The bond whose cleavage leads to the next most significant fraction of the products is labeled ② etc.

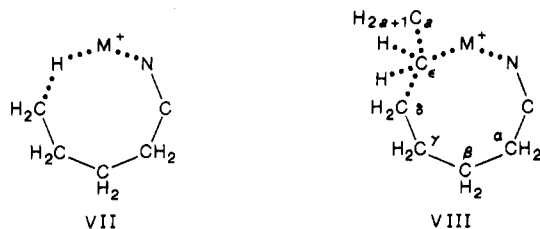


If one compares the products and their distributions for the nitriles and the corresponding alcohols and alkyl halides,⁶ it is apparent that the skeletal bond that is cleaved to a greatest extent (labeled ①) is farthest from the functional group in the nitrile cases, which would be expected from an end-on complexation model. Larger rings would be required to bring atoms of the alkyl group close to the metal. On the other hand, the effect is not that dramatic for the smaller nitriles. In fact, cleavage of many of the skeletal bonds would not be predicted if a fairly constrained end-on complexation is maintained. There are some differences in reactivity unique to the nitriles when compared to other polar compounds but not as dramatic as might be expected from the initial formation of the proposed end-on complex.

The data suggest that, while alkyl halides and alcohols may prefer to interact with parts of the alkyl group via 5- and 6-membered ring intermediates⁶ such as V and VI,



larger nitriles appear to preferentially utilize 8-membered ring intermediates. For example, the fact that H_2 elimination is observed only for nitriles with $n = 4$ or larger may suggest that intermediate VII is important.



Intermediate VIII could explain why certain C-C and C-H bonds are most often cleaved. For example, structure VIII suggests that, via an 8-membered ring, the ϵ -C comes into close proximity to the metal, making the two C-C bonds that contain that ϵ -C candidates for insertion (as well as the ϵ -C-H bonds). Consider the data for $C_8H_{17}CN$ in Table I. Insertion via intermediate VIII into the C-

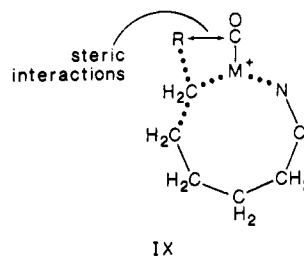
(δ)-C(ϵ) bond leads to loss of butene, which represents 24% of the total products; insertion into the C(ϵ)-C(ζ) bond leads to loss of propene and propane, which represent a total of 32% of the products formed. A similar analysis of the $C_7H_{15}CN$ data also suggests that intermediate VIII can account for a substantial fraction of the products formed (>50%). However, for the shorter chains, attack of C-C bonds closer to the functional group accounts for a substantial fraction of the products. Both VII and VIII involve 8-membered rings. Thus, the end-on geometry is certainly influencing but need not dominate the observed chemistry. Presumably a distribution of cyclic intermediates of various ring sizes may be sampled by the metal, presenting a variety of "choices". Whether attack of a skeletal bond will follow or not depends on additional considerations, such as the subsequent thermodynamics of each insertion process.

Ligand Effects. Tables I and III show the effects of the addition of a carbonyl ligand to the metal center on the products formed, and their distributions. The effects are dramatic. What is typically considered to be a "ligand substitution" process

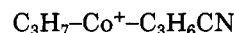


dominates. (For larger reactant molecules, the neutral loss corresponding to 28 daltons could also represent ethylene loss, with retention of the CO ligand—however, the binding energy of ethylene to M^+ appears to be slightly larger than that for CO.^{4,21}) What is most obvious from Table I is that very little chemistry is apparent for $CoCO^+$ except with the largest nitriles. Attack of C-C bonds much farther out on the alkyl chain dominates when a CO is bound to the metal. The order in which skeletal bonds are preferred for insertion is dramatically altered. Only in the octyl cyanide is C-C cleavage evident—and then only involving the two skeletal bonds most distant from the functional group.

We propose two possible scenarios in which the CO could play a role leading to this dramatic change in product distributions for a metal center when this ligand is attached. Both are steric in nature. In the first case, the CO prevents the metal from getting close to the more interior C-C bonds, due to steric effects, shown schematically in IX.



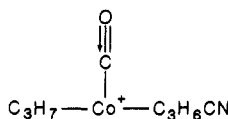
In a second scenario, the CO does not interfere, allowing the metal to "sample" the same preferred complex geometries as it does when it is ligand-free. However, the relative stabilities of the insertion intermediates determine which bonds will actually be attacked. For example, in the case of hexyl cyanide, the Co^+ can apparently attack the central C-C bond to form the insertion intermediate:



This intermediate must, then, be both geometrically and energetically accessible. However, when a CO is present,

(21) Hanratty, M. A.; Beauchamp, J. L.; Illies, A. J.; vanKoppen, P.; Bowers, M. T. *J. Am. Chem. Soc.* 1988, 110, 1.

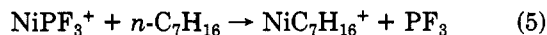
the analogous intermediate



may be less stable due to interactions of the fairly large alkyl groups with the third ligand, CO. The most favored insertion intermediates might then become those in which one of the σ -bonded groups on the metal is relatively small (such as H or CH₃), consistent with the reactions observed for CoCO⁺ with octyl cyanide, and the data for the other MCO⁺ ions in Table III. Similar behavior has been observed in other systems. A dramatic example is in the chemistry of Ni⁺, NiCO⁺, and NiPF₃⁺ with heptane.²² Ni⁺ inserts into a number of skeletal bonds in heptane, resulting in the elimination of C₂-, C₃-, and C₄-containing neutral molecules. Dihydrogen elimination is also observed. In contrast, NiCO⁺ forms two products.

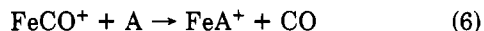


When the ligand is changed to PF₃, no chemistry at all is apparent, except for ligand substitution.



This would be the trend expected for the types of steric effects proposed, since the cone angle²³ for PF₃, which reflects its relative size as a ligand, is larger than that for CO, suggesting that its steric effects would be more dramatic.

Relationship to Prior Work. Two points are to be made here. The first is that results presented here and elsewhere suggest that CA experiments may be difficult to interpret and need not correlate with the analogous bimolecular ion/molecule reactions. The second point is that, while there need not be similarities between these very different experiments, they do provide similar results in the case of Co⁺/RCN chemistry. Schwarz et al.^{8a} suggest that these ions are formed by ion/molecule reactions of FeCO⁺ and Fe(CO)₂⁺, and the mechanism by which the ions are formed has "no implications for the chemistry of mass-selected Fe(RCN)⁺ ions".^{8a} The implication is that an apparent ligand substitution reaction is a literal ligand substitution and that all of the chemistry occurs after the energetic collision with a neutral helium atom. Can it be assumed that reactions such as

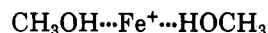


leave A intact? If not, what possible forms could FeA⁺ have?

Such reactions cannot always be considered literally as ligand substitutions. The observation of such a reaction only indicates that all of the atoms of the neutral reactant are now associated with the metal ion. For small molecules such as methanol, it has been suggested² that such processes are not simple ligand displacements. Consider the following:



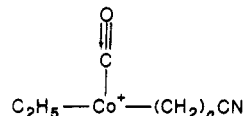
This sequence of reactions has been interpreted as an indication that the product of reaction 7 has the form CH₃-Fe⁺-OH, suggested by the subsequent reaction in which the CH₃ is displaced. Labeling experiments show that the methyl group lost in (8) originates exclusively from the ion, negating the occurrence of (8) through a symmetric intermediate involving two equivalent "methanol ligands" such as



Similar experiments² involving MC₂H₅I⁺ ions formed by reaction of MCO⁺ with ethyl iodide suggest that the ion exists, at least in part, as M(C₂H₄)(HI)⁺. Thus, ligand substitution need not guarantee that the incoming molecule remains intact.

Ions of the type MCO⁺ do react with organic molecules and induce rearrangement to smaller molecules. This is known. Consider the molecule ABC, which can be converted into AC and B by a metal ion. If this also occurs for MCO⁺, the complex that finally dissociates to yield the observed products is M⁺(CO)(AC)(B). The ligands that are lost are those with the lower metal-ligand binding energies. Frequently, the ligand lost is a small alkane—which would be expected since the alkane is a poorer base than the unsaturated molecule left behind, or CO. When MCO⁺ reacts with an alkyl chloride, one may see loss of HCl with retention of CO, again consistent with the relative proton affinities of the molecules involved. However, it would also be appropriate in some cases for M⁺(CO)-(AC)(B) to lose one ligand, CO. Thus, for larger ABC species, the ion current at an *m/z* corresponding to MABC⁺ may contain a collection of structures such as M⁺(AC)(B).

Suppose MCO⁺ reacts with a nitrile and inserts into a C-C bond forming the intermediate



If $n \geq 2$, there are two groups from which a β -H may shift. These two possibilities yield two intermediates, M⁺(CO)(C₂H₄)(H(CH₂)_nCN) and M⁺(CO)(C₂H₆)(C_n-H_{2n-1}CN). On the basis of proton affinities of these species, one might expect the former to lose ethylene or CO, while the latter would preferentially lose the alkane. Thus, the "ligand substitution" species MC_{n+2}H_{2n+5}CN⁺ may take the form M⁺(C₂H₄)(H(CH₂)_nCN) but not M⁺(C₂H₆)(C_nH_{2n-1}CN). This may explain why collisional activation of some [FeRCN]⁺ ions leads to loss of C₂H₄, but not loss of C₂H₆. The discussion of the Fe⁺/CH₃OH system above may explain why CA spectra also show loss of C₂H₅. Thus, the question remains as to whether the energetic collision of a transition-metal-containing ion such as [MRCN]⁺ leads to a "collisional activation" or to a collision-induced dissociation. The collisional activation experiment need not directly parallel the reactivity of the bare metal ion with the neutral substrate, since the ion selected for study need not contain the intact organic molecule. This depends on the chemistry by which the selected ion is formed. If there are, indeed, ligand effects that alter the reactivity of MCO⁺ relative to that for M⁺, then the distribution of the various MRCN⁺ geometries may not resemble the ion/molecule reaction products for M⁺ with RCN. In fact, the combination of the ion/molecule reaction results and the CA data can provide interesting contrasts, and both are useful for understanding the observed chemistry. The minor processes observed in the CA experiments (such as loss of C₂H₅) may provide more

(22) (a) Radecki, B. D. Ph.D. Thesis, Michigan State University, 1985.
 (b) Radecki, B. D.; Allison, J. presented at the 33rd ASMS Conference on Mass Spectrometry and Allied Topics, San Diego, CA, May 1985.
 (23) Tolman, C. A. *Chem. Rev.* 1977, 77, 313.
 (24) Lias, S. G.; Liebman, J. F.; Levin, R. D. J. *Phys. Chem. Ref. Data* 1984, 13, 695-808.

information than the dominant products, since such minor products are not formed in exothermic bimolecular processes.

While such possible complications should be expected, the results of CA^{8c} of [CoRCN]⁺ ions are very similar to the chemistry presented here. There are, of course, differences in product distributions and in the observation of the least abundant products; however, the correlations are substantial. For example, no reaction products were observed for Co⁺ with CH₃CN and C₂H₅CN, and there was no evidence for chemistry between these species in the analogous CA experiments. In the case of C₃H₇CN, loss of C₂H₄ is observed in both experiments; however, no loss of H₂ was observed in the ICR experiments. In the larger nitriles such as C₆H₁₃CN and C₇H₁₅CN, it is interesting to note that loss of methane is reported from the CA experiments, but not in the ICR experiments. There are many reasons why this may occur. The ICR experiment may be less sensitive in detecting minor products. Also, the reaction may be slightly endothermic—but sufficient energy is available in the collisional activation to allow it to occur. However, since the CA results parallel the ion/molecule reaction results presented here, ions of the

type [CoRCN]⁺ formed by ligand substitution processes are apparently simple adduct ions, with the RCN still intact to a great extent.

IV. Conclusions

The -CN group appears to have unique directing abilities in the reactions of transition-metal ions with alkyl nitriles. An end-on geometry of the initially formed complex appears to explain at least some of the reactivity that follows, in which atoms of the alkyl chain far from the functional group are involved. When a CO is attached to the metal ion, the reactivity appears to change dramatically. This may be due to steric interactions at a number of points along the reaction coordinate. Before the "reactivity" of MCO⁺ with alkyl cyanides can be evaluated, further work must be undertaken to determine the structure(s) of the various MRCN⁺ product ions.

Registry No. CH₃CN, 75-05-8; C₂H₅CN, 107-12-0; C₃H₇CN, 109-74-0; C₄H₉CN, 110-59-8; C₅H₁₁CN, 628-73-9; C₆H₁₃CN, 629-08-3; C₇H₁₅CN, 124-12-9; C₈H₁₇CN, 2243-27-8; Fe⁺, 14067-02-8; Co⁺, 16610-75-6; Ni⁺, 14903-34-5; Mn⁺, 14127-69-6; Cr⁺, 14067-03-9; FeCO⁺, 35038-14-3; CoCO⁺, 28963-35-1; NiCO⁺, 71837-05-3; NiPF₃⁺, 115512-35-1; MnCO⁺, 115512-36-2; CrCO⁺, 75474-48-5.

Synthesis of an Unstable Vinyl-Substituted Diiron- μ -Alkenyl Complex. Iron-Iron Bond Cleavage and Rearrangement to an Iron-Substituted Butadiene-Iron Complex

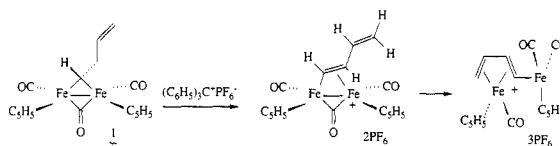
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Received November 19, 1987

Reaction of diiron- μ -alkylidene complex [C₅H₅(CO)Fe]₂(μ -CO)(μ -CHCH₂CH=CH₂) (1) with (C₆H₅)₃C⁺PF₆⁻ led to cleavage of the iron-iron bond and formation of [C₅H₅(CO)Fe] $\{\eta^4$ -1-[C₅H₅(CO)₂Fe]-buta-1,3-diene $\}^+$ PF₆⁻ (3PF₆) in 86% yield by abstraction of a β -hydride and rearrangement of an intermediate μ -alkenyl complex, [C₅H₅(CO)Fe]₂(μ -CO)(μ - η^1, η^2 -(E)-CH=CHCH=CH₂)⁺PF₆⁻ (2PF₆). The related tetraphenylborate salt 3BPh₄ was characterized by single-crystal X-ray crystallography: monoclinic, P2₁/n, a = 9.876 (2) Å, b = 25.703 (6) Å, c = 13.155 (3) Å, β = 90.16 (2)°, and Z = 4. A similar 4-phenyl-substituted butadiene-iron complex, [C₅H₅(CO)Fe] $\{\eta^4$ -1-[C₅H₅(CO)₂Fe]-4-phenylbuta-1,3-diene $\}^+$ BF₄⁻ (12BPh₄), was synthesized by condensation of phenylacetaldehyde with diiron- μ -ethyldiene complex [C₅H₅(CO)Fe]₂(μ -CO)(μ -CCH₃)⁺BF₄⁻ (10) followed by two rearrangements. 12BPh₄ was shown to be in equilibrium with rearrangement intermediate μ -alkenyl complex [C₅H₅(CO)Fe]₂(μ -CO)(μ - η^1, η^2 -(E,E)-CH=CHCH=CHC₆H₅)⁺B(C₆H₅)₄⁻ (11BPh₄).

In the course of our investigations on the extensive chemistry of hydrocarbyl-bridged diiron systems [C₅H₅(CO)Fe]₂(μ -CO)(μ -CR), we reacted diiron- μ -alkylidene complex [C₅H₅(CO)Fe]₂(μ -CO)(μ -CHCH₂CH=CH₂) (1)¹ with (C₆H₅)₃C⁺PF₆⁻. We anticipated that β -hydride abstraction would occur to give vinyl-substituted μ -alkenyl-diiron complex [C₅H₅(CO)Fe]₂(μ -CO)(μ - η^1, η^2 -(E)-CH=CHCH=CH₂)⁺PF₆⁻ (2PF₆) since Knox,² Pettit,³ and we⁴ had prepared diiron- μ -alkenyl complexes by β -hydride abstraction from μ -alkylidene complexes. Other methods are also available for the preparation of μ -alkenyl complexes.⁴⁻⁶



When a solution of 1 was stirred with (C₆H₅)₃C⁺PF₆⁻ in CH₂Cl₂, a bright orange crystalline compound 3PF₆ precipitated from solution over 2 h. ¹H NMR and IR spectroscopy indicated that this new material was not the expected μ -alkenyl complex 2PF₆. No bridging carbonyl stretch was observed in the IR; only terminal carbonyl

(1) Casey, C. P.; Ghodes, M. A.; Meszaros, M. W. *Organometallics* 1986, 5, 196.

(2) Dyke, A. F.; Knox, S. A. R.; Naish, P. J.; Orpen, A. G. *J. Chem. Soc., Chem. Commun.* 1980, 441.

(3) Kao, S. C.; Lu, P. P. Y.; Pettit, R. *Organometallics* 1982, 1, 411.

(4) Casey, C. P.; Marder, S. R.; Adams, B. R. *J. Am. Chem. Soc.* 1985, 107, 7700.

(5) Dyke, A. F.; Knox, S. A. R.; Morris, M. J.; Naish, P. J. *J. Chem. Soc., Dalton Trans.* 1983, 1417.

(6) (a) Casey, C. P.; Meszaros, M. W.; Fagan, P. J.; Bly, R. K.; Colborn, R. E. *J. Am. Chem. Soc.* 1986, 108, 4053. (b) Casey, C. P.; Meszaros, M. W.; Marder, S. R.; Bly, R. K.; Fagan, P. J. *Organometallics* 1986, 5, 1873. (c) Casey, C. P.; Meszaros, M. W.; Colborn, R. E.; Roddick, D. M.; Miles, W. H.; Ghodes, M. A. *Organometallics* 1986, 5, 1879.