CAD spectrum of $C_4H_4^{\bullet+}$ generated from benzene and pyridine at threshold. Bowers and co-workers have recently suggested that the *m/z* 26/27 peak ratio can be approximately equated to the ratio of $\mathbf{1}^{\bullet+}$ and vinylacetylene radical cation in the ion beam.[2c,39] Our ratios of 6.2, 4.2, and 4.1 from **1**, benzene, and pyridine, respectively, suggest a preponderance of $\mathbf{1}^{\bullet+}$, although some linear ions may be present in the spectrum of **1**. It is significant that a greater proportion of *m/z* 26 occurs in the latter spectrum, as would be expected if this ion arises from the dissociation of $\mathbf{1}^{\bullet+}$. Interestingly, Tureček et al. have recently reported that a CAD spectrum of C_4H_4 produced by pyrolysis of 2-chloromethylenecyclopropane showed a *m/z* 26/27 peak ratio of 3.2, as compared with a ratio of 4.2 for $C_4H_4^{\bullet+}$ from benzene.[40] These ratios are in accord with their conclusion that vinylacetylene is the major C_4H_4 product of pyrolysis.

In summary, all currently available evidence points to a value of ca. 281 kcal/mol for $\Delta H_f{}^\circ{}_0$ of the lowest energy structure of $C_4H_4^{\bullet+}$. This, along with *m/z* 26/27 ratios from CAD spectra of $C_4H_4^{\bullet+}$ strongly supports the conclusion that the predominant structure of $C_4H_4^{\bullet+}$ *at threshold* is the methylenecyclopropene radical cation ($\mathbf{1}^{\bullet+}$).

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Registry No. 1, 4095-06-1; $\mathbf{1}^{\bullet+}$, 79105-72-9; **2**, 1120-53-2; **3**, 106-99-0; **5**, 2961-80-0; $\mathbf{5}^{\bullet+}$, 100815-68-7; methylenecyclopropane, 6142-73-0; 2-bromomethylenecyclopropane, 90246-24-5.

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Gas-Phase Organometallic Chemistry of Ni^+, $NiCO^+$, $NiPF_3^+$, and $NiC_5H_5^+$ with Aromatic Compounds

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Abstract: The gas-phase chemistry of Ni^+ and the monoligated nickel cations $NiCO^+$, $NiPF_3^+$, and $NiC_5H_5^+$ with a series of aromatic compounds is reported here. The phenyl group is largely unreactive and does not appear to prohibit the metal ion from interacting with other parts of these molecules. For some phenyl compounds, C_6H_5X, no reaction is observed for Ni^+. When Ni^+ does react, products such as $NiC_6H_4^+$ and $NiC_5H_5^+$ are formed—depending on the chemical composition of the attached functional group (X). Ni^+ reacts with benzyl compounds by insertion into the $C_6H_5CH_2$–X bond, frequently followed by charge transfer to form $C_7H_7^+$ as a product. The Ni^+ ion is observed to decarbonylate aromatic carbonyl compounds. When a single ligand is attached to the Ni^+, changes in the chemistry are observed. In many cases, the reactivity decreases as the size of the ligand increases, suggesting the importance of steric interactions even for these monoligated species. There are some exceptions, where $NiC_5H_5^+$ is most reactive, even though the cyclopentadienyl ligand is the largest. It is suggested that some charge transfer may occur in $NiC_5H_5^+$, resulting in increased positive charge on the metal, leading to increased reactivity.

The gas-phase chemistry of transition-metal ions with organic molecules has been extensively studied in recent years by using ion cyclotron resonance (ICR) and ion beam techniques. The reactions of metal and metal-containing ions have yielded fundamental insights into systems that activate bonds in organic molecules.[1] The organic molecules that have been studied include alkanes and alkenes, as well as a variety of monofunctional compounds such as halogens, alcohols, acids, esters, ketones, ethers, amines, nitro compounds, and nitriles. Some multifunctional compounds have also been studied,[2,3] and in addition, the effect of the basic structural features of linear, branched, and cyclic geometries has been investigated. The major reaction mechanisms have been discussed and reviewed.[1]

For small compounds such as alkyl halides (RX),[4] reaction products appear to be formed via a series of elementary steps. First, a transition-metal ion such as Fe^+ inserts into the C–X bond to yield the intermediate R–Fe^+–X. If the R group is an ethyl group or larger, a β-H shifts to yield a complex of the form $(C_nH_{2n})Fe^+(HX)$. The complex dissociates in a competitive ligand loss step.[3] For more complex functional groups (e.g., carboxylic acids), insertion into bonds within the functional group can also be important.[5,6]

The role of the alkyl group in such reactions has been studied. The extent of branching can affect the overall reactivity. For example, ions such as Co^+ do not appear to insert into the C_3H_7–CN bond in *n*-propyl cyanide, but the insertion does occur for isopropyl cyanide.[7] For straight-chain polar organic compounds, the length of the chain is an important factor in determining the number and types of products. For example, Co^+ reacts with ethanol by inserting into the C–OH bond, which ultimately

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leads to the products CoH_2O^+ and $CoC_2H_4^+$. Insertion into C–C or C–H bonds does not appear to occur.[4] However, the products of the reaction of Co^+ with heptanol[8] suggest that insertion into the C–OH bond is a very minor pathway, compared to attack of C–C and C–H bonds in the alkyl group. Apparently, the metal may initially interact with the functional group; however, parts of the alkyl group that are "remote" to the functional may be brought into close proximity to the metal ion via cyclic intermediates—making a variety of C–C and C–H bonds candidates for insertion by the metal.

While extensive work has been performed on a variety of organic compounds, very little has been reported for aromatic molecules. The phenyl group (cyclo-C_6H_5–) may behave much differently than other R groups. Presented here is a survey of the reactions of Ni^+ with a variety of polar compounds that contain a phenyl group.

Several examples of the reactions of aromatic compounds with gas-phase transition-metal ions have been published. Corderman and Beauchamp[9] reported that $NiCp^+$ (Cp = cyclo-C_5H_5) decarbonylates a variety of carbonyl-containing compounds. For example, decarbonylation was observed for a variety of aldehydes, reactions 1 and 2, including benzaldehyde which forms benzene and CO.

$$NiCp^+ + RC(O)H \rightarrow NiCpCO^+ + RH \qquad (1)$$

$$NiCp^+ + RC(O)H \rightarrow NiCpRH^+ + CO \qquad (2)$$

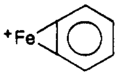
In 1979, Dietz, Chatellier, and Ridge[10] reported that Fe^+ can induce the dehydrohalogenation of halobenzenes, reaction 3. In

$$Fe^+ + C_6H_5X \rightarrow FeC_6H_4^+ + HX \qquad X = F, Cl, Br \qquad (3)$$

the case of iodobenzene, reactions 4 and 5 were observed. Reactions 4 and 5 are analogous to those reported for Fe^+ with methyl iodide. Consideration of the reaction thermodynamics leads to the following proposed bond dissociation energies: $D(Fe^+–C_6H_4) > 66$ kcal/mol; $D(Fe^+–C_6H_5) > 64$ kcal/mol. The $FeC_6H_4^+$ may be an Fe^+–benzyne complex[10] or may take the form of structure I.

$$Fe^+ + C_6H_5I \rightarrow FeC_6H_5^+ + I \quad (85\%) \qquad (4)$$

$$Fe^+ + C_6H_5I \rightarrow FeI^+ + C_6H_5 \quad (15\%) \qquad (5)$$



I

Recently, Chowdhury and Wilkins[11] reported the gas-phase chemistry of Au^+ with benzene, toluene, and ethylbenzene. Most of the products were due to hydride abstraction. (Note: the Au–H bond energy, 71 ± 3 kcal/mol,[11] is greater than the Ni–H bond energy,[12] 60 kcal/mol.) For example, Au^+ reacts with toluene by reaction 6. It was determined that 90% of the ionic product

$$PhCH_3 + Au^+ \rightarrow C_7H_7^+ + AuH \qquad (6)$$

was in the form of the benzyl cation, with the remaining 10% having a tropylium structure. In a reaction such as 6, the hydride stripping need not require insertion into a bond (in particular for closed shell ions such as Au^+, which may not readily insert). This contrasts with reactions such as 7, which presumably proceeds[4]

$$Ni^+ + C_3H_7Cl \rightarrow C_3H_7^+ + NiCl \qquad (7)$$

via an insertion intermediate, $C_3H_7–Ni^+–Cl$. Charge transfer following insertion may occur in (7). While the ionization energy of the isopropyl radical[13] (7.55 eV) is comparable to that for Ni (7.64 eV), the NiCl moiety has a much higher ionization energy, 11.4 eV.[14] Analogous processes may then be expected for compounds of the type $PhCH_2X$, following metal ion insertion into the C–X bond, since the ionization energy of $PhCH_2^{\bullet}$ is 7.3 eV.

Table I. Some Relevant Proton Affinities[a]

molecule	proton affin, kcal/mol	molecule	proton affin, kcal/mol
C_6H_6	181.3	$PhCH_3$	189.3
CH_3CHO	186.6	$PhNO_2$	193.4
C_2H_5OH	188.3	$PhCHO$	200.2
CH_3COOH	190.2	$PhOCH_3$	200.3
$(CH_3)_2O$	192.1	$PhNH_2$	209.5
CH_3NO_2	192.5	$PhCH_2NH_2$	216.8
$(CH_3)_2CO$	196.7		
CH_3NH_2	214.1		

[a] Data obtained from ref 16.

On the basis of our present understanding of gas-phase organometallic ion/molecule reactions, would we expect aromatic compounds to react as their saturated alkyl analogues, or would we expect the phenyl group to dominate the initial interactions? Gas-phase basicity data may provide some insights into this question. It has been noted that relative metal ion (M^+)–ligand interaction energies correlate with the ligand's proton affinity (PA).[15] Larger gas-phase basicities indicate larger M^+–L interactions for simple π- and n-donor bases. Table I lists some relevant proton affinity data.[16] The basicities of the functional groups, as indicated by the PAs of small compounds such as acetaldehyde, ethanol, etc., are larger than that of benzene, suggesting that the presence of a phenyl group need not prohibit M^+ interactions with other parts of an aromatic molecule.

Reported here is the observed chemistry of Ni^+ with a series of aromatic compounds (phenyl and benzyl compounds). These results provide a framework with which the behavior of the phenyl group may be put into perspective, relative to other C_nH_m– groups such as alkyl groups. In most cases, the phenyl group is unreactive, but affects the thermochemistry of the system through inductive effects, as will be discussed.

Also, the reactions of three ligated nickel ions, $NiCO^+$, $NiPF_3^+$, and $NiCp^+$, with the same aromatic compounds are presented. The gas-phase chemistry of ligated transition-metal ions, ML^+, is a rapidly growing field of study;[17] ligands that have been studied include σ-bonded species (H, CH_3), multiply bonded species (e.g., O, S, CH_{0-2}), and others in which the bonding may be more complex (e.g., CO, NO, C_5H_5, Cl, and other metal atoms). Changes in reactivity of the metal ion due to the presence of the various ligands correlate with a number of chemical aspects of the ligands. For the systems studied here, a variety of factors could contribute to the changes in the chemistry of Ni^+ that are observed when a ligand is attached; we focus here on the possible influence of steric factors.

Experimental Section

All experiments were performed on an ion cyclotron resonance (ICR) mass spectrometer of conventional design which was constructed at Michigan State University and has been described elsewhere.[18] Only

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Table II. Reactions of Ni^+ with Aromatic Compounds: $Ni^+ + PhX \rightarrow$ Products

X	products	$D(Ph-X)$[a]	$D(PhCH_2-R)$[a]	relev thermochem, ΔH[a]
		Group 1		
H	no reactn obsd	104		$PhH \rightarrow C_6H_4 + H_2$, 80
Cl	no reactn obsd	88		$PhCl \rightarrow C_6H_4 + HCl$, 65
Br	$NiC_6H_4^+ + HBr$	75		$PhBr \rightarrow C_6H_4 + HBr$, 67
I	$NiC_6H_4^+ + HI$ (45%) $NiC_6H_5^+ + I$ (55%)	61		$PhI \rightarrow C_6H_4 + HI$, 57
CN	no reactn obsd	119		$PhCN \rightarrow C_6H_4 + HCN$, 79
OH	no reactn obsd	104	*b*	$PhOH \rightarrow C_6H_4 + H_2O$, 65
OCH_3	$NiPhH^+ + CH_2O$	88	*c*	$PhOCH_3 \rightarrow PhH + CH_2O$, 8 $PhOCH_3 \rightarrow C_6H_4 + CH_3OH$, 69
NH_2	no reacn obsd	88	*d*	$PhNH_2 \rightarrow C_6H_4 + NH_3$, 64
NO_2	$NiC_5H_5^+ + CO + NO$ (84%) $NiC_6H_5O^+ + NO$ (16%)	65		$PhNO_2 \rightarrow C_5H_5 + CO + NO$, 41 $PhNO_2 \rightarrow C_6H_5O + NO$, 18
		Group 2		
CH_2H	no reactn obsd	93	78	$PhCH_3 \rightarrow C_6H_4 + CH_4$, 70
CH_2Cl	$C_7H_7^+ + NiCl$	94	60	implication: $D(Ni-Cl) > 56$
CH_2Br	$C_7H_7^+ + NiBr$	99	45	$PhCH_2Br \rightarrow C_6H_4 + CH_3Br$, 73 implication: $D(Ni-Br) > 42$
CH_2OH	$C_7H_7^+ + NiOH$ (75%) $NiPhCHO^+ + H_2$ (25%)	91	72	implication: $D(Ni-OH) > 72$ $PhCH_2OH \rightarrow PhCHO + H_2$, 15 $PhCH_2OH \rightarrow PhH + CH_2O$, 17
CH_2NH_2	$NiPhCHNH^+ + H_2$	89	59	
CH_2CH_3	$NiPhCHCH_2^+ + H_2$	90	63	$PhC_2H_5 \rightarrow PhCHCH_2 + H_2$, 30 $PhC_2H_5 \rightarrow C_6H_4 + C_2H_6$, 73
$CH(OH)CH_3$	$NiPhCH_3^+ + CH_2O$ (69%) $NiPhCHCH_2^+ + H_2O$ (31%)	88	81	$PhCHOHCH_3 \rightarrow PhCH_3 + CH_2O$, 18 $PhCHOHCH_3 \rightarrow PhC_2H_3 + H_2O$, 13
$(CH_2)_3CH_3$	$NiPhCH_3^+ + C_3H_6$	94	63	$PhBu \rightarrow PhCH_3 + C_3H_6$, 20 $PhBu \rightarrow PhH + C_4H_8$, 23 $PhBu \rightarrow PhC_2H_5 + C_2H_4$, 23
c-C_6H_5	no reactn obsd	105		$Ph_2 \rightarrow C_6H_4 + PhH$, 80

[a] All thermochemical information in kilocalories per mole, derived from data in ref 21. [b] $D(PhO-H) = 87$ kcal/mol. [c] $D(PhO-CH_3) = 60$ kcal/mol. [d] $D(PhNH-H) = 82$ kcal/mol.

Table III. Reactions of Ni^+ with Aromatic Carbonyl Compounds: $Ni^+ + PhX \rightarrow$ Products

X	products	$D(Ph-X)$	$D(PhC(O)-R)$	relev thermochem, ΔH
C(O)H	$NiPhH^+ + CO$	78	89	$PhCHO \rightarrow PhH + CO$, 4 $PhCHO \rightarrow C_6H_4 + CH_2O$, 82
$C(O)CH_3$	$NiPhCH_3^+ + CO$	91	82	$PhCOCH_3 \rightarrow PhCH_3 + CO$, 9
C(O)OH	$NiPhOH^+ + CO$	105	108	$PhCOOH \rightarrow PhOH + CO$, 23 $PhCOOH \rightarrow PhH + CO_2$, −2
$C(O)OCH_3$	$NiPhOCH_3^+ + CO$	103	97	$PhCO_2CH_3 \rightarrow PhOCH_3 + CO$, 29 $PhCO_2CH_3 \rightarrow PhCH_3 + CO_2$, −10
C(O)Ph	$Ni(Ph)_2^+ + CO$	86	86	$PhCOPh \rightarrow Ph_2 + CO$, 1 $PhCOPh \rightarrow C_6H_4 + PhCHO$, 77
C(O)Cl	no reactn obsd	91	84	$PhCOCl \rightarrow PhCl + CO$, 15
$CH_2C(O)H$	$NiPhCH_3^+ + CO$	89	*a*	$PhCH_2CHO \rightarrow PhCH_3 + CO$, 2

[a] $D(PhCH_2-CHO) = 50$ kcal/mol; $D(PhCH_2C(O)-H) = 86$ kcal/mol.

two modifications to the system have been made. First, the three-section, 6.25 in. long ICR cell has been modified from a square to rectangular cross-section (0.5 in. × 0.75 in.). All experiments were performed in drift mode, with continuous electron ionization. The second modification is that mass spectra are now obtained with a frequency-swept detector that was designed, built, and installed by Dr. John Wronka and has been described elsewhere.[19] Data were obtained by scanning the frequency-swept detector over the range of frequencies necessary to produce a spectrum, with the magnetic field of the Varian V-7800 electromagnet held constant at 16 kG. The aromatic compound and organometallic compound were admitted to the cell in approximately a 1:1 ratio, to a total pressure of 6×10^{-6} Torr. Typically, 11 mass spectra were signal averaged to improve the signal-to-noise ratio. Data were collected with a MacADIOS data acquisition system (GW Instruments, Cambridge, MA) using a MacIntosh Plus computer. The data acquisition program was written in Microsoft BASIC. After a single-resonance mass spectrum was acquired, a second, fixed-frequency oscillator (tuned to the frequency of a reactant ion) is turned on. The irradiated ion is thus ejected from the source region of the cell, and another mass spectrum of the reaction mixture is acquired. Any ions in the spectrum that were products resulting from the reaction of the irradiated ion would not appear in the second spectrum. The spectrum acquired with the double-resonance oscillator on is then subtracted from that obtained with the double-resonance oscillator off. This difference spectrum consists of all ion/molecule reaction products of the irradiated ion.[20] Double-resonance spectra were obtained for all ions of interest in this way.

All chemicals used in this work were high-purity commercial samples which were used as supplied, except for the liquid samples which were subjected to multiple freeze–pump–thaw cycles to remove noncondensable gases. Butylbenzene, benzyl bromide, benzyl chloride, benzylamine, and phenylacetaldehyde were obtained from Aldrich Chemical Co. Benzonitrile, acetophenone, phenol, and benzoyl chloride were obtained from Baker Chemical Co. Bromobenzene, chlorobenzene, nitrobenzene, benzaldehyde, benzoic acid, and benzyl alcohol were obtained from Fisher Scientific. Benzene and benzophenone were obtained from E. M. Science. Methylbenzyl alcohol was obtained from Eastman Organic Chemicals. Iodobenzene was obtained from Chem Service. Toluene, analine, anisole, and ethylbenzene was obtained from Matheson, Coleman, and Bell. Nickel tetracarbonyl and tetrakis(trifluorophosphine)nickel were obtained from Alfa Inorganics. Cyclopentadienylnickel nitrosyl was obtained from Strem Chemicals.

Results and Discussion

The compounds that have been studied are divided into three groups. The reactions of Ni^+ with the phenyl and benzyl compounds are listed in Table II. Table III contains the results for

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aromatic carbonyl compounds. Both tables contain a variety of thermochemical data[21] that are useful in understanding the observed chemistry.

We will first consider the reactant molecules labeled as group 1 in Table II, the simple Ph–X molecules. Similar to the reactions reported[10] for Fe^+, we do observe the formation of an $M^+C_6H_4$ product in some cases:

$$Ni^+ + C_6H_5X \rightarrow NiC_6H_4^+ + HX \qquad X = Br, I \quad (8)$$

To form the HX product, a C–X and a C–H bond must be cleaved. Presumably the reaction proceeds by initial insertion into the C–X bond, rather than into the C–H bond, since the former is weaker. The reaction is not observed when X = H, Cl, CN, OH, NH_2, OCH_3, and NO_2. The X = OCH_3 and NO_2 cases will be discussed separately. In general, the reaction analogous to (8) is not observed when the Ph–X bond is strong and when $\Delta H_{rxn}(PhX \rightarrow C_6H_4 + HX)$ is relatively high. When this reaction product is not observed, it may be because the initial insertion is thermodynamically prohibited, or that the overall reaction is endothermic. In the case of $PhNH_2$ the barrier may be in the insertion step, since Ni^+ has not been observed to insert into the C–N bond of primary amines.[22] Since the overall reaction for X = Cl would be exothermic (based on the energetics of the process for X = Br), we may conclude that the initial insertion does not occur. We note that, in the context of typical gas-phase organometallic ion/molecule reactions that have been observed, reaction 8 is certainly unusual. In reaction 9, 19 kcal/mol is required to convert ethyl bromide to

$$Ni^+ + C_2H_5Br \rightarrow NiC_2H_4^+ + HBr \qquad (9)$$

ethylene and HBr; thus the reaction will be exothermic if the Ni^+–ethylene bond is stronger than 19 kcal/mol, which it surely is. In contrast, 67 kcal/mol is required to convert PhBr to benzyne and HBr. The reaction is observed only because the binding energy in the $NiC_6H_4^+$ product is greater than 67 kcal/mol. This substantial bond energy may reflect σ-(M–C) bond formation in the product.

Very different reactions are observed for $PhOCH_3$ and $PhNO_2$. In the case of $PhOCH_3$, insertion into the Ph–O bond appears to occur, to give the $Ph–Ni^+–OCH_3$ intermediate. This is the first case where insertion leads to two groups on the metal that possess β-H atoms that can shift. Since the products {benzene and formaldehyde} are more stable than {benzyne and methanol} by 61 kcal/mol (and the difference in binding energies of benzene and benzyne to Ni^+ is small compared to this number), the lower energy pathway available here is apparently selected, and the shift of an H atom *from* the methoxy group dominates the chemistry.

The reactions of $PhNO_2$ are very different from the other reactions reported; however, nitroalkanes also exhibit chemistry with transition-metal ions that is much different than that observed for alcohols and alkyl halides. In 1984, Cassady, Freiser, McElvany, and Allison reported the reactions of Co^+ with a series of nitroalkanes.[6] In addition to reactions that proceed via insertion into the $C–NO_2$, C–H, and C–C bonds, additional intermediates were apparently formed such as $RO–Co^+–NO$. Mechanisms were suggested that would allow for access of such an intermediate.[6] In light of this, it is not surprising that NO elimination from $PhNO_2$ was observed. However, the major product is $C_5H_5Ni^+$, with loss of NO and CO. We propose that the products are formed in the sequence shown in reaction 10. We note that the C_6H_5O

$$Ni^+ + PhNO_2 \rightarrow PhO\text{-}Ni^+\text{-}NO \xrightarrow{-NO} PhO\text{-}Ni^+ \xrightarrow{-CO} C_5H_5Ni^+ \quad (10)$$

group has a similar skeletal structure to cyclohexanone. The energy required to convert $C_6H_5O^\bullet$ to $C_5H_5^\bullet$ and CO, 23.2 kcal/mol, is similar to that required to decarbonylate cyclohexanone to C_5H_{10} and CO (this value varies from 22.7 to 9.2 kcal/mol, depending on whether the C_5H_{10} is 1-pentene or cyclopentane).

Finally we note that, for X = OH, OCH_3, and NH_2, the possibility exists for insertion into bonds in the functional group (as is observed for $PhNO_2$). While an insertion process such as reaction 11 for phenol may occur, there is no β-H available to

$$PhOH + Ni^+ \rightarrow PhO\text{-}Ni^+\text{-}H \qquad (11)$$

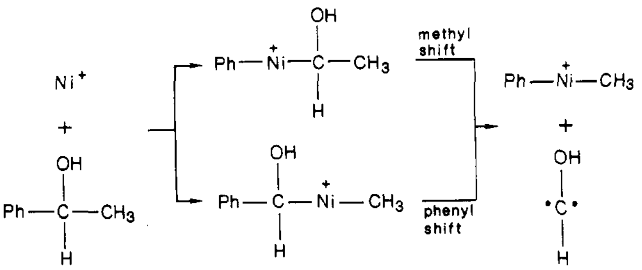
shift, and the only option for this intermediate may be to convert back into reactants.

The discussion will now move to the molecules in group 2 of Table II, the benzyl compounds. In the chemistry with these molecules, insertion into the Ph–X bond is not observed, but rather insertion into the $PhCH_2$–R bond dominates, reflecting the relative weakness of this bond. This is graphically seen in variations of the C–C bond energies in *n*-butylbenzene. The Ph–C bond is more than 30 kcal/mol stronger than the $PhCH_2$–C bond! This correlates with the observation that only loss of propene is observed, although when Ni^+ reacts with *n*-butane, ethane loss and H_2 loss is observed. For benzyl chloride, benzyl bromide, and benzyl alcohol, the only or major product is $C_7H_7^+$. (Thermodynamic discussions[21] will assume that the product is the benzyl cation.) As indicated in the introduction, such reactions are reasonable since the relative ionization energies predict charge transfer to the C_7H_7 moiety, and the strength of the bond in the neutral that is formed is substantial. Listed in Table II are the lower limits on various Ni–X bonds that are implied by assuming that the observed reactions are exothermic or thermoneutral. These are consistent with reported bond energies:[23] D(Ni–Cl) = 88 kcal/mol, D(Ni–Br) = 85 kcal/mol. Also, the relatively weak Ni–H bond,[12] 60 kcal/mol, would make the analogous reaction endothermic for toluene.

When X in Ph–X has at least two skeletal atoms, and both have one or more H atoms on them, H_2 elimination is observed. This suggests that a site of unsaturation is formed in the X group—i.e., ethyl benzene is converted to styrene, benzyl alcohol becomes benzaldehyde, etc. Presumably, the benzyl C–H bond is the initial site of insertion in these cases.

Unexpected products are observed in the case of methylbenzyl alcohol. Water loss is observed, as is typical for aliphatic alcohols, indicative of insertion into the C–OH bond. An unexpected process is elimination of formaldehyde. One could conceive of elimination of CH_2O via either an initial insertion into the Ph–C bond or the $C–CH_3$ bond, as shown in Scheme I.

Scheme I



Unfortunately, the possible insertions shown, followed by a methyl or phenyl shift, yield a diradical, not formaldehyde. An alternative mechanism would involve loss of H_2 first, followed by loss of CO. It has been reported that Ni^+ will induce the elimination of H_2 from alcohols, presumably via insertion into the O–H bond. More importantly, we report it here for benzyl alcohol. Elimination of H_2 yields the corresponding carbonyl compound as $Ni(PhC(O)CH_3)^+$. As will be discussed shortly (Table III), Ni^+ can decarbonylate acetophenone—thus we suggest a two-step pathway, with the neutral product(s) being {H_2 + CO}, not CH_2O.

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[21] Thermodynamic data were taken and derived from the following sources: (a) Reference 14. (b) Reference 13. (c) Weast, R. C.; Astle, M. J., Eds. *Handbook of Chemistry and Physics*; CRC Publishing Co.: Boca Raton, FL, 1983. (d) Rosenstock, H. M.; Larkins, J. T.; Walker, J. A. *Int. J. Mass Spectrom. Ion Phys.* **1973**, *11*, 309. In cases where no data were available, heats of fomration were estimated from group equivalent tables given in ref 14.

[22] Babinec, S. J.; Allison, J. *J. Am. Chem. Soc.* **1984**, *106*, 7718.

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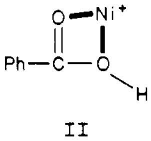
This is also supported by the NiL^+ reactions that will be discussed in following sections.

The reactions of Ni^+ with a series of aromatic carbonyl compounds are listed in Table III. For all of the compounds except benzoyl chloride, decarbonylation is observed. A number of reports have appeared concerning the chemistry of transition-metal ions with carbonyl compounds.[5,24,25] The 1976 Corderman and Beauchamp publication was cited earlier.[9] It is interesting to note that, while $CpNi^+$ was observed to decarbonylate molecules such as CH_3CHO, the analogous reaction was not observed for acetyl chloride and bromide.[9] Freiser et al.[24,26] have studied the chemistry of Cu^+ and Fe^+ with ketones. Also, cyclic ketones were used in a number of publications since Fe^+ appears to form a metallacycle upon decarbonylation.[24,25,27,28] In 1984, Halle, Crowe, Armentrout, and Beauchamp[25] reported the chemistry of M^+ with several ketones and aldehydes. They suggest that, for ketones, $R_1C(O)R_2$, transition-metal ions appear to insert into both R_i–C bonds. However, in molecules such as aldehydes, insertion into the C–CO bond is favored over insertion into the H–CO bond as an initial mechanistic step.

We note that reactions similar to reaction 8 for carbonyl compounds, reaction 12, are not observed. Relatively large amounts of energy are required. For the above reaction to be exothermic, the Ni^+–C_6H_4 bond energy would have to be greater than 82 kcal/mol. Thus, such pathways are thermodynamically prohibited in these compounds. In comparison, decarbonylation requires little energy. We also note that, for benzoic acid and methyl benzoate, CO_2 elimination is a thermodynamically favored process, but does not occur. For aliphatic organic acids, CO_2 elimination is not observed,[5] so failure to observe the reaction is not related to the presence of the aromatic group here. Consider the case of benzoic acid. The decarbonylation may occur via the PhC(O)–Ni^+–OH intermediate, and would require a phenyl shift. If insertion lead to an intermediate of the form Ph–Ni^+–COOH, the geometry about the acid group, due to the sp^2 hybridization of the carbonyl C may place the H too far from the metal for a H shift to occur. Thus, CO_2 elimination may be a mechanistically inaccessible process. However, an OH shift may occur, again leading to decarbonylation.

$$Ni^+ + Ph\text{–}C(O)H \rightarrow NiC_6H_4^+ + CH_2O \qquad (12)$$

In decarbonylation reactions, when both bonds to the carbonyl group are cleaved, it is difficult to suggest whether one bond is attacked preferentially in the initial step. The bond energies in Table III suggest that either would be possible. In the case of benzoic acid, insertion into the C–OH bond may be favored, due to preferred initial interactions such as those shown in structure II. In the case of phenylacetaldehyde, $PhCH_2C(O)H$, the very weak $PhCH_2$–C bond is presumably the site of attack to form $PhCH_2$–Ni^+–C(O)H; a H shift leads to decarbonylation.



II

The results presented in Tables II and III show fairly clearly how the presence of a phenyl group can influence these gas-phase ion/molecule reactions. In most cases, it behaves as an unreactive "terminal" group such as H– or CH_3–. Actually, the bond energies place it between the two, e.g., $D(H\text{–}CH_3) > D(Ph\text{–}CH_3) > D(CH_3\text{–}CH_3)$. While an H can be removed from a phenyl group such as in the Ph–I reaction, this certainly does not suggest that phenyl behaves as an alkyl group such as an ethyl group. In fact the energy required to eliminate HI from methyl iodide is closer to that for Ph–I than it is for C_2H_5I. What we have seen as the major influence of the phenyl group is in its inductive effects, substantially weakening neighboring bonds—as seen in the benzyl compounds. We suggest that this effect may be very useful. Since the phenyl ring does not hamper access of the metal ion to other parts of the molecule, one may be able to add a phenyl group to various positions on an alkyl chain, create "unusually" weak bonds, and determine how such thermodynamic variations of the molecule affect the chemical reactivity.

The Gas-Phase Chemistry of NiL^+ (L = CO, PF_3, Cp) with Aromatic Compounds. The observed chemistry of $NiCO^+$, $NiPF_3^+$, and $NiCp^+$ with the aromatic compounds that are the focus of this work is summarized in Table IV. First, a few comments are in order on these ligands and how their presence may affect the chemistry of the metal ion in these gas-phase reactions.

$NiCO^+$. Of the ligands studied in such gas-phase ion/molecule reactions to date, CO has been among the most popular, since volatile transition-metal carbonyl compounds are readily accessible for mass spectrometric studies.[1,4,15,29] Recent theoretical calculations suggest that, while the bonding in neutral MCO species (where M is a first row transition metal) may be described by a Dewar–Chatt-type interaction, this is not the case for the analogous cation. In MCO^+ the metal–ligand bonding is essentially electrostatic in nature.[30,31] Thus, the electronic structure of the metal in MCO^+ is essentially the same as that in the bare metal ion. We have recently discussed the chemistry of MCO^+ ions;[30] in general they react very similarly to M^+. There are some cases in which the CO can become involved in the chemistry; that is, MCO^+ can react with a molecule AB via intermediates such as A–M^+–C(O)–B. However, the CO is usually simply a spectator, having little effect on the chemistry. Recent work suggests that $D(Ni^+\text{–}CO)$ is approximately 25–30 kcal/mol.[30] While CO has an appreciable electron affinity[32] [EA(CO) = 31.6 kcal/mol], little charge transfer occurs, i.e., the charge on the nickel atom is +1.0.

$NiPF_3^+$. Little has been done to date in the gas phase with the PF_3 ligand. Reaction 13 has been observed,[15c] which indicates

$$CoCO^+ + PH_3 \rightarrow CoPH_3^+ + CO \qquad (13)$$

that PH_3 is more strongly bound than CO to Co^+. If, as has been suggested, the proton affinity of simple ligands reflect their relative binding energies to transition-metal ions, PF_3 would be more weakly bound than PH_3 [PA(PF_3), 166.5 kcal/mol < PA(PH_3), 188.6 kcal/mol].[16] PF_3 has a negative electron affinity, so charge transfer would lead to dissociation. Ligand substitution processes such as reaction 14 suggest that PF_3 exists as an intact ligand,

$$NiPF_3^+ + PhX \rightarrow NiPhX^+ + PF_3 \qquad (14)$$

as opposed to a structure such as F–Ni^+–PF_2. From appearance potential measurements[33] on the ions derived from electron ionization of $Ni(PF_3)_4$, it has been suggested that $\Delta H_f(NiPF_3^+)$ = 35 kcal/mol. Based on $\Delta H_f(Ni^+)$ = 279 kcal/mol[14] and $\Delta H_f(PF_3)$ = –219.6 kcal/mol,[14] this would lead to a bond strength of $D(Ni^+\text{–}PF_3)$ = 24.6 kcal/mol. With this information it is difficult to decide whether PF_3 would be expected to be more or less strongly bound to Ni^+ than is CO. To order the relative metal–ligand binding energies, we studied the ion/molecule reactions in a mixture of $Ni(CO)_4$ and PF_3. Reaction 15 was observed. We

$$NiCO^+ + PF_3 \rightarrow NiPF_3^+ + CO \qquad (15)$$

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(24) Burnier, R. C.; Byrd, G. D.; Freiser, B. S. *J. Am. Chem. Soc.* **1981**, *103*, 4360.

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(26) Burnier, R. C.; Byrd, G. D.; Freiser, B. S. *Anal. Chem.* **1980**, *52*, 1641.

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Table IV. Reactions of Monoligated Ni^+ with Aromatic Compounds: $NiL^+ + P$ (Parent Molecule) $\rightarrow$ Products

P	products (with NiL^+ =)		
	$NiCO^+$	$NiPF_3^+$	$NiCp^+$
PhH	$NiP^+ + L$	$NiP^+ + L$	$NiLP^+$
PhCl	$NiP^+ + L$	$NiP^+ + L$	$NiLC_6H_4^+ + HCl$
PhBr	$NiP^+ + L$	$NiP^+ + L$	$NiLC_6H_4^+ + HBr$
PhI	$NiP^+ + L$	no reactn	$NiLC_6H_4^+ + HI$
PhCN	$NiP^+ + L$	$NiP^+ + L$	no reactn
PhOH	$NiP^+ + L$	$NiP^+ + L$	no reactn
$PhOCH_3$	$NiPhH^+ + CH_2O + L$ (17%) $NiP^+ + L$ (60%) $NiLP^+$ (23%)	$NiP^+ + L$	$NiLP^+$
$PhNH_2$	$NiP^+ + L$	$NiP^+ + L$	no reactn
$PhNO_2$	$NiP^+ + L$ (72%) $NiLP^+$ (28%)	$NiP^+ + L$	$NiLP^+$
$PhCH_2H$	$NiP^+ + L$	$NiP^+ + L$	$NiLP^+$
$PhCH_2Cl$	no reactn	$C_7H_7^+ + NiCl(L)$	$C_7H_7^+ + NiCl(L)$
$PhCH_2Br$	$C_7H_7^+ + NiBr(L)$	$C_7H_7^+ + NiBr(L)$ (80%) $NiP^+ + L$ (20%)	no reactn
$PhCH_2OH$	$NiPhCHO^+ + H_2 + L$ (37%) $NiP^+ + L$ (63%)	$NiPhCHO^+ + H_2 + L$ (22%) $NiP^+ + L$ (78%)	no reactn
$PhCH_2NH_2$	$NiPhCHNH^+ + H_2 + L$ (68%) $NiP^+ + L$ (32%)	$NiPhCHNH^+ + H_2 + L$ (31%) $NiP^+ + L$ (69%)	$NiLPhCHNH^+ + H_2$ (58%) $NiLPhCN^+ + 2H_2$ (42%)
$PhCH_2CH_3$	$NiPhCHCH_2^+ + H_2 + L$ (41%) $NiP^+ + L$ (59%)	$NiP^+ + L$	no reactn
$PhCH(OH)CH_3$	$NiPhCOCH_3^+ + H_2 + L$	$NiPhCHCH_2^+ + H_2O + L$ (70%) $NiPhCOCH_3^+ + H_2 + L$ (30%)	$NiLPhCHCH_2^+ + H_2O$
$Ph(CH_2)_3CH_3$	$NiPhCH_3^+ + C_3H_6 + L$ (44%) $NiP^+ + L$ (56%)	$NiP^+ + L$	no reactn
PhC(O)H	$NiPhH^+ + CO + L$ (29%) $NiP^+ + L$ (71%)	$NiP^+ + L$	$NiLPhH^+ + CO$
$PhC(O)CH_3$	$NiPhCH_3 + CO + L$ (42%) $NiP^+ + CO$ (58%)	$NiPhCH_3^+ + CO + L$ (20%) $NiP^+ + L$ (80%)	$NiLP^+$
PhC(O)OH	$NiPhOH^+ + CO + L$ (32%) $NiP^+ + L$ (68%)	$NiP^+ + L$	no reactn
$PhC(O)OCH_3$	$NiPhOCH_3^+ + CO + L$ (45%) $NiP^+ + L$ (55%)	$NiP^+ + L$	$NiLP^+$
PhC(O)Ph	$NiP^+ + L$	$NiP^+ + L$	no reactn
PhC(O)Cl	no reactn	no reactn	no reactn
$PhCH_2C(O)H$	$NiPhCH_3^+ + CO + L$ (32%) $NiP^+ + L$ (68%)	$NiPhCH_3^+ + CO + L$ (17%) $NiP^+ + L$ (83%)	no reactn

suggest that the two bond energies are similar, with $D(Ni^+{-}PF_3) > D(Ni^+{-}CO)$ by a few kilocalories per mole.

$NiCp^+$. The cyclopentadienyl ligand appears to be much different concerning its effects on the chemistry of a metal than the other two ligands studied here. Jacobson and Freiser[34a] studied the chemistry of $CoCp^+$ and report some bond energies that suggest that $CoCp^+$ forms stronger bonds than does Co^+ [for example, $D(Co^+{-}C_4H_6) < D(CpCo^+{-}C_4H_6)$, $D(Co^+{-}Cp) < D(CpCo^+{-}Cp)$]. They report that $D(Co^+{-}Cp) = 85 \pm 10$ kcal/mol, which is larger than $D(Co^+{-}C_6H_6)$, 70 ± 4 kcal/mol. This suggests that a bonding mechanism other than a simple electrostatic one may be operative for the Cp group. It has been suggested that the Cp group can be actively involved in the chemistry of the attached metal—molecular fragments can be "stored" on the Cp ring,[34] as well as on the metal ion. For example, reaction 16 has been discussed[34a] by suggesting that the CH_2 may

$$CoCp^+ + C_4H_8 \rightarrow CoCp(CH_2)^+ + C_3H_6 \qquad (16)$$

not be bound to the metal, but may be incorporated into the ring to yield a Co(methylcyclopentadienyl)$^+$ product.

The Cp ligand appears to be strongly bound to Ni^+. In Table IV, this ligand is never displaced by an aromatic compound, while CO and PF_3 are. Also, the molecular ion of CpNiNO reacts with all of the aromatic compounds studied here in a ligand displacement reaction, reaction 17, with the Cp never being displaced.

$$CpNiNO^+ + PhX \rightarrow CpNiPhX^+ + NO \qquad (17)$$

It is possible that some charge transfer takes place between the metal ion and the Cp group to yield a structure of the type $Ni^{(1+\delta)+}Cp^{\delta-}$. Charge transfer of this type has been observed for ligands such as the chlorine atom.[35] The electron affinity of C_5H_5 has been reported to be <42.3 kcal/mol.[36] If additional positive charge is generated on the metal with this ligand, it may explain the strength of the $Ni^+{-}Cp$ bond, as well as the increased bond energies to Co^+ when the Cp ligand is present, relative to those for Co^+ alone. The reaction of $PhNO_2$ with Ni^+ in Table II to form $NiC_5H_5^+$ suggests that $D(Ni^+{-}C_5H_5) > 41$ kcal/mol, if the C_5H_5 exists as an intact ligand in the reaction product. We note that in organometallic chemistry,[37] the Cp ligand is frequently considered to take the form Cp^-; charge transfer from the metal to Cp would yield an aromatic ligand (6 π-electrons).

Expected Trends in the Reactions of NiL^+. Based on what is known about these three ligands, some reaction trends may be proposed. However, first a comment should be made on the "pitfalls" of overinterpreting the data[7] in Table IV. Consider the two reactions:

$$Ni^+ + ABC \rightarrow NiB^+ + AC \qquad (18)$$

$$NiCO^+ + ABC \rightarrow NiABC^+ + CO \qquad (19)$$

One may be tempted to suggest that, while Ni^+ reacts with ABC, $NiCO^+$ only undergoes a ligand substitution reaction (i.e., does not insert into bonds, etc.). However, this may not be the case. If $NiCO^+$ induces the rearrangement of ABC to AC and B, the species that dissociates to the final products is $Ni^+(AC)(B)(CO)$. The order in which ligands are lost appear to reflect their relative

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[34] (a) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1985**, *107*, 7399. (b) Corderman, R. R.; Beauchamp, J. L. *Inorg. Chem.* **1978**, *17*, 68.

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bond energies to the metal ion. Thus, if AC = H_2, it would be preferentially lost relative to CO, and if a reaction occurred, it would be apparent. However, if the products AC and B are the more strongly bound ligands, reaction 19 will be observed. Thus reaction 19 provides no information (in the latter case) as to whether rearrangement of ABC to AC and B has occurred. Thus, it is important, when comparing the chemistry of Ni^+ and NiL^+, to consider the possible reaction products and their proton affinities.[7] In this way, one may be able to conclude whether or not the presence of the ligand affects the chemistry, or whether such information cannot be obtained from the experimental results presented.

We interpret reactions such as

$$NiCO^+ + PhCl \rightarrow NiPhCl^+ + CO \tag{20}$$

as ligand displacement reactions. If chlorobenzene reacted on the metal center to form C_6H_4 and HCl, HCl is more weakly bound than CO and would be lost. That is, if the HCl elimination occurred, we would expect to see either $NiC_6H_4^+$ or $NiCOC_6H_4^+$ as a $NiCO^+$ product. Note that $NiCp^+$ does not participate in ligand substitution reactions, presumably reflecting the strong Ni^+–Cp bond energy.

Changes in the chemistry of NiL^+ as L varies would be expected to parallel the relative bond energies, which we expect to be

$$D(Ni^+\text{–}CO) < D(Ni^+\text{–}PF_3) < D(Ni^+\text{–}Cp)$$

Also, the relative sizes of the three ligands may introduce steric effects. We have found the "cone angle" concept[38] to be useful in this regard; it suggests that the Cp ligand is the largest, occupying a "cone" from the origin (metal center) with an angle of 136°, with PF_3 next at 104°, and CO the smallest, 95°. These steric effects may favor the formation of intermediates in which at least one of the groups attached to the metal is small, such as H. Steric effects may hinder the insertion process in which two bulky groups are bound to the metal (in addition to the ligand). In addition to steric effects, differences in the chemistry of the Ni^+ when Cp is attached may reflect either an increased positive charge on the metal or reactions that involve storage of some molecular fragment on the ring.

The trends in reactivity that will be highlighted from the data in Table IV fall into a few simple categories. There are some reactions in which $NiCp^+$ appears to be more reactive than the other NiL^+, and even Ni^+, which may be due to the increased positive charge on the metal. We suggest that many of the trends are due to steric effects.

Increased Reactivity of $NiCp^+$. This is observed in the reactions of the halobenzenes in Table IV. Ni^+ reacts with bromo- and iodobenzene to eliminate HX, but not with chlorobenzene. Only ligand substitution reactions appear to be occurring with these compounds for $NiCO^+$ and $NiPF_3^+$. In contrast, $NiCp^+$ eliminates HX from all three PhX compounds. The thermochemical data[21] in Table II suggest that the failure of Ni^+ to react with PhCl may be due to the relatively strong Ph–Cl bond (rather than the overall reaction enthalpy). If the Ni in $NiCp^+$ has a charge of greater than +1.0, polarization effects may lead to the formation of stronger bonds. That is, $NiCp^+$ may react with PhCl because

$$[D(CpNi^+\text{–}Cl) + D(Cp(Cl)Ni^+\text{–}Ph)] > [D(Ni^+\text{–}Cl) + D(ClNi^+\text{–}Ph)]$$

With the Cp ligand, there are, of course, many other possibilities such as coupling of the C_6H_4 group to the Cp ring.

Why Focus on Steric Effects? Since the ordering of size of the three ligands studied here parallels their binding energies to Ni^+, trends in the data may obviously reflect effects of either or both property(ies). One approach is to suggest that variations in $D(M^+\text{–}L)$ lead to variations in chemistry. Suppose, when Ni^+ complexes with some PhX compound, 60 kcal/mol is generated and assists in accessing, in fact is required for accessing, the insertion intermediate structure. Now consider the reaction of NiL^+. When it forms the initial complex, 60 kcal/mol is released, and 30 kcal/mol is consumed in rapid cleavage of the Ni^+–L bond. The resulting complex, $NiPhX^+$ now has only 30 kcal/mol which may be insufficient for further reaction to occur (a relatively "cold" $NiPhX^+$ complex), the result being only ligand displacement. These considerations would predict that the reactivity of NiL^+ would decrease as $D(Ni^+\text{–}L)$ increases—for those cases in which ligand displacement reactions occur. We note that Schilling and Beauchamp[39] recently proposed a similar argument to explain the unreactive behavior of Pr^+ and Eu^+ with small alkanes—citing the possible importance of the "chemical activation" that occurs upon complexation and its relationship to barriers earlier in the reaction. This energetic argument has some attractive features, and may seem more reasonable than a steric argument. However, we do not suggest it here, alone, because we cannot determine where in the course of the reactions, the ligand is lost.

Do the reactions for $NiCO^+$ and $NiPF_3^+$ proceed via pathway **A** or **B** in reaction 21? The ligand is consistently lost in the

$$\begin{tikzcd} ML^+ + AB \arrow[r] & M(L)(AB)^+ \arrow[r, "-L", "\mathbf{A}"'] \arrow[d, "\mathbf{B}"'] & M(AB)^+ \arrow[d] \\ & M(L)(C)(D)^+ \arrow[r, "-L{,}D"] & MC^+ + D \end{tikzcd} \tag{21}$$

reactions in Table IV, supporting pathway **A**; however, this would be expected by either pathway for weakly bound ligands. We suggest that the ligand need not be lost promptly, but may reside on the metal until the final ligand loss step, after rearrangement of the organic molecule is complete. There are a number of cases in which this has been observed;[3,4,8,18] a few examples are presented below.

$$CoCO^+ + n\text{-}C_4H_9X \rightarrow CoCOC_4H_8^+ + HX \quad X = F, Cl, Br \tag{22}$$

$$CoCO^+ + n\text{-}C_3H_7Cl \rightarrow CoCOC_3H_6^+ + HCl \tag{23}$$

$$CoCO^+ + n\text{-}C_3H_7Cl \rightarrow CoCOHCl^+ + C_3H_6 \tag{24}$$

$$CoCO^+ + C_2H_5NH_2 \rightarrow CoCO(C_2H_5N)^+ + H_2 \tag{25}$$

$$CoCO^+ + C_2H_5NH_2 \rightarrow CoCO(CH_3N)^+ + CH_4 \tag{26}$$

The weakly bound CO need not be promptly lost, or lost at all, when ML^+ complexes with the neutral organic molecule. We have found such an assumption to be consistent in considerations of the ligand loss processes.

If ligand loss does not occur initially, then the correlation of reactivity with $D(M^+\text{–}L)$ is inappropriate to discuss. The following discussion will assume that prompt ligand loss is not required, leaving steric factors as features of these reactions that may influence the reactivity. We believe that these considerations have merit, since consideration of metal–ligand binding energy influences does not explain the observation that facile reactions occur for ML^+ ions when the initial insertion step involves attack of a C–H, O–H, or N–H bond.

Trends Reflecting Steric Effects. We propose two types of steric effects. In the first case, a reaction may be "turned off" due to the presence of a bulky ligand. That is, while Ni^+ may react with ABCH via the intermediate A–Ni^+–BCH, the steric interactions may prevent access of the analogous intermediate when a bulky ligand is present. A second steric effect can be seen when the products of Ni^+ reflect attack of several bonds. For the molecule ABCH, the product distributions may suggest that the intermediate III is formed to a greater extent than intermediate IV.

A-Ni^+-BCH	ABC-Ni^+-H
III	IV

However, with a bulky ligand on the metal, steric interactions would be less if the C–H bond were attacked, making intermediate VI more stable than V. Consider, for example, the reactions of $PhCH_2X$, X = Cl and Br. Ni^+ reacts by halide abstraction with

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(38) Tolman, T. A. *Chem. Rev.* **1977**, *77*, 313.

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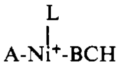
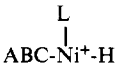

$\mathrm{A}\text{-}\overset{\overset{\mathrm{L}}{|}}{\mathrm{Ni}}{}^{+}\text{-}\mathrm{BCH}$

V


$\mathrm{ABC}\text{-}\overset{\overset{\mathrm{L}}{|}}{\mathrm{Ni}}{}^{+}\text{-}\mathrm{H}$

VI

both compounds. $NiPF_3^+$ does so as well. $NiCO^+$ only reacts with $PhCH_2Br$. This may suggest that the ionization energies (IE) follow the order IE(NiCO) < IE($NiPF_3$);[40] thus the presence of the CO may hinder the charge-transfer step that leads to the formation of the $C_7H_7^+$ product (assuming that the insertion step occurs). However, $NiCp^+$ only reacts with the chloride. This may be a case where the energetically more facile reaction (for the $PhCH_2Br$) does not occur because the Br atom is too large, preventing access of the $PhCH_2$–Ni^+Cp–Br intermediate. This further suggests that the formation of $C_7H_7^+$ occurs via an insertion intermediate, not a stripping process.

The decrease in reactivity with increasing ligand size is more apparent in the data for the aromatic carbonyl compounds in Table IV. Here reactivity (i.e., ability to induce decarbonylation) follows the order

$$NiCO^+ > NiPF_3^+ > NiCp^+$$

decreasing as the size of the ligand increases. Consider first $PhC(O)CH_3$. If decarbonylation proceeds via intermediates of the type Ph–Ni^+(L)–$C(O)CH_3$, we would expect decreasing reactivity as the size of L increases. We note that the cone angles[38] of C_6H_5 and $C(O)CH_3$ are both estimated to be 100°. Thus, 42% of the products correspond to decarbonylation for $NiCO^+$, 20% for $NiPF_3^+$, and 0% for $NiCp^+$. The ability of the metal in $NiCp^+$ to form stronger bonds apparently cannot compensate for the steric energies involved. However, this may not be the case for PhC(O)H. $NiCp^+$ does decarbonylate benzaldehyde, suggesting that the reaction proceeds by insertion into the C–H bond; this will minimize steric interactions since one molecular fragment on the metal is an H, with a cone angle[38] of only 75°. Why then doesn't $NiCp^+$ decarbonylate $PhCH_2C(O)H$? This may reflect the fact that the weak benzyl–C bond favors insertion at that point—that is, that decarbonylation of $Ph(CH_2)C(O)H$ proceeds through intermediate VII, not VIII.

$PhCH_2\text{-}Ni^+\text{-}C(O)H$ $\quad$ $PhCH_2C(O)\text{-}Ni^+\text{-}H$

VII $\quad$ VIII

The increased probability that NiL^+ will favor intermediates of the type ABC–$Ni(L)^+$–H is seen in a number of instances. Consider benzyl alcohol, $PhCH_2OH$. Ni^+ reacts with this compound to form $C_7H_7^+$, and to eliminate H_2, presumably via intermediates IX and X, respectively. In contrast, $NiCO^+$ and $NiPF_3^+$ only appear to react via an intermediate analogous to X; again the extent of reaction decreases as the size of the ligand increases. In fact, many of the cases where $NiPF_3^+$ and $NiCp^+$ react correspond to those mechanisms in which insertion into a C–H or N–H bond occurs. Also note that there is only one case where $NiCO^+$ does *not* induce a decarbonylation of an aromatic carbonyl when Ni^+ does. The exception is PhC(O)Ph, in which the two groups that would be on the metal upon insertion are the largest. Thus, in this case, even the smallest ligand, CO, appears to exert steric influences.

$Ph(CH_2)\text{-}Ni^+\text{-}OH$ $\quad$ $PhCH_2O\text{-}Ni^+\text{-}H$

IX $\quad$ X

In the experiments performed to yield the data in Tables II–IV, the reactions of the multiligated ions such as $Ni(CO)_{2-4}^+$ were also studied. These are not reported here since they are generally uninteresting. Typically, only ligand displacement reactions are observed. There were only two cases in which NiL_2^+ ions were observed to react:

$$Ni(PF_3)_2^+ + PhCH_2OH \rightarrow NiPhCHO^+ + H_2 + 2PF_3 \tag{27}$$

and

$$Ni(CO)_2^+ + PhCH(OH)CH_3 \rightarrow NiPhCOCH_3^+ + H_2 + 2CO \tag{28}$$

When two ligands are present, steric effects would certainly be increased, which would be consistent with decreased "reactivity". These two cases in which NiL_2^+ ions react are both systems in which hydrogen elimination occurs. That is, they proceed via intermediates with minimal steric energy in the insertion intermediate, since they place a H on the metal as one of the two fragments of the molecule.

It was suggested that, in the case of $PhCH(OH)CH_3$, the loss of CH_2O was actually a two-step process—elimination of H_2 followed by elimination of CO. This is supported by the reactions of the ligated species, where H_2 elimination is observed. Following H_2 elimination, cleavage of the Ni^+–L bond appears to occur rather than decarbonylation of the ketone that is formed as a result of dehydrogenation.

Finally, we note only one case in which the presence of a ligand actually leads to new products. All three NiL^+ ions react with benzylamine, $PhCH_2NH_2$, to eliminate H_2, consistent with our suggestion that reactions that proceed by insertion into C–H, O–H, or N–H bonds are least affected by steric interactions. However, $NiCp^+$ alone induces the elimination of a second dihydrogen:

$$NiCp^+ + PhCH_2NH_2 \rightarrow CpNiPhCN^+ + 2H_2 \tag{29}$$

If H_2 elimination occurs, sufficient energy may be released when the resulting PhCHNH interacts with the $Ni^{(1+\delta)+}$ center to overcome the barrier that leads to the elimination of a second H_2. Reaction 30 requires 33 kcal/mol, thus the metal–PhCN binding energy must be greater than this value.

$$PhCH_2NH_2 \rightarrow PhCN + 2H_2 \tag{30}$$

In the discussion of the chemistry of ML^+ cations, we suggest that steric interaction energies in some insertion intermediates may make them energetically less favorable, when L is large. One may not be able to distinguish between steric effects at this point in the mechanism, from those in the immediate precursor—the initially formed ion/molecule complex. That is, the presence of L may affect the ability of the metal to get close to some bonds more so than others, prior to insertion.

We have discussed two extreme scenarios here for considering how ligated transition-metal ions react in the gas phase. Obviously, a conclusion on which dominates cannot be made from the data presented here. This does, however, suggest future studies that can begin to approach some of the questions raised. Systems can be selected that will focus on the role of steric effects, and the role of ligand binding energy.

Conclusions

In these gas-phase organometallic ion/molecule reactions the phenyl group behaves chemically, in some ways, intermediate to the methyl and ethyl groups. H transfer from the phenyl group is a high-energy process, much closer in energy to that required for H transfer from a methyl group than an ethyl group. The formation of the strong benzyne–Ni^+ bond makes H abstraction from C_6H_5 possible in a few cases. When other pathways are open, such as the elimination of a small neutral molecule from the functional group, this latter pathway is preferred.

A major effect of the presence of a phenyl group in an organic molecule is its inductive effects. This can be seen in reactions of substituted benzyl compounds. The weak $C_6H_5CH_2$–X bond plays an important role in the observed chemistry. This bond is the only bond attacked for most of the benzyl compounds studied. Charge transfer to the $C_6H_5CH_2$ moiety following insertion into this bond occurs due to the low ionization potential of this group.

The effect of ligands on metal centers is of major importance in the understanding of transition-metal chemistry in condensed phases. The reactions of $NiPF_3^+$ follow closely the reactions of $NiCO^+$, with slightly less reactivity observed for the $NiPF_3^+$ ion. The metal–ligand bonding in $NiCO^+$ and $NiPF_3^+$ is probably very similar, so this result is not surprising. The slightly less reactivity

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[40] Would the IE(NiCO) be expected to be less than IE($NiPF_3$)? This may not be unreasonable if one considers the situation when Ni is surrounded by four ligands: IE($Ni(CO)_4$) = 8.28 eV,[14] which is less than IE($Ni(PF_3)_4$) = 9.6 eV.[33]

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of $NiPF_3^+$ reflects the steric crowding involved upon insertion produced by this larger ligand. Much of the chemistry of the NiL^+ ions can be explained by considering the formation of intermediates that would exhibit low steric interactions. The reactivity of $NiCp^+$ with the halobenzenes indicates that this ligand affects the metal ion much differently than either CO or PF_3. Charge transfer to the cyclopentadienyl group to increase its aromatic character may explain why this ion is more reactive than the other NiL^+ species in these examples. In other cases the steric hindrance of the bulky Cp group appears to block reaction pathways.

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The Relaxed and Spectroscopic Energies of Olefin Triplets

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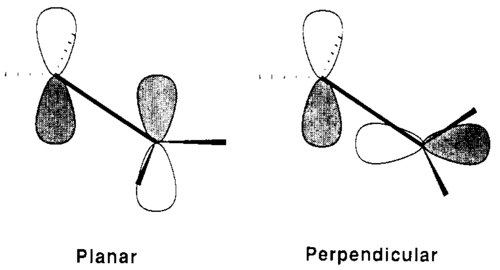
Abstract: The relaxed energies and lifetimes of a series of olefin triplets have been determined by time-resolved photoacoustic calorimetry using a novel cell configuration which allows improved precision. The planar triplet energies of a number of olefins were measured by oxygen and heavy-atom perturbation methods. For styrene triplets, the difference between the relaxed and planar triplet energies varies from 0 to 10 kcal/mol depending on the degree of twisting allowed. Stilbene triplets show a potential surface rather flat between trans and perpendicular geometries. New Benson group equivalents for a number of free radical additivities derived from recent literature values of heats of formation of radicals are tabulated. The energies of acyclic, fully relaxed triplets are in excellent agreement with the values calculated by the Benson method using the new radical group values and the assumption that the triplet is satisfactorily modeled as a "1,2-biradical".

The triplet state of alkenes is an intermediate in many long-known photoreactions, examples including photosensitized cis–trans isomerization,[1,2] photorearrangements,[3] and photocycloadditions.[4] In general, such processes will originate from a thermally relaxed triplet. While transient spectroscopy with standard optical detection allows observation of these species,[5] it does not provide thermochemical information. Normally the excited energies are estimated by spectroscopic methods such as conventional absorption or luminescence. Since the relaxed triplet energies are frequently quite different from vertical energies, i.e., the energies at ground-state geometry, the relaxed energies will frequently be spectroscopically inaccessible due to severe Franck–Condon restriction. To understand the energy surfaces of alkenes better, and particularly to provide thermochemical information from which further considerations of alkene triplet reactivity might follow, we have determined the relaxed triplet energies of a substantial number of related alkenes by time-resolved photoacoustic calorimetry[6,7] (PAC) together with their spectroscopic energies by heavy-atom solvent[8] or oxygen-perturbed[9] absorption. Comparison of the two quantitates the energy difference between the planar and perpendicular forms (sketched below) when the latter is not prohibited by structural constraint.



Experimental Section

Oxygen-perturbed absorption spectra were run on a photodiode array spectrometer (Hewlett-Packard, Model 8450A) with resolution of 1 nm and sensitivity of 10^{-4} in absorbance. The high-pressure sample cell, shown in Figure 1, has a 5-cm light path for vapor samples and 1-cm light path for liquid samples. The spectra of low boiling point samples were taken by placing several drops of the compound under study in the bottom of the high-pressure cell, allowing 5 min for vaporization. In the cases of higher boiling compounds, the spectra were taken in the liquid phase. Normally, 1 mL of solution containing 0.2–0.4 g of compound was placed in a standard 1-cm UV quartz cell which can be placed in the high-pressure cell. The system was then pressurized with 20–40 atm of oxygen. Because the diffusion of oxygen in the liquid phase is very slow, the spectra were recorded after the cell had been gently shaken for 5 min to reach equilibrium. Further shaking produced no further change in the spectra. The spectra under 1 atm were also recorded to provide references. Evaluation of the singlet–triplet absorption spectra were carried out by subtracting the references from the perturbed spectra obtained under high-pressure condition.

External heavy-atom perturbed spectra were also run on the photodiode array spectrometer. Dibromomethane and methyl iodide were used as heavy-atom perturbers. Methyl iodide is a highly light-sensitive

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