J. Phys. Chem. A **1999,** *103,* 6373−6382

Gas-Phase Coordination of Mg^+, $(c\text{-}C_5H_5)Mg^+$, and $(c\text{-}C_5H_5)_2Mg^+$ with Small Inorganic Ligands

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Received: March 10, 1999; In Final Form: June 7, 1999

The coordination of the electronic ground states of Mg^+, $(c\text{-}C_5H_5)Mg^+$, and $(c\text{-}C_5H_5)_2Mg^+$ with the inorganic molecules H_2, NH_3, H_2O, N_2, CO, NO, O_2, CO_2, N_2O, and NO_2 has been investigated in the gas phase at room temperature and moderate pressures. Reaction rate coefficients and product distributions were measured with the selected-ion flow tube (SIFT) technique operating at 294 ± 3 K and a helium buffer-gas pressure of 0.35 ± 0.01 Torr. Rate coefficients were measured for all observed ligation steps (or upper limits in the case of nonreactions), and bond connectivities in the coordinated ions were probed with multicollision-induced dissociation. The rates and extent of ligation were found to depend on the degree of ligation with $c\text{-}C_5H_5$ and the nature and size of the inorganic ligand. Mg^+ was found to be unreactive except with ammonia, which was found to add slowly ($k = 4 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}). Single ligation of Mg^+ with $c\text{-}C_5H_5$ substantially *enhances* the efficiency of ligation; the initial ligation is rapid ($k > 5 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}) with all ligands except H_2, N_2, and O_2. Double ligation with $c\text{-}C_5H_5$ substantially *reduces* the efficiency of ligation; no ligation was observed with the “full-sandwich” magnesocene cation. Fast bimolecular *ligand-switching* reactions occur instead, but only with NH_3 and H_2O, indicating that these two molecules ligate more strongly to $(c\text{-}C_5H_5)Mg^+$ than does $c\text{-}C_5H_5$ itself. Higher-order ligation was observed between Mg^+ and NH_3 and between the “half-sandwich” $(c\text{-}C_5H_5)Mg^+$ cation and CO, NO, NH_3, H_2O, CO_2, N_2O, and NO_2. After a slow initiation step, ammonia added to Mg^+ up to four times to generate $Mg(NH_3)_4{}^+$. Higher-order ligation reactions of $(c\text{-}C_5H_5)Mg^+$ with CO, NO, NH_3, CO_2, N_2O, and NO_2 proceed with diminishing rates adding up to at most three ligands. H_2O is an exception; at least six H_2O molecules were observed to add sequentially to $(c\text{-}C_5H_5)Mg^+$. Variations in the observed rate of this addition have been attributed to the completion of an “inner” coordination shell and the onset of hydrogen bonding in an “outer” coordination shell that accounts for the continuing rapid ligation. Higher-order ligands were removed sequentially by multicollision-induced dissociation with He atoms; there was no evidence for intramolecular interligand interactions leading to unimolecular bond redisposition after ligation.

Introduction

The chemistries of magnesium cations continue to be of interest in a wide range of disciplines including atmospheric chemistry, organometallic chemistry, and circumstellar/interstellar chemistry. Pioneering measurements of the reactivity of Mg^+ in the gas phase were reported as early as 1968 by Ferguson and Fehsenfeld[1] who were motivated by the role of this ion in the chemistry of the earth’s ionosphere. In 1963 rocket-borne mass spectrometers had identified Mg^+ in the earth’s upper atmosphere in stratified layers at 105 and 120 km where magnesium is thought to be deposited by meteor ablation.[2] Ferguson and Fehsenfeld drew attention to the nonreactivity of Mg^+ expected on the basis of energetics in bimolecular reactions with the abundant stable atmospheric gases O_2, N_2, and CO_2, but they also were able to demonstrate with rate measurements the substantial bimolecular reactivity of this ion with the less stable, less abundant atmospheric constituents O_3, Cl_2, Br_2, H_2O_2, HNO_3, and CCl_4.[3] There is continuing interest in the atmospheric chemistry of Mg^+, particularly as it proceeds in meteor trains,[4] the atmospheres of stars,[5] and the atmospheres of Neptune and the other giant planets;[6] more kinetic data for reactions of this ion, for example with H_2 and hydrocarbons, have been called for.[6] Little progress has been made in this regard, although systematic studies of the kinetics of reactions of Mg^+ with a large variety of inorganic and organic molecules using a selected-ion flow tube (SIFT)/glow discharge technique have been initiated in the laboratory of Babcock.[7] Preliminary results from this laboratory indicate no reactions with the inorganic molecules H_2, N_2, CO, NO, H_2O, SO_2, NH_3, NO_2, and N_2O at room temperature in helium carrier gas (at ca. 0.3 Torr), although addition reactions were reported for CO_2 and H_2S as well as hydrocarbons generally, except methane.[7]

A prime focus in organomagnesium chemistry has been the intrinsic nature of Mg^+−ligand interactions and the influence of such interactions on the chemistry of bare and ligated Mg^+. Previous theoretical investigations, as well as systematic gas-phase experiments, have led to structures and total energies of isolated ligated Mg^+ ions as well as intrinsic Mg^+−L binding energies. Theoretical studies of ligated Mg^+ have been reported primarily by Bauschlicher and co-workers[8−13] for singly ligated MgL^+ cations with L = H_2, N_2, CO and many organic molecules and for multiply ligated $MgL_n{}^+$ cations with L = H_2O and NH_3. Gardner et al. have computed the ionic species MgX^+ and $MgX_2{}^+$ (X = H, F, Cl, and OH).[14] The weakly bound ligated

10.1021/jp9908505 CCC: $18.00

$Mg^+{-}D_2$, $Mg^+{-}N_2$, $Mg^+{-}O_2$, $Mg^+{-}H_2O$, $Mg^+{-}N_2O$, and $Mg^+{-}CO_2$ ions in which the bonding is primarily electrostatic in nature, as well as multiply ligated CO_2 cations, have been examined experimentally using photoexcitation and dissociation spectroscopy.[15] Sequential bond energies for multiply ligated $Mg^+(H_2O)_n$ cations with n up to 4 have been determined from observed thresholds for collision-induced dissociation with xenon proceeding within a guided ion beam mass spectrometer.[16] The photoabsorption and photodissociation of $Mg^+(H_2O)_n$ have been investigated experimentally for $n = 1$ and 2.[17] The latter has been shown to lead to the evaporation of water molecules as well as the production of $MgOH^+$.[17] Also, the dehydrogenation reaction 1 has been seen to occur spontaneously upon hydration at room temperature for $n > 4$.[18]

$$Mg^+(H_2O)_n + H_2O \rightarrow MgOH^+(H_2O)_n + H \qquad (1)$$

Relative $Mg^+{-}L$ ligand bond energies can be deduced from measurements of reaction *kinetics* by establishing the preferred directions of ligand-switching reactions of types 2a and 2b.

$$ML'^+ + L'' \rightarrow ML''^+ + L' \qquad (2a)$$

$$ML'_nL''_m{}^+ + L'' \rightarrow ML'_{n-1}L''_{m+1}{}^+ + L' \qquad (2b)$$

Preliminary results of such investigations with $M = Mg^+$ and various organic and inorganic ligands have been reported using the SIFT technique.[7]

We report here systematic SIFT investigations of the reactivity of Mg^+ toward inorganic molecules and of changes in Mg^+ reactivity when the Mg^+ cation is ligated with one and two cyclopentadienyl radicals. The Mg^+, $(c\text{-}C_5H_5)Mg^+$, and $(c\text{-}C_5H_5)_2Mg^+$ ions were generated from magnesocene by electron-impact ionization and were allowed to thermalize by collisional deactivation with He atoms prior to reaction. The reactivity of ground-state Mg^+ with inorganic gases was examined first, and then the change in reactivity was explored with the singly and doubly ligated ions $(c\text{-}C_5H_5)Mg^+$ and $(c\text{-}C_5H_5)_2Mg^+$. It will be seen that the reactivity of Mg^+ changes dramatically with single and double ligation and that the inorganic ligands themselves exhibit a variety of degrees of coordination with $(c\text{-}C_5H_5)Mg^+$ in sequential ligation reactions.

The reactivities of Mg^+, $(c\text{-}C_5H_5)Mg^+$, and $(c\text{-}C_5H_5)_2Mg^+$ were assessed through measurements of rate coefficients for ligation at room temperature and at operating helium pressures that are sufficiently high to allow collisional stabilization of the ligated ions. Under such operating conditions ligation occurs by termolecular reactions of type 3.

$$ML_n{}^+ + L + He \rightarrow ML_{n+1}{}^+ + He \qquad (3)$$

Measured rate coefficients for sequential ligation provide a measure of intrinsic coordination numbers, since the rate coefficents for ligation reactions of type 3 are sensitive to the bond energy of the ligated species, $D(M^+{-}L_{n+1})$. This is because the gas-phase ligation proceeds in two steps,

$$ML_n{}^+ + L \rightleftharpoons (ML_{n+1}{}^+)^* \qquad (4a)$$

$$(ML_{n+1}{}^+)^* + He \rightarrow ML_{n+1}{}^+ + He \qquad (4b)$$

and the lifetime of the intermediate $(ML_{n+1}{}^+)^*$ against dissociation back to reactants is dependent on both the degrees of freedom in $(ML_{n+1}{}^+)^*$ effective in intramolecular energy redisposition in the transient intermediate and its attractive well depth $D(M^+{-}L_{n+1})$.[19] We have recently applied this approach to the determination of intrinsic coordination numbers for Fe^+ coordinated by a variety of inorganic and organic molecules.[20,21] When the standard free energy change of ligation becomes sufficiently small, the reverse reaction may become significantly fast and drive the ligation reaction 3 toward equilibrium. In such instances, an equilibrium data analysis can provide a measure of the standard free energy of ligation.

Finally, the ligated Mg^+ ions produced in this study also were explored with multicollision-induced dissociation experiments. Such experiments provide indications of bond connectivities in the stabilized ligated species $ML_{n+1}{}^+$ and provide estimates of relative bond strengths.

Experimental Section

The results reported here were obtained using a selected-ion flow tube (SIFT) apparatus that has been described previously.[22,23] All measurements were performed at 294 ± 3 K and at a helium buffer gas pressure of 0.35 ± 0.01 Torr. The reactant ions, Mg^+, $(c\text{-}C_5H_5)Mg^+$, and $(c\text{-}C_5H_5)_2Mg^+$ were all generated in a low-pressure ion source from $(c\text{-}C_5H_5)_2Mg$ by electron impact ionization at electron energies of 35, 50, and 10 eV, respectively. Some collisional dissociation of $(c\text{-}C_5H_5)_2Mg^+$ and $(c\text{-}C_5H_5)Mg^+$ was observed to accompany ion injection into the flow tube; about 75% of the full-sandwich fragmented to the half-sandwich, while about 18% of the half-sandwich broke to form Mg^+ in the flow tube. The injected ions were thermalized by collisions (about 4×10^5) with helium buffer gas before entering the reaction region further downstream. Reactant neutrals were introduced into the reaction region either as a pure gas or, in the case of H_2O, as a dilute (0.2−5%) mixture in helium. The H_2O was distilled and deionized before use. All other reactant neutrals were obtained from Matheson Gas Products and were of high purity (generally >99%). The rate coefficients and product distributions were measured in the usual manner.[22,23] The rate coefficients for primary reactions reported here are estimated to have an absolute accuracy of ±30%. Higher-order rate coefficients were obtained by fitting the experimental data to the solution of the system of differential equations for a chain of successive reactions. Reverse reactions were ignored in this analysis but, when appropriate, a check was made for approach to equilibrium by plotting the ratio of the product to reactant ion concentrations vs reactant concentration. When equilibrium is achieved, such a plot becomes linear and the rate coefficient in the forward direction determined by the fitting is regarded as a lower limit to the true value. Bond connectivities in the product ions were investigated with multicollision-induced dissociation (CID) experiments by raising the sampling nose cone voltage from 0 to −80 V while concomitantly varying the potentials of front and rear quadrupole focusing lenses so that mass discrimination is not introduced.[24]

Results and Discussion

Table 1 summarizes, in order of increasing molecular weight of the reactant, the rate coefficients measured for *primary* reactions of Mg^+, $(c\text{-}C_5H_5)Mg^+$, and $(c\text{-}C_5H_5)_2Mg^+$. Rate coefficients deduced for higher-order reactions are summarized in Table 2. All rate coefficients are *apparent* bimolecular rate coefficients at 294 ± 3 K and a helium buffer gas pressure of 0.35 ± 0.01 Torr. Standard enthalpy changes referred to in the text were derived from the values found in the compilation of Lias et al.[25] unless indicated otherwise.

TABLE 1: Measured Rate Coefficients for Reactions of the Ground States of Mg^+, $(c\text{-}C_5H_5)Mg^+$, and $(c\text{-}C_5H_5)_2Mg^+$ with Selected Inorganic Ligands Proceeding at 294 ± 3 K in Helium Buffer Gas at a Total Pressure of 0.35 ± 0.01 Torr[a]

ligand	Mg^+	$(c\text{-}C_5H_5)Mg^+$	$(c\text{-}C_5H_5)_2Mg^+$
H_2	NR, $<10^{-14}$ $[1.5 \times 10^{-9}]$	NR, $<5 \times 10^{-13}$ $[1.5 \times 10^{-9}]$	NR, $<10^{-14}$ $[1.5 \times 10^{-9}]$
NH_3	4.0×10^{-12} $[2.5 \times 10^{-9}]$	1.2×10^{-9} $[2.1 \times 10^{-9}]$	*1.2×10^{-9}* $[2.0 \times 10^{-9}]$
H_2O	NR, $<10^{-14}$ $[2.8 \times 10^{-9}]$	1.6×10^{-9} $[2.3 \times 10^{-9}]$	*2.6×10^{-10}* $[2.2 \times 10^{-9}]$
N_2	NR, $<10^{-13}$ $[8.6 \times 10^{-10}]$	3.8×10^{-11} $[6.7 \times 10^{-10}]$	NR, $<10^{-13}$ $[6.3 \times 10^{-10}]$
CO	NR, $<10^{-13}$ $[9.4 \times 10^{-10}]$	1.7×10^{-10} $[7.3 \times 10^{-10}]$	NR, $<10^{-13}$ $[6.9 \times 10^{-10}]$
NO	NR, $<10^{-13}$ $[8.8 \times 10^{-10}]$	5.2×10^{-11} $[6.8 \times 10^{-10}]$	NR, $<10^{-13}$ $[6.4 \times 10^{-10}]$
O_2	NR, $<10^{-14}$ $[8.0 \times 10^{-10}]$	NR, $<10^{-13}$ $[6.1 \times 10^{-10}]$	NR, $<10^{-13}$ $[5.7 \times 10^{-10}]$
CO_2	NR, $<10^{-13}$ $[1.0 \times 10^{-9}]$	7.1×10^{-10} $[7.4 \times 10^{-10}]$	NR, $<10^{-13}$ $[6.8 \times 10^{-10}]$
N_2O	NR, $<10^{-13}$ $[1.1 \times 10^{-9}]$	3.1×10^{-10} $[7.8 \times 10^{-10}]$	NR, $<10^{-13}$ $[7.3 \times 10^{-10}]$
NO_2	NR, $<10^{-13}$ $[1.1 \times 10^{-9}]$	7.4×10^{-10} $[8.1 \times 10^{-10}]$	NR, $<10^{-13}$ $[7.5 \times 10^{-10}]$

[a] Reaction and collision rate coefficients are given in units of cm^3 $molecule^{-1}$ s^{-1}. All the observed reactions, except those italicized, are addition reactions. The two italicized reactions are ligand-switching reactions. The relative uncertainty in all reaction rate coefficient does not exceed 10%; however, the absolute error may be as high as 30%. Collision rate coefficients are given in square brackets and calculated using TC theory.[6] NR denotes no reaction.

A. Mg^+ Reactions. Mg^+ was found to be *unreactive* with all the molecules investigated with the exception of ammonia. No ligand-association reactions,

$$Mg^+ + L\ (+\ He) \rightarrow \text{no reaction} \tag{5}$$

or reactions leading to bimolecular products, were observed between Mg^+ and H_2, H_2O, or O_2, $k_1 < 10^{-14}$ cm^3 $molecules^{-1}$ s^{-1}, and between Mg^+ and N_2, CO, NO, CO_2, N_2O, or NO_2, $k_1 < 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1}. However, as we have reported recently,[26] ammonia did ligate sequentially to form ammonia adducts according to the following reaction sequence for n from 0 to 4.

$$Mg(NH_3)_n{}^+ + NH_3 \rightarrow Mg(NH_3)_{n+1}{}^+ \tag{6}$$

The rate coefficient for the ligation of bare Mg^+ with ammonia under our operating conditions was measured to be $4.1 \pm 1.2 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}.

Except for the result with ammonia and carbon dioxide, these observations are qualitatively in agreement with the preliminary results reported by Babcock et al.[7] These authors did not observe addition with ammonia, perhaps because it is a very slow reaction, and did report the clustering of CO_2 with Mg^+, perhaps because of a greater energy content for Mg^+. For the reaction of Mg^+ with H_2O, both our results and those of Babcock et al.[7] are inconsistent with the results of Castleman et al.[18] who report that water ligates Mg^+ in a flow-tube apparatus in He under similar conditions of pressure and temperature (a reaction rate coefficient was not reported). Also, hydrated M^+ ions were produced by Fuke et al.[17] in helium in a previous photodissociation study of magnesium−water cluster ions. The one important difference between these various experiments is the mode of production of Mg^+, which is achieved by laser vaporization of the metal in the experiments of Fuke et al.[17] and Castleman et al.[18] It is conceivable, as already has been pointed out by Babcock et al.,[7] that a large fraction of the Mg^+ ions generated by laser vaporization is excited and that only excited Mg^+ adds to water. It is also interesting to note that a slow addition reaction of Mg^+ with O_2 has been observed to proceed in Ar buffer gas under operating conditions otherwise similar to ours with a three-body rate coefficient of $\sim 2.5 \times 10^{-30}$ cm^6 $molecule^{-2}$ s^{-1}.[27] Apparently, argon is more effective than helium in stabilizing the transient intermediate $(MgO_2{}^+)^*$.

The failure to observe bimolecular reaction products for the reactions with Mg^+ at the room temperature of our operating conditions can be attributed to endothermicity. For example, available standard enthalpies of formation[25] indicate that oxidation reactions 7a and 7b

$$Mg^+ + O_2 \rightarrow MgO^+(^2\Pi) + O \tag{7a}$$

$$\rightarrow MgO + O^+ \tag{7b}$$

are endothermic by more than 80 and 170 kcal mol^{-1}, respectively. We have used a method described previously[28] at the CCSD(T)(full)/6-311++G(2df,p)//MP2(full)/6-311++G-(d,p) level of theory to calculate these endothermicities and found them to be 66 and 156 kcal mol^{-1}, respectively, at 298 K. The standard enthalpy of formation at 298 K for the $^2\Pi$ ground state of MgO^+ was computed to be 219.7 kcal mol^{-1}, which is lower than the experimental value of 238 ± 8 kcal mol^{-1}.[25] The calculated ionization energy of MgO is 7.980 eV, which is in good agreement with a previous theoretical value of 8.09 eV obtained at the singles-plus-doubles configuration interaction (SDCI) level[29] and the reported experimental value of 7.9 ± 0.1 eV, which was determined using Fourier transform mass spectrometry.[30] Guided ion beam mass spectrometry has provided a much higher value of 8.76 ± 0.22 eV, but it is based on a controversial value for the bond energy of MgO.[31]

A recent computation at MP2(FU)/6-311G**//MP2(FU)/6-311G** predicts an endothermicity for the hydrogenation reaction 8 of 220 kcal mol^{-1}.[32]

$$Mg^+ + H_2 \rightarrow MgH^+ + H \tag{8}$$

Insufficient thermochemical data are available for the standard enthalpy change for the analogous reaction between Mg^+ and N_2. Oxidation reactions analogous to reaction 7 with H_2O, CO, NO, CO_2, N_2O, or NO_2 and hydrogenation reactions analogous to reaction 8 with NH_3 and H_2O are also endothermic according

TABLE 2: Measured Rate Coefficients (in Units of cm^3 $molecule^{-1}$ s^{-1}) for the Sequential Ligation Reactions $(c\text{-}C_5H_5)Mg(L)_n{}^+ + L \rightarrow (c\text{-}C_5H_5)Mg(L)_{n+1}{}^+$ Proceeding at 294 ± 3 K in Helium Buffer Gas at a Total Pressure of 0.35 ± 0.01 Torr

n/L	N_2	CO	CO_2	NO	N_2O	NO_2	NH_3	H_2O
0	3.8×10^{-11}	1.7×10^{-10}	7.1×10^{-10}	5.2×10^{-11}	3.1×10^{-10}	7.4×10^{-10}	1.2×10^{-9}	1.6×10^{-9}
1	$<1 \times 10^{-13}$	$\geq 2.6 \times 10^{-12}$	$\geq 3.7 \times 10^{-11}$	1.2×10^{-11}	2.0×10^{-11}	$\geq 9.6 \times 10^{-12}$	1.4×10^{-9}	1.4×10^{-9}
2			$<5 \times 10^{-13}$	$<1 \times 10^{-13}$	$<1 \times 10^{-13}$		3.7×10^{-10}	2.7×10^{-10}
3							$<1 \times 10^{-13}$	2.4×10^{-10}
4								2.2×10^{-10}
5								2.4×10^{-10}
6								2.3×10^{-10}

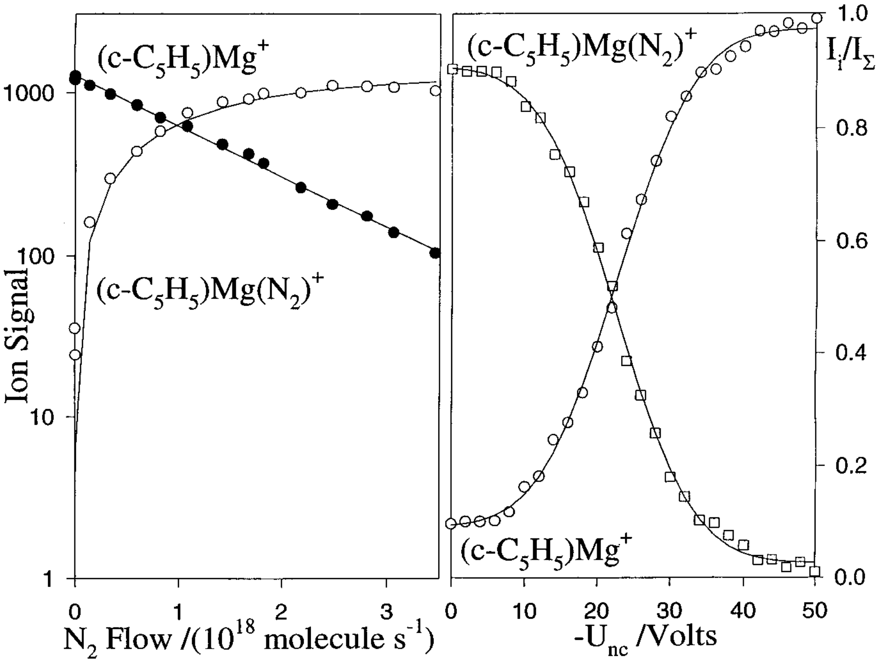

Figure 1. (Left) Experimental data for the reaction of (c-C_5H_5)Mg^+ with N_2. The measurements were performed at 294 ± 3 K and at a helium buffer gas pressure of 0.35 ± 0.01 Torr. (c-C_5H_5)Mg^+ was generated from pure (c-C_5H_5)$_2$Mg in a low-pressure ionization source by 25 eV electron-impact dissociative ionization. The solid lines represent a fit of the experimental data with the solution of the differential equations appropriate to the observed sequential reactions. (Right) Multicollision CID results for (c-C_5H_5)Mg$(N_2)^+$ in the laboratory energy scale and at a N_2 flow of 2.5 × 10^{18} molecules s^{-1}.

to the available thermochemical data.[25] However, the oxidation reaction 9 with N_2O, which has a computed endothermicity of 5 ± 8 kcal mol^{-1},[25] is a borderline case.

$$Mg^+ + N_2O \rightarrow MgO^+ + N_2 \qquad (9)$$

Failure to observe ligation with Mg^+ under SIFT operating conditions can be attributed to a combination of low binding energy and low degrees of freedom of the adduct ion, since these are the parameters that determine the lifetime against unimolecular dissociation of the transient intermediate adduct ion, which needs to be stabilized for ligation to take place in the gas phase.[19] Ammonia has the largest number of atoms and degrees of freedom of all the ligands investigated and, although not all of the binding energies for the other molecules are known, probably also has the highest binding energy with Mg^+. We have computed $D_0(Mg^+{-}NH_3) = 37.7$ kcal mol^{-1} (or $D_{298} = 39.7$ kcal mol^{-1}) at MP4SDTQ(fc)/6-311++G(2df,p)//B3LYP/6-31+G(d), and this value is larger than the binding energy with water, which has a computed $D_0 = 30.6$ kcal mol^{-1} at MCPF level using a TZ2P basis set[11] and an experimentally determined value of 28.4 ± 3.0 kcal mol^{-1} at 0 K.[33]

B. (c-C_5H_5)Mg^+ Reactions. In contrast to the chemistry of Mg^+, (c-C_5H_5)Mg^+ was found to be generally reactive and to initiate higher-order ligation chemistry. The measured rate coefficients for the primary and higher-order ligation reactions of (c-C_5H_5)Mg^+ with N_2, CO, CO_2, NO, NO_2, N_2O, NH_3, and H_2O are summarized in Tables 1 and 2. All of the observed reactions were addition reactions of type 10:

$$(c\text{-}C_5H_5)Mg(L)_n{}^+ + L \rightarrow (c\text{-}C_5H_5)Mg(L)_{n+1}{}^+ \qquad (10)$$

There was no evidence for the oxidation of magnesium to form (c-C_5H_5)MgO^+.

No reactions were observed with H_2 ($k < 5 \times 10^{-13}$ cm^3 $molecules^{-1}$ s^{-1}) and O_2 ($k < 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1}). (c-C_5H_5)Mg^+ was observed to react with N_2 only slowly ($k = 3.8 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}), as indicated in Figure 1. A second addition was not observed in the flow range of the experiments. The experimental dissociation onset for (c-C_5H_5)Mg$(N_2)^+$ in Figure 1 is 12 V (lab energy). This small value indicates that a weak bond is being fragmented,[24] and this is consistent with the rather low value for the effective bimolecular rate coefficient for ligation.

Figure 2 presents the observed reaction profiles for the reactions of (c-C_5H_5)Mg^+ with L = CO, NO, CO_2, N_2O. In each case two ligands were observed to add sequentially over the range of reactant flow employed, although there was also evidence for the addition of a third molecule of CO. The kinetics of ligation is similar for these four ligands in that a relatively fast addition of the first ligand is followed by an apparently much slower addition of the second ligand. An equilibrium analysis of the second ligation step indicates that a number of these secondary ligations achieve equilibrium in the flow range employed. This is evident in Figure 3, which indicates the attainment of equilibrium in the second ligation step with CO and CO_2 and the approach to equilibrium in the second ligation step with NO and N_2O. Table 3 provides a summary of the equilibrium constants deduced from the plots shown in Figure 3. The CID profiles in Figure 4 show a straightforward sequential loss of ligands, but with a substantial difference in onset between the loss of the first and the second ligand, the first ligand being more strongly bound. Also, the CID profile for (c-C_5H_5)Mg$(NO)_2^+$ is unique in that it shows an inflection, which suggests the presence of two isomers of (c-C_5H_5)Mg$(NO)_2^+$. One isomer could contain a magnesium−oxygen bond and the other a magnesium−nitrogen bond. These two isomers would fragment at different nose cone voltages and hence lead to an inflection in the CID profile. The more strongly bound isomer appears to be the more abundant.

Figure 5 shows that three molecules of NO_2 add sequentially to (c-C_5H_5)Mg^+ under our operating conditions, although the first addition is decidedly the fastest ($k = 7.4 \times 10^{-10}$ cm^3

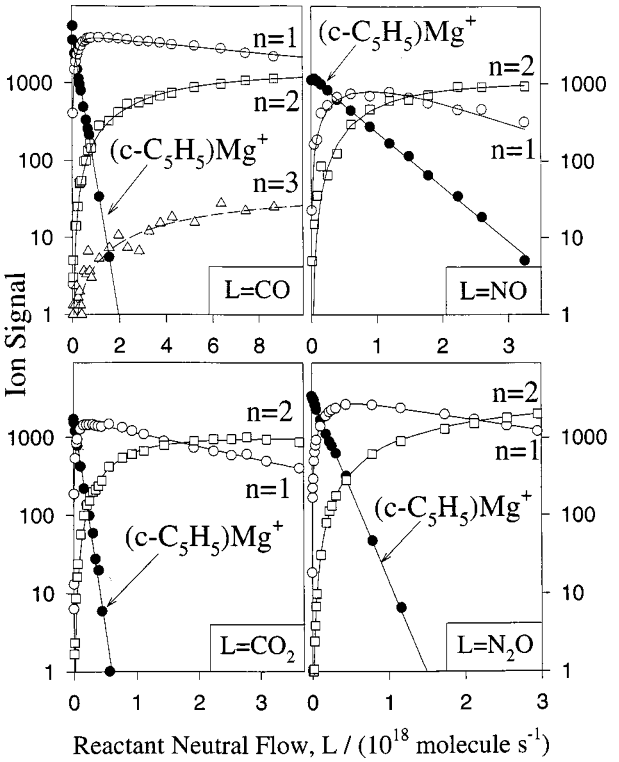

Figure 2. Experimental data for reaction 10 with L = CO, NO, CO_2, and N_2O. The measurements were performed at 294 ± 3 K and at a helium buffer gas pressure of 0.35 ± 0.01 Torr. (c-C_5H_5)Mg^+ was formed by electron-impact dissociative ionization of Mg(c-C_5H_5)$_2$ at 25 eV. The solid lines represent a fit of the experimental data with the solution of the differential equations appropriate to the observed sequential reactions. The dashed line has not been fitted to the data.

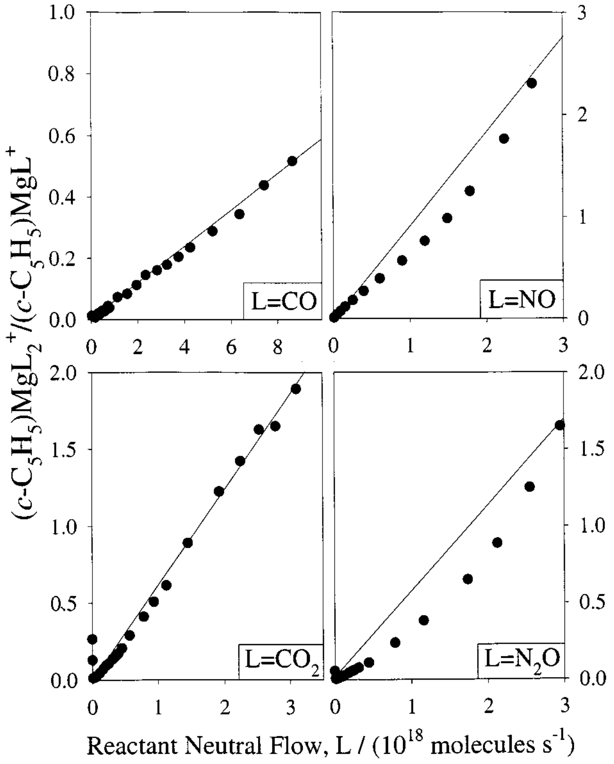

Figure 3. Ion-signal ratio plots showing the approach to, and attainment of, equilibrium for some of the data shown in Figure 2.

TABLE 3: Room-Temperature Equilibrium Constants (Standard State = 1 atm) and Standard Free Energy Changes (in kcal mol^{-1}) for Ligation Reactions (c-C_5H_5)Mg(L)$_n^+$ + L → (c-C_5H_5)Mg(L)$_{n+1}^+$

L	n	K_{eq}	$\Delta G°$
N_2	0	$\geq 2.1 \times 10^7$	$-(\geq 10)$
CO	1	4.6×10^5	-7.7
NO	1	$\geq 6.4 \times 10^6$	$-(\geq 9.3)$
CO_2	1	4.4×10^6	-9.1
N_2O	1	$\geq 4.1 \times 10^6$	$-(\geq 9.0)$
NO_2	1	1.9×10^6	-8.5
	2	7.8×10^6	-9.4

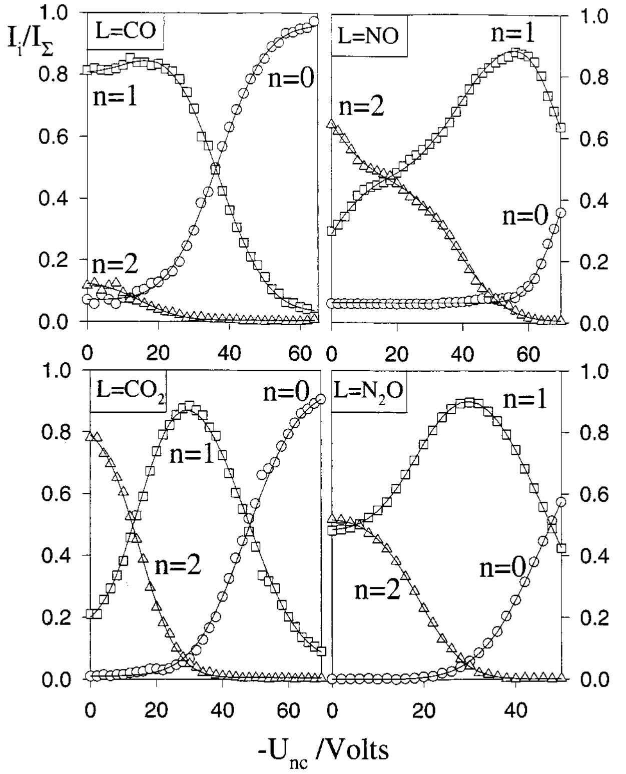

Figure 4. Multicollision CID results for (c-C_5H_5)Mg(L)$_n^+$ with L = CO, NO, CO_2, and N_2O in the laboratory energy scale. The measurements were performed with a helium buffer−collision gas at a total pressure of 0.35 ± 0.01 Torr. (c-C_5H_5)Mg^+ was generated from pure (c-C_5H_5)$_2$Mg in a low-pressure ionization source by 25 eV electron-impact dissociative ionization, selected, injected into the flow tube, and then allowed to react with the neutral ligand, L, upstream of the CID region. The flows of the ligands, L, are as follows (in molecules s^{-1}): CO at 2.0×10^{18}, NO at 3.0×10^{18}, CO_2 at 1.3×10^{18}, and N_2O at 2.5×10^{18}.

molecule^{-1} s^{-1}). The ligation reactions for the addition of the next two NO_2 molecules appeared to achieve equilibrium (see Table 3). The CID profiles indicate that the NO_2 ligands are removed sequentially and that the threshold for dissociation drops with increasing ligation.

The reaction profile of the ligation chemistry of (c-C_5H_5)-Mg^+ with H_2O is shown on the left-hand side of Figure 6. Ligation with up to seven molecules was observed in the range of chosen additions of water vapor. A fit to the observed reaction profiles indicates that the ligation remains rapid all the way. Equilibrium analyses of ion ratios indicated that the ligation reactions were far removed from equilibrium up to the addition of at least three water molecules, and this is reasonably consistent with the measured onsets for dissociation. For higher additions the ion profiles were not sufficiently developed to provide reliable estimates of equilibrium constants and dissociation onsets could not be measured because of the low signal intensities. The onset observed for the dissociation of (c-C_5H_5)-Mg(H_2O)$_3^+$ deserves further comment. The inflections in the dissociation curve of (c-C_5H_5)Mg(H_2O)$_3^+$ and the concomitant

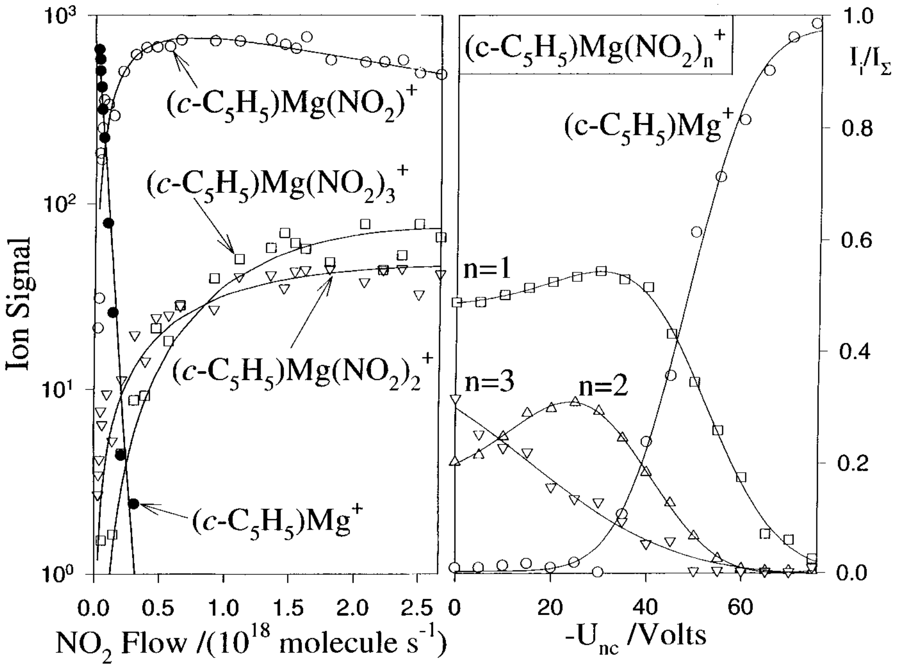

Figure 5. (Left) Experimental data for the reaction of (c-C_5H_5)Mg^+ with NO_2 in helium buffer gas at 294 ± 3 K and 0.35 ± 0.01 Torr. (c-C_5H_5)Mg^+ was produced initially by 25 eV electron-impact dissociative ionization of magnesocene vapor. The solid lines represent a fit of the experimental data with the solution of the differential equations appropriate to the observed sequential reactions. (Right) Multicollision CID results for (c-C_5H_5)$Mg(NO_2)_n^+$ in the laboratory energy scale and a flow of $NO_2 = 2.5 \times 10^{18}$ molecules s^{-1}.

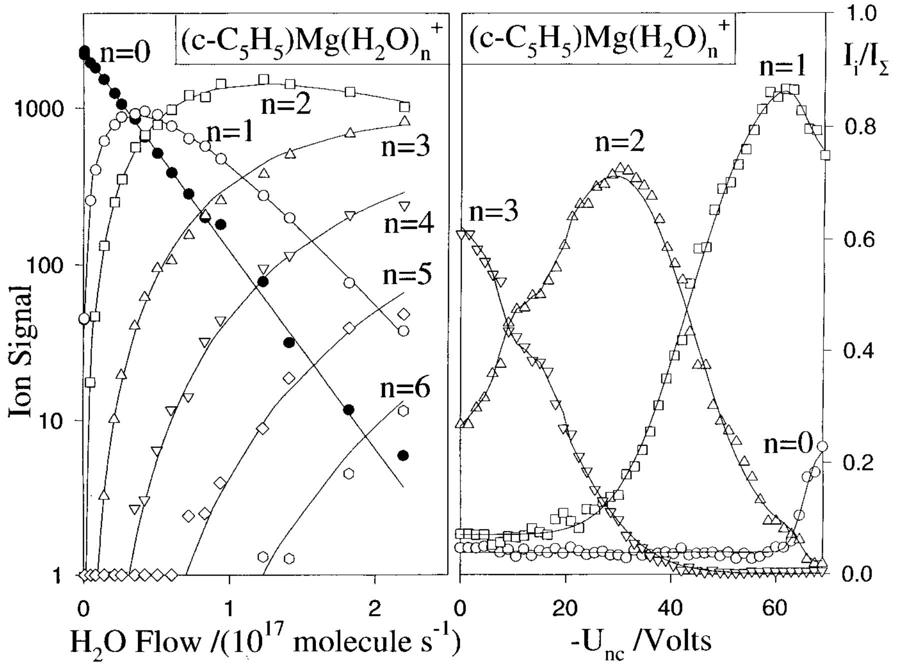

Figure 6. (Left) Experimental data for the reaction of (c-C_5H_5)Mg^+ with H_2O. The measurements were performed at 294 ± 3 K and at a helium buffer gas pressure of 0.35 ± 0.01 Torr. (c-C_5H_5)Mg^+ was formed initially by 25 eV electron-impact dissociative ionization of Mg(c-C_5H_5)$_2$. The solid lines represent a fit of the experimental data with the solution of the differential equations appropriate to the observed sequential reactions. (Right) Multicollision CID results for (c-C_5H_5)$Mg(H_2O)_n^+$ in the laboratory energy scale and a flow of $H_2O = 2.5 \times 10^{17}$ molecules s^{-1}.

appearance curve of (c-C_5H_5)$Mg(H_2O)_2^+$ in Figure 6 indicate the presence of two states or isomers of (c-C_5H_5)$Mg(H_2O)_3^+$. We interpret the data in terms of the presence of two isomers of (c-C_5H_5)$Mg(H_2O)_3^+$, since the third water ligand may coordinate directly to magnesium or hydrogen-bond to one of the two directly coordinated water molecules. The CID curve for (c-C_5H_5)$Mg(H_2O)_3^+$ suggests that the smaller fraction of these ions has a lower onset for dissociation. This fraction is attributed to the hydrogen-bonded isomers, since the hydrogen bond will be weaker than the bond resulting from direct coordination. The larger fraction of the ions are then more strongly bonded, and this is consistent with the standard free energy of ligation estimated to be less than −10 kcal mol^{-1} from an equilibrium ratio analysis of the kinetic data.

We have shown recently that three ammonia molecules sequentially ligate to the half-sandwich and do so rapidly with rate coefficients of 1.2×10^{-9}, 1.4×10^{-9}, and 3.7×10^{-10} cm^3 molecule^{-1} s^{-1}.[26] All three additions were far removed from equilibrium, and there was no evidence for the addition of a fourth ammonia ligand. CID experiments showed the sequential

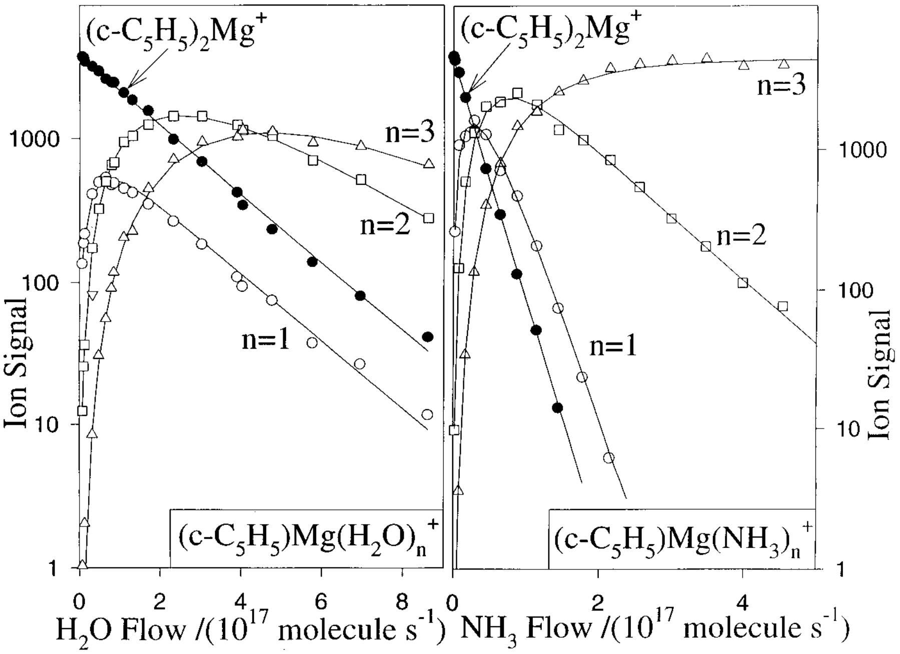

Figure 7. Experimental data for the reactions of $(c\text{-}C_5H_5)_2Mg^+$ with H_2O (left) and NH_3 (right). The measurements were performed at 294 ± 3 K and at a helium buffer-gas pressure of 0.35 ± 0.01 Torr. $(c\text{-}C_5H_5)_2Mg^+$ was generated from pure $(c\text{-}C_5H_5)_2Mg$ in a low-pressure ionization source by 5 eV electron-impact dissociative ionization. The solid lines represent a fit of the experimental data with the solution of the differential equations appropriate to the observed sequential reactions.

removal of ammonia ligands from $(c\text{-}C_5H_5)Mg(NH_3)_3{}^+$ by collisional dissociation.[26] Inflections were observed in the dissociation curve of $(c\text{-}C_5H_5)Mg(NH_3)_3{}^+$ and the concomitant appearance curve of $(c\text{-}C_5H_5)Mg(NH_3)_2{}^+$, and these were interpreted in terms of the possible presence of two isomers of $(c\text{-}C_5H_5)Mg(NH_3)_3{}^+$, as is suggested here for $(c\text{-}C_5H_5)Mg(H_2O)_3{}^+$. However, the fraction of what presumably again is a weaker bound hydrogen-bonded isomer is very low.

C. $(c\text{-}C_5H_5)_2Mg^+$ Reactions. The full-sandwich $(c\text{-}C_5H_5)_2Mg^+$ cation was observed to react only with NH_3 and H_2O. The observed reactions with these two molecules correspond to ligand substitution or switching as in reaction 11.

$$(c\text{-}C_5H_5)_2Mg^+ + L \rightarrow (c\text{-}C_5H_5)Mg(L)^+ + (c\text{-}C_5H_5) \quad (11)$$

Ligand switching was not observed with L = H_2, N_2, CO, NO, O_2, CO_2, N_2O, and NO_2, *nor was simple addition*. The measured upper limits to the rate coefficients for reactions of $(c\text{-}C_5H_5)_2Mg^+$ with these molecules were in the range between $<10^{-14}$ and $<10^{-13}$ cm^3 $molecule^{-1}$ s^{-1}.

Figure 7 presents reaction profiles for the reactions of $(c\text{-}C_5H_5)_2Mg^+$ with NH_3 and H_2O. The first step in the observed chemistry in both cases is a rapid ligand switching with one of the cyclopentadienyl rings in $(c\text{-}C_5H_5)_2Mg^+$. The ligand substitution is followed by the sequential addition of two ligands in the case of NH_3 and more than two ligands in the case of H_2O, in a manner similar to that observed for the higher-order reactions of the half-sandwich cation, and with similar rates.

The switching reactions with NH_3 and H_2O are not equally fast; the switching reaction with H_2O is about 5 times slower than that with NH_3, which reacts at close to the collision rate (see Table 1). The rapid occurrence of switching implies that these two molecules ligate more strongly to $(c\text{-}C_5H_5)Mg^+$ than $c\text{-}C_5H_5$ itself, viz. that $D_{298}((c\text{-}C_5H_5)Mg^+{-}NH_3)$ and $D_{298}((c\text{-}C_5H_5)Mg^+{-}H_2O) > D_{298}((c\text{-}C_5H_5)Mg^+{-}\ c\text{-}C_5H_5)$. Conversely, the failure to observe switching with H_2, N_2, CO, NO, O_2, CO_2, N_2O, and NO_2 implies that these molecules ligate less strongly.

D. Variation in the Rate of Ligation with the Number of $(c\text{-}C_5H_5)$ Ligands. The results of the measurements reported here show a strong dependence of the rate of ligation with the number of $(c\text{-}C_5H_5)$ ligands. We have seen that Mg^+ is unreactive except with ammonia, which ligates slowly ($k = 4 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}). Single ligation of Mg^+ with $c\text{-}C_5H_5$ substantially *enhances* reactivity; the initial ligation of the “half-sandwich” $(c\text{-}C_5H_5)Mg^+$ cation is rapid ($k > 5 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}) with all ligands except H_2, N_2, and O_2. Double ligation with $c\text{-}C_5H_5$ substantially *reduces* reactivity. No ligation was observed with the “full-sandwich” magnesocene cation, although fast bimolecular *ligand-switching* reactions were observed to occur with NH_3 and H_2O.

We attribute the enhanced rates of ligation of the half-sandwich to increased collisional stabilization of the intermediate ligated complex. The increase in collisional stabilization is a consequence of an increase in the lifetime of the intermediate complex that is expected from the increase in the number of degrees of freedom that may participate in energy redisposition.

Mg^+ in the full-sandwich appears to be coordinatively saturated, and we take this to account for the observed inertness of the full-sandwich to further ligation, even by longer-range electrostatic bonding. The observed nonreactivity of the full-sandwich cation also suggests that there is no strong bonding of any of the ligands investigated with the $c\text{-}C_5H_5$ ring substituents themselves, as might be expected.

E. Variation in the Rate of Ligation with the Number of Ligands, L. Ammonia was the only one of the 10 molecules investigated that ligated Mg^+ with a measurable rate coefficient and did so sequentially. We have discussed previously the trend in the observed kinetics of this sequential ligation.[26] We have proposed that the precipitous drop in the observed rate of ligation of the fourth ligand and the existence of a weakly bonded population of ligated ions in the measured CID spectra for $Mg(NH_3)_3{}^+$ and $Mg(NH_3)_4{}^+$ may signify a change in the nature of the bonding from direct bonding to hydrogen bonding in a second coordination shell with the addition of the third ligand.

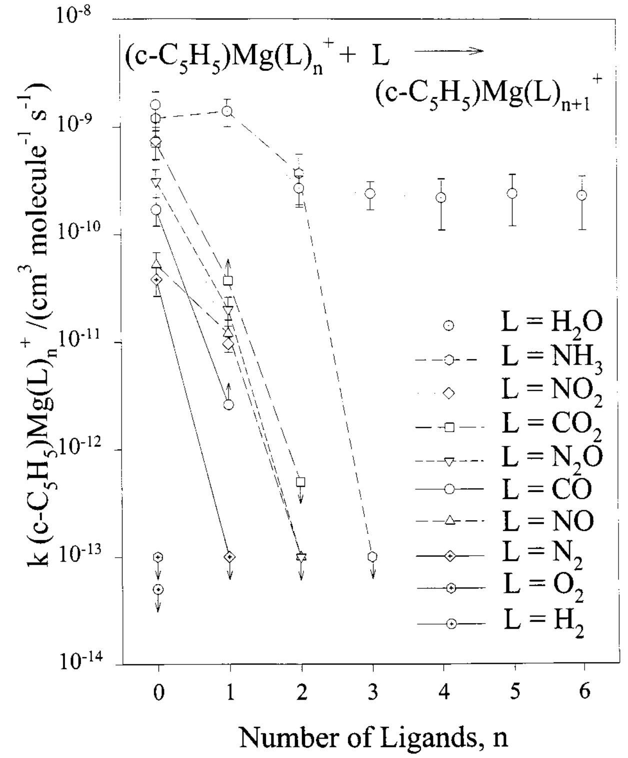

Figure 8. Semilogarithmic correlation of the rate coefficient for the sequential ligation of (c-C_5H_5)Mg^+ by H_2, O_2, N_2, CO, CO_2, NO, NO_2, N_2O, NH_3, and H_2O with the number of ligands n added in the gas phase at 294 ± 3 K and at a helium buffer gas pressure of 0.35 ± 0.01 Torr.

The range in the rates of ligation of (c-C_5H_5)Mg^+ with different ligands and their dependence on the number of ligands are shown in Figure 8. Measured rate coefficients for ligation with a single molecule range from 1.6×10^{-9} to $< 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1}, and the number of ligands observed to add sequentially ranges from 1 to >7. Only hydrogen and oxygen were observed *not* to ligate to (c-C_5H_5)Mg^+ under our chosen operating conditions.

The magnitude of the rate of ligation of (c-C_5H_5)Mg^+ under our operating conditions, presumed here to occur by collisional stabilization, is determined in part by the strength, and therefore the nature, of the bonding interaction between the ligand and (c-C_5H_5)Mg^+ or (c-C_5H_5)$Mg(L)_n^+$. This interaction can be covalent or purely electrostatic or, as is expected to be the case in the observed water ligation, may involve hydrogen bonding with existing ligands. (c-C_5H_5)$Mg^+{-}L$ binding energies are generally not known. But we can say that for multiple additions in which degrees of freedom continue to rise, a sharp drop in rate under our operating conditions must reflect a sharp drop in ligand-binding energy. This being the case, we can define a primary coordination number, as we have done previously, as the number of ligands added sequentially before the occurrence of a sharp drop in the rate of ligation.[21] For the systems investigated here, the primary coordination number should be equal to the number of ligands that bond directly with the Mg in the (c-C_5H_5)Mg^+ cation. The definition, or "sharpness", of this coordination number of course will depend on the sharpness of the transition in ligation energy. Our previous measurements indicate that a transition between a strong coordinate bond to a weak electrostatic bond upon ligation can lead to a drop in the rate of ligation by 2 or more orders of magnitude.[21] A transition from strong coordinate "inner-shell" bonding to "outer-shell" hydrogen bonding should lead to a smaller drop in rate, since hydrogen bonding is usually stronger than electrostatic bonding. Concurrent "inner-shell" ligation and "outer-shell" ligation will obfuscate the determination of primary coordination numbers. The measured multicollision-induced dissociation profiles provide additional information on relative bond strengths and so may be used in conjunction with the measured kinetics to better determine the coordination number. Accordingly, on the basis of results shown in Figure 8, the following coordination numbers can be assigned for coordination with (c-C_5H_5)Mg^+: 0 for O_2 and H_2, 1 for N_2, 1 or 2 for CO and NO_2, and 2 for NO, N_2O, and CO_2.

The situation with ammonia and water is different, since both of these molecules either may bond directly to the Mg center in an inner coordination sphere or may bond in an outer coordination sphere by weaker hydrogen bonding. In this case we must distinguish between a *primary* coordination number corresponding to ligation in an inner coordination sphere and a *secondary* coordination number corresponding to ligation in an outer coordination sphere as we have done recently in our studies of the ligation of FeO^+ with water molecules.[20]

Our previously reported results for the ligation of (c-C_5H_5)-Mg^+ with ammonia indicate rapid sequential ligation with three ammonia molecules and a drop of $>10^3$ in the rate of ligation with a fourth molecule.[26] There is only a small drop (a factor of 3.8) in the rate of ligation of the third molecule, and the CID experiments indicate only a very small proportion of a weakly bonded isomer of (c-C_5H_5)$Mg(NH_3)_3^+$ that is likely formed by hydrogen bonding. The sequential ligation of (c-C_5H_5)Mg^+ with ammonia is therefore consistent with a primary coordination number of 3.

The break in the kinetics of ligation with H_2O observed at $n = 2$ in Figure 8 suggests an apparent primary coodination number for H_2O of only 2 and a secondary coordination number of >5. The third water molecule apparently is bonded weakly compared to the first two and presumably by hydrogen bonding. However, the CID data suggest that the third hydrate is a mixture of directly coordinated and hydrogen-bonded isomers, which suggests a primary coordination number of 3. A transition from direct to hydrogen bonding has been shown to occur theoretically for the addition of water to the bare Mg^+ ion; the fourth water molecule in $Mg^+(H_2O)_4$ is predicted to bond more strongly to the other water molecules by hydrogen bonding than to the metal itself.[13,34] However, threshold CID measurements of the bond dissociation of $Mg(H_2O)_n^+$ with $n = 1-4$ reported by Dalleska et al.[33] showed no evidence for a break that would suggest the formation of a hydration shell.

F. Structures and Bonding. Our multiple-CID experiments indicate that the ligands that were observed to add sequentially to Mg^+ and to (c-C_5H_5)Mg^+ are all removed *sequentially* by collision-induced dissociation. There was no evidence for the occurrence of intramolecular ligand−ligand interactions leading to bond redisposition in the ligated ions of the type we have reported previously for several hydrocarbon-ligated Fe^+ ions.[21] Production of MgL^+ was not observed over the available range in CID energy. Apparently, the (c-C_5H_5)$Mg{-}L^+$ bond is the weakest bond in each case. Also, all the CID profiles reported here, with the exception of those for (c-C_5H_5)$Mg(NO)_2^+$ and (c-C_5H_5)$Mg(H_2O)_3^+$, are consistent with the presence of only one isomer of the ligated ion.

As far as we are aware, there are no previous determinations, either experimental or theoretical, of the structures and bonding of coordinated (c-C_5H_5)MgL_n^+ cations. Some *plausible* structures for these ions are presented in Figure 9. We have discussed previously, in detail, the structures and bonding of $Mg(NH_3)_n^+$ ($n = 1-4$).[26] Our experiments show that three molecules of

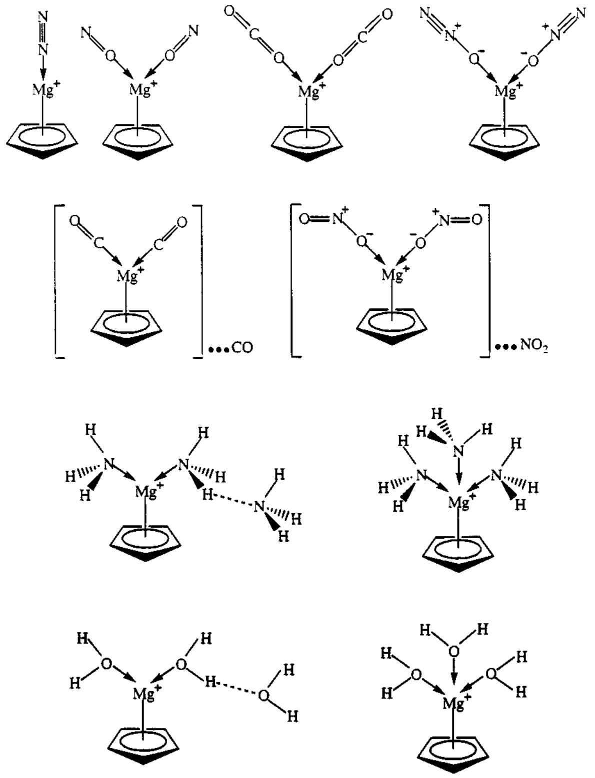

Figure 9. Proposed structures for several ligated (c-C_5H_5)Mg^+ cations.

NH_3 add sequentially to (c-C_5H_5)Mg^+ and are removed sequentially by multicollision-induced dissociation. The three ammonia molecules are expected to ligate directly to the magnesium and to attach through the lone pair on the nitrogen as shown in Figure 9. There was some evidence in the CID profile of (c-C_5H_5)Mg$(NH_3)_3^+$ for the formation of small amounts of the hydrogen-bonded isomer also shown in Figure 9.

The "end-on" structure of (c-C_5H_5)Mg$(N_2)^+$ proposed in Figure 9 is based on what is known about $CH_3N_2^+$, HN_2^+,[35] and Mg$(N_2)^+$. Results of a spectroscopic study of Mg$(N_2)^+$ produced in a molecular beam environment using a pulsed nozzle laser vaporization cluster source support a linear ground-state "end-on" arrangement as in $Mg^+ \leftarrow N{\equiv}N$ ($C_{\infty v}$, $^2\Sigma^+$).[10] Furthermore, Bauschlicher's[8] theoretical studies and those of Tachikawa et al.[36] support this arrangement for the ground state with a small binding energy, $D_0(Mg^+{-}N_2) = 2.4$ kcal mol^{-1}. On the basis of these results, we propose that the half-sandwich ligated by N_2 would bond through the lone pair on one of the nitrogen atoms, forming a complex with a 5-fold axis of symmetry.

Studies by Sodupe and Bauschlicher[10] on $Mg^+{-}CO_2$ systems determined that a linear ion−molecule complex is the result of the first addition of CO_2 to Mg^+ with the bonding dominated by charge−quadrupole interactions. The second ligation of Mg^+ by CO_2 gives a structure that has an OMgO angle of ~90° and an MgOC angle of ~170°. On the basis of these results, a possible structure for (c-C_5H_5)Mg^+ with two CO_2 ligands is shown in Figure 9. $CO{-}Mg^+$ has also been examined by Bauschlicher's group.[9] Ligation through both sites of CO was investigated. MCPF calculations using an ANO basis set showed that ligation through the carbon is preferred by 3.2 kcal mol^{-1} over coordination through oxygen, and the structure proposed in Figure 9 for the half-sandwich complex is based upon these results.

Only one of three possible isomers of (c-C_5H_5)Mg$(NO)_2^+$ is shown in Figure 9. Computational studies at B3LYP/3-21G* in our laboratory indicate that the oxygen in NO is the preferred site of ligation to the closed-shell ion Mg^{2+}. Addition to the nitrogen atom of NO is only slightly less exothermic. Two plausible isomers of (c-C_5H_5)Mg$(H_2O)_3^+$ are shown in Figure 9, one with an inner shell containing two water molecules and the second with an inner shell of three water molecules.

G. Standard Free Energies of Ligation. Table 3 summarizes the standard free energies of ligation deduced from the measured values (or limiting values) of equilibrium constants for reactions of type 10. No previous values, either experimental or theoretical, are available for comparison. Standard entropies of ligation are also unavailable so that standard enthalpies of formation cannot be deduced from the standard free energies. The values for $\Delta G°$ (ligation) summarized in Table 3 range from -7.7 to $-(\geq 12.2)$ kcal mol^{-1}. Values for $\Delta S°$ (ligation) are likely to be more negative than -25 cal K^{-1} judging from available experimental values for entropy changes for ion−cluster dissociation.[37] A statistical thermodynamic assessment indicates values for $\Delta S°$(translation) of -35.5 ± 0.5 cal K^{-1}. $\Delta S°$ (rotation) is not known but will be much smaller, say less than ca. -5 cal K^{-1}, and $\Delta S°$(vibration) should be negligible. Thus, $\Delta H°$(ligation), and also $\Delta E°$(ligation), will be uniformly at least ca. 9 kcal mol^{-1} more negative than $\Delta G°$(ligation).

The low values of the free energies (and estimated enthalpies) for the second ligation of (c-C_5H_5)Mg^+ with CO and CO_2 and the higher values for the second ligation with NO and N_2O are consistent with the results of collision-induced dissociation experiments shown in Figure 4. These indicate very low onset energies for the dissociation of (c-C_5H_5)Mg$(CO)_2^+$ and (c-C_5H_5)Mg$(CO_2)_2^+$ and higher dissociation energies for the bulk of (c-C_5H_5)Mg$(NO)_2^+$ and (c-C_5H_5)Mg$(N_2O)_2^+$.

The standard free energies of ligation deduced from the measured equilibrium constants for reaction 10 with L = NO_2 are -8.5 and -9.4 kcal mol^{-1} for $n = 1$ and 2, respectively. These low free energies of ligation are again consistent with the observed thresholds for multicollision-induced dissociation; (c-C_5H_5)Mg$(NO_2)_3^+$ exhibits a very early threshold for dissociation, while the early onset of (c-C_5H_5)Mg$(NO_2)^+$ indicates an early threshold for the dissociation of (c-C_5H_5)Mg$(NO_2)_2^+$, which is present initially and is also produced by the dissociation of (c-C_5H_5)Mg$(NO_2)_3^+$.

H. Circumstellar $MgNH_2$. Two Mg-containing molecules, MgNC and MgCN, have been identified by radioastronomers in observations of metal-bearing compounds toward the circumstellar shell of the late-type carbon star IRC +10216.[38,39] Specifically, these Mg compounds appear in the *outer* shell of IRC +10216 "where temperatures and densities are sufficiently low such that the chemistry is kinetically controlled and photochemical and *ion−molecule reactions occur*".[39] We propose here, on the basis of the measured kinetics for the reaction of Mg^+ with ammonia, that ion−molecule reactions analogous to those proposed for the formation of MgNC[37] can lead to the formation of the $MgNH_2$ molecules in these environments. The proposed mechanism involves the initial ligation of Mg^+ with ammonia by radiative association, reaction 12, followed by dissociative recombination with electrons, reaction 13.

$$Mg^+ + NH_3 \rightarrow MgNH_3^+ + h\nu \qquad (12)$$

$$MgNH_3^+ + e \rightarrow MgNH_2 + H \qquad (13)$$

Conclusions

The application of the SIFT technique has allowed an evaluation of the intrinsic kinetics of ligation of Mg^+,

(c-C_5H_5)Mg^+, and (c-C_5H_5)$_2$$Mg^+$ with inorganic ligands at room temperature in helium at 0.35 Torr. The rates and extent of ligation depend on the degree of ligation with c-C_5H_5 and the nature and size of the inorganic ligand. Thermalized Mg^+ ions did not react with any of the inorganic ligands chosen for study, except NH_3, and this can be attributed to low ligand-binding energies and relatively small numbers of degrees of freedom in the ligated complexes. Single ligation of Mg^+ with c-C_5H_5 substantially *enhances* the efficiency of ligation. Double ligation with c-C_5H_5 substantially *reduces* the efficiency of ligation; no ligation was observed with the "full-sandwich" magnesocene cation. Fast bimolecular *ligand-switching* reactions occur instead but only with NH_3 and H_2O, indicating that these two molecules ligate more strongly to (c-C_5H_5)Mg^+ than does c-C_5H_5 itself. Higher-order ligation reactions of (c-C_5H_5)Mg^+ with CO, NO, NH_3, CO_2, N_2O, and NO_2 proceed with diminishing rates, adding up to at most three ligands. H_2O is an exception; at least six H_2O molecules were observed to add sequentially to (c-C_5H_5)Mg^+. Variations in the observed rate of this addition can be attributed to the completion of an "inner" coordination shell and the onset of hydrogen bonding in an "outer" coordination shell that accounts for the continuing rapid ligation. Higher-order ligands are removed sequentially by multicollision CID with He atoms; there is no evidence for intramolecular interligand interactions leading to unimolecular bond redisposition after ligation.

Acknowledgment. Continued financial support from the Natural Science and Engineering Research Council of Canada is greatly appreciated.

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