

# Gas-Phase Coordination of $\text{Mg}^+$ , $(c\text{-C}_5\text{H}_5)\text{Mg}^+$ , and $(c\text{-C}_5\text{H}_5)_2\text{Mg}^+$ with Small Inorganic Ligands

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The coordination of the electronic ground states of  $\text{Mg}^+$ ,  $(c\text{-C}_5\text{H}_5)\text{Mg}^+$ , and  $(c\text{-C}_5\text{H}_5)_2\text{Mg}^+$  with the inorganic molecules  $\text{H}_2$ ,  $\text{NH}_3$ ,  $\text{H}_2\text{O}$ ,  $\text{N}_2$ ,  $\text{CO}$ ,  $\text{NO}$ ,  $\text{O}_2$ ,  $\text{CO}_2$ ,  $\text{N}_2\text{O}$ , and  $\text{NO}_2$  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  $294 \pm 3$  K and a helium buffer-gas pressure of  $0.35 \pm 0.01$  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  $c\text{-C}_5\text{H}_5$  and the nature and size of the inorganic ligand.  $\text{Mg}^+$  was found to be unreactive except with ammonia, which was found to add slowly ( $k = 4 \times 10^{-12}$   $\text{cm}^3$  molecule $^{-1}$  s $^{-1}$ ). Single ligation of  $\text{Mg}^+$  with  $c\text{-C}_5\text{H}_5$  substantially enhances the efficiency of ligation; the initial ligation is rapid ( $k > 5 \times 10^{-11}$   $\text{cm}^3$  molecule $^{-1}$  s $^{-1}$ ) with all ligands except  $\text{H}_2$ ,  $\text{N}_2$ , and  $\text{O}_2$ . Double ligation with  $c\text{-C}_5\text{H}_5$  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  $\text{NH}_3$  and  $\text{H}_2\text{O}$ , indicating that these two molecules ligate more strongly to  $(c\text{-C}_5\text{H}_5)\text{Mg}^+$  than does  $c\text{-C}_5\text{H}_5$  itself. Higher-order ligation was observed between  $\text{Mg}^+$  and  $\text{NH}_3$  and between the “half-sandwich”  $(c\text{-C}_5\text{H}_5)\text{Mg}^+$  cation and  $\text{CO}$ ,  $\text{NO}$ ,  $\text{NH}_3$ ,  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{N}_2\text{O}$ , and  $\text{NO}_2$ . After a slow initiation step, ammonia added to  $\text{Mg}^+$  up to four times to generate  $\text{Mg}(\text{NH}_3)_4^+$ . Higher-order ligation reactions of  $(c\text{-C}_5\text{H}_5)\text{Mg}^+$  with  $\text{CO}$ ,  $\text{NO}$ ,  $\text{NH}_3$ ,  $\text{CO}_2$ ,  $\text{N}_2\text{O}$ , and  $\text{NO}_2$  proceed with diminishing rates adding up to at most three ligands.  $\text{H}_2\text{O}$  is an exception; at least six  $\text{H}_2\text{O}$  molecules were observed to add sequentially to  $(c\text{-C}_5\text{H}_5)\text{Mg}^+$ . 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 redistribution 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  $\text{Mg}^+$  in the gas phase were reported as early as 1968 by Ferguson and Fehsenfeld<sup>1</sup> 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  $\text{Mg}^+$  in the earth's upper atmosphere in stratified layers at 105 and 120 km where magnesium is thought to be deposited by meteor ablation.<sup>2</sup> Ferguson and Fehsenfeld drew attention to the nonreactivity of  $\text{Mg}^+$  expected on the basis of energetics in bimolecular reactions with the abundant stable atmospheric gases  $\text{O}_2$ ,  $\text{N}_2$ , and  $\text{CO}_2$ , 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  $\text{O}_3$ ,  $\text{Cl}_2$ ,  $\text{Br}_2$ ,  $\text{H}_2\text{O}_2$ ,  $\text{HNO}_3$ , and  $\text{CCl}_4$ .<sup>3</sup> There is continuing interest in the atmospheric chemistry of  $\text{Mg}^+$ , particularly as it proceeds in meteor trains,<sup>4</sup> the atmospheres of stars,<sup>5</sup> and the atmospheres of Neptune and the other giant planets;<sup>6</sup> more kinetic data for reactions of this ion, for example with  $\text{H}_2$  and hydrocarbons,

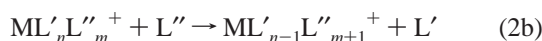
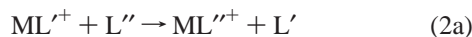
have been called for.<sup>6</sup> Little progress has been made in this regard, although systematic studies of the kinetics of reactions of  $\text{Mg}^+$  with a large variety of inorganic and organic molecules using a selected-ion flow tube (SIFT)/glow discharge technique have been initiated in the laboratory of Babcock.<sup>7</sup> Preliminary results from this laboratory indicate no reactions with the inorganic molecules  $\text{H}_2$ ,  $\text{N}_2$ ,  $\text{CO}$ ,  $\text{NO}$ ,  $\text{H}_2\text{O}$ ,  $\text{SO}_2$ ,  $\text{NH}_3$ ,  $\text{NO}_2$ , and  $\text{N}_2\text{O}$  at room temperature in helium carrier gas (at ca. 0.3 Torr), although addition reactions were reported for  $\text{CO}_2$  and  $\text{H}_2\text{S}$  as well as hydrocarbons generally, except methane.<sup>7</sup>

A prime focus in organomagnesium chemistry has been the intrinsic nature of  $\text{Mg}^+$ –ligand interactions and the influence of such interactions on the chemistry of bare and ligated  $\text{Mg}^+$ . Previous theoretical investigations, as well as systematic gas-phase experiments, have led to structures and total energies of isolated ligated  $\text{Mg}^+$  ions as well as intrinsic  $\text{Mg}^+$ –L binding energies. Theoretical studies of ligated  $\text{Mg}^+$  have been reported primarily by Bauschlicher and co-workers<sup>8–13</sup> for singly ligated  $\text{MgL}^+$  cations with  $L = \text{H}_2$ ,  $\text{N}_2$ ,  $\text{CO}$  and many organic molecules and for multiply ligated  $\text{MgL}_n^+$  cations with  $L = \text{H}_2\text{O}$  and  $\text{NH}_3$ . Gardner et al. have computed the ionic species  $\text{MgX}^+$  and  $\text{MgX}_2^+$  ( $X = \text{H}$ ,  $\text{F}$ ,  $\text{Cl}$ , and  $\text{OH}$ ).<sup>14</sup> The weakly bound ligated

$\text{Mg}^+-\text{D}_2$ ,  $\text{Mg}^+-\text{N}_2$ ,  $\text{Mg}^+-\text{O}_2$ ,  $\text{Mg}^+-\text{H}_2\text{O}$ ,  $\text{Mg}^+-\text{N}_2\text{O}$ , and  $\text{Mg}^+-\text{CO}_2$  ions in which the bonding is primarily electrostatic in nature, as well as multiply ligated  $\text{CO}_2$  cations, have been examined experimentally using photoexcitation and dissociation spectroscopy.<sup>15</sup> Sequential bond energies for multiply ligated  $\text{Mg}^+(\text{H}_2\text{O})_n$  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.<sup>16</sup> The photoabsorption and photodissociation of  $\text{Mg}^+(\text{H}_2\text{O})_n$  have been investigated experimentally for  $n = 1$  and 2.<sup>17</sup> The latter has been shown to lead to the evaporation of water molecules as well as the production of  $\text{MgOH}^+$ .<sup>17</sup> Also, the dehydrogenation reaction 1 has been seen to occur spontaneously upon hydration at room temperature for  $n > 4$ .<sup>18</sup>



Relative  $\text{Mg}^+-\text{L}$  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.



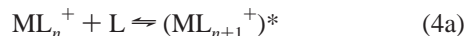
Preliminary results of such investigations with  $\text{M} = \text{Mg}^+$  and various organic and inorganic ligands have been reported using the SIFT technique.<sup>7</sup>

We report here systematic SIFT investigations of the reactivity of  $\text{Mg}^+$  toward inorganic molecules and of changes in  $\text{Mg}^+$  reactivity when the  $\text{Mg}^+$  cation is ligated with one and two cyclopentadienyl radicals. The  $\text{Mg}^+$ ,  $(c\text{-C}_5\text{H}_5)\text{Mg}^+$ , and  $(c\text{-C}_5\text{H}_5)_2\text{Mg}^+$  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  $\text{Mg}^+$  with inorganic gases was examined first, and then the change in reactivity was explored with the singly and doubly ligated ions  $(c\text{-C}_5\text{H}_5)\text{Mg}^+$  and  $(c\text{-C}_5\text{H}_5)_2\text{Mg}^+$ . It will be seen that the reactivity of  $\text{Mg}^+$  changes dramatically with single and double ligation and that the inorganic ligands themselves exhibit a variety of degrees of coordination with  $(c\text{-C}_5\text{H}_5)\text{Mg}^+$  in sequential ligation reactions.

The reactivities of  $\text{Mg}^+$ ,  $(c\text{-C}_5\text{H}_5)\text{Mg}^+$ , and  $(c\text{-C}_5\text{H}_5)_2\text{Mg}^+$  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.



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



and the lifetime of the intermediate  $(\text{ML}_{n+1}^+)^*$  against dissociation back to reactants is dependent on both the degrees of freedom in  $(\text{ML}_{n+1}^+)^*$  effective in intramolecular energy redistribution in the transient intermediate and its attractive well

depth  $D(\text{M}^+-\text{L}_{n+1})$ .<sup>19</sup> We have recently applied this approach to the determination of intrinsic coordination numbers for  $\text{Fe}^+$  coordinated by a variety of inorganic and organic molecules.<sup>20,21</sup> 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  $\text{Mg}^+$  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  $\text{ML}_{n+1}^+$  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.<sup>22,23</sup> All measurements were performed at  $294 \pm 3$  K and at a helium buffer gas pressure of  $0.35 \pm 0.01$  Torr. The reactant ions,  $\text{Mg}^+$ ,  $(c\text{-C}_5\text{H}_5)\text{Mg}^+$ , and  $(c\text{-C}_5\text{H}_5)_2\text{Mg}^+$  were all generated in a low-pressure ion source from  $(c\text{-C}_5\text{H}_5)_2\text{Mg}$  by electron impact ionization at electron energies of 35, 50, and 10 eV, respectively. Some collisional dissociation of  $(c\text{-C}_5\text{H}_5)_2\text{Mg}^+$  and  $(c\text{-C}_5\text{H}_5)\text{Mg}^+$  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  $\text{Mg}^+$  in the flow tube. The injected ions were thermalized by collisions (about  $4 \times 10^5$ ) 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  $\text{H}_2\text{O}$ , as a dilute (0.2–5%) mixture in helium. The  $\text{H}_2\text{O}$  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.<sup>22,23</sup> The rate coefficients for primary reactions reported here are estimated to have an absolute accuracy of  $\pm 30\%$ . 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.<sup>24</sup>

## Results and Discussion

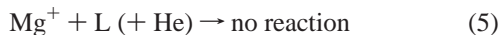
Table 1 summarizes, in order of increasing molecular weight of the reactant, the rate coefficients measured for primary reactions of  $\text{Mg}^+$ ,  $(c\text{-C}_5\text{H}_5)\text{Mg}^+$ , and  $(c\text{-C}_5\text{H}_5)_2\text{Mg}^+$ . Rate coefficients deduced for higher-order reactions are summarized in Table 2. All rate coefficients are apparent bimolecular rate coefficients at  $294 \pm 3$  K and a helium buffer gas pressure of  $0.35 \pm 0.01$  Torr. Standard enthalpy changes referred to in the text were derived from the values found in the compilation of Lias et al.<sup>25</sup> unless indicated otherwise.

**TABLE 1: Measured Rate Coefficients for Reactions of the Ground States of Mg<sup>+</sup>, (c-C<sub>5</sub>H<sub>5</sub>)Mg<sup>+</sup>, and (c-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Mg<sup>+</sup> with Selected Inorganic Ligands Proceeding at 294 ± 3 K in Helium Buffer Gas at a Total Pressure of 0.35 ± 0.01 Torr<sup>a</sup>**

ligand	Mg <sup>+</sup>	(c-C <sub>5</sub> H <sub>5</sub> )Mg <sup>+</sup>	(c-C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> Mg <sup>+</sup>
H <sub>2</sub>	NR, <10 <sup>-14</sup> [1.5 × 10 <sup>-9</sup> ]	NR, <5 × 10 <sup>-13</sup> [1.5 × 10 <sup>-9</sup> ]	NR, <10 <sup>-14</sup> [1.5 × 10 <sup>-9</sup> ]
NH <sub>3</sub>	4.0 × 10 <sup>-12</sup> [2.5 × 10 <sup>-9</sup> ]	1.2 × 10 <sup>-9</sup> [2.1 × 10 <sup>-9</sup> ]	1.2 × 10 <sup>-9</sup> [2.0 × 10 <sup>-9</sup> ]
H <sub>2</sub> O	NR, <10 <sup>-14</sup> [2.8 × 10 <sup>-9</sup> ]	1.6 × 10 <sup>-9</sup> [2.3 × 10 <sup>-9</sup> ]	2.6 × 10 <sup>-10</sup> [2.2 × 10 <sup>-9</sup> ]
N <sub>2</sub>	NR, <10 <sup>-13</sup> [8.6 × 10 <sup>-10</sup> ]	3.8 × 10 <sup>-11</sup> [6.7 × 10 <sup>-10</sup> ]	NR, <10 <sup>-13</sup> [6.3 × 10 <sup>-10</sup> ]
CO	NR, <10 <sup>-13</sup> [9.4 × 10 <sup>-10</sup> ]	1.7 × 10 <sup>-10</sup> [7.3 × 10 <sup>-10</sup> ]	NR, <10 <sup>-13</sup> [6.9 × 10 <sup>-10</sup> ]
NO	NR, <10 <sup>-13</sup> [8.8 × 10 <sup>-10</sup> ]	5.2 × 10 <sup>-11</sup> [6.8 × 10 <sup>-10</sup> ]	NR, <10 <sup>-13</sup> [6.4 × 10 <sup>-10</sup> ]
O <sub>2</sub>	NR, <10 <sup>-14</sup> [8.0 × 10 <sup>-10</sup> ]	NR, <10 <sup>-13</sup> [6.1 × 10 <sup>-10</sup> ]	NR, <10 <sup>-13</sup> [5.7 × 10 <sup>-10</sup> ]
CO <sub>2</sub>	NR, <10 <sup>-13</sup> [1.0 × 10 <sup>-9</sup> ]	7.1 × 10 <sup>-10</sup> [7.4 × 10 <sup>-10</sup> ]	NR, <10 <sup>-13</sup> [6.8 × 10 <sup>-10</sup> ]
N <sub>2</sub> O	NR, <10 <sup>-13</sup> [1.1 × 10 <sup>-9</sup> ]	3.1 × 10 <sup>-10</sup> [7.8 × 10 <sup>-10</sup> ]	NR, <10 <sup>-13</sup> [7.3 × 10 <sup>-10</sup> ]
NO <sub>2</sub>	NR, <10 <sup>-13</sup> [1.1 × 10 <sup>-9</sup> ]	7.4 × 10 <sup>-10</sup> [8.1 × 10 <sup>-10</sup> ]	NR, <10 <sup>-13</sup> [7.5 × 10 <sup>-10</sup> ]

<sup>a</sup>Reaction and collision rate coefficients are given in units of cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. 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.<sup>6</sup> NR denotes no reaction.

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



or reactions leading to bimolecular products, were observed between Mg<sup>+</sup> and H<sub>2</sub>, H<sub>2</sub>O, or O<sub>2</sub>,  $k_1 < 10^{-14}$  cm<sup>3</sup> molecules<sup>-1</sup> s<sup>-1</sup>, and between Mg<sup>+</sup> and N<sub>2</sub>, CO, NO, CO<sub>2</sub>, N<sub>2</sub>O, or NO<sub>2</sub>,  $k_1 < 10^{-13}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. However, as we have reported recently,<sup>26</sup> ammonia did ligate sequentially to form ammonia adducts according to the following reaction sequence for  $n$  from 0 to 4.



The rate coefficient for the ligation of bare Mg<sup>+</sup> with ammonia under our operating conditions was measured to be 4.1 ± 1.2 × 10<sup>-12</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>.

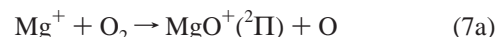
Except for the result with ammonia and carbon dioxide, these observations are qualitatively in agreement with the preliminary results reported by Babcock et al.<sup>7</sup> These authors did not observe addition with ammonia, perhaps because it is a very slow reaction, and did report the clustering of CO<sub>2</sub> with Mg<sup>+</sup>, perhaps because of a greater energy content for Mg<sup>+</sup>. For the reaction of Mg<sup>+</sup> with H<sub>2</sub>O, both our results and those of Babcock et al.<sup>7</sup>

**TABLE 2: Measured Rate Coefficients (in Units of cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>) for the Sequential Ligation Reactions (c-C<sub>5</sub>H<sub>5</sub>)Mg(L) <sub>$n$</sub> <sup>+</sup> + L → (c-C<sub>5</sub>H<sub>5</sub>)Mg(L) <sub>$n+1$</sub> <sup>+</sup> Proceeding at 294 ± 3 K in Helium Buffer Gas at a Total Pressure of 0.35 ± 0.01 Torr**

$n/L$	N <sub>2</sub>	CO	CO <sub>2</sub>	NO	N <sub>2</sub> O	NO <sub>2</sub>	NH <sub>3</sub>	H <sub>2</sub> O
0	3.8 × 10 <sup>-11</sup>	1.7 × 10 <sup>-10</sup>	7.1 × 10 <sup>-10</sup>	5.2 × 10 <sup>-11</sup>	3.1 × 10 <sup>-10</sup>	7.4 × 10 <sup>-10</sup>	1.2 × 10 <sup>-9</sup>	1.6 × 10 <sup>-9</sup>
1	<1 × 10 <sup>-13</sup>	≥2.6 × 10 <sup>-12</sup>	≥3.7 × 10 <sup>-11</sup>	1.2 × 10 <sup>-11</sup>	2.0 × 10 <sup>-11</sup>	≥9.6 × 10 <sup>-12</sup>	1.4 × 10 <sup>-9</sup>	1.4 × 10 <sup>-9</sup>
2			<5 × 10 <sup>-13</sup>	<1 × 10 <sup>-13</sup>	<1 × 10 <sup>-13</sup>		3.7 × 10 <sup>-10</sup>	2.7 × 10 <sup>-10</sup>
3							<1 × 10 <sup>-13</sup>	2.4 × 10 <sup>-10</sup>
4								2.2 × 10 <sup>-10</sup>
5								2.4 × 10 <sup>-10</sup>
6								2.3 × 10 <sup>-10</sup>

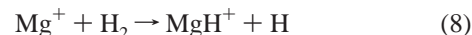
are inconsistent with the results of Castleman et al.<sup>18</sup> who report that water ligates Mg<sup>+</sup> in a flow-tube apparatus in He under similar conditions of pressure and temperature (a reaction rate coefficient was not reported). Also, hydrated M<sup>+</sup> ions were produced by Fuke et al.<sup>17</sup> 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<sup>+</sup>, which is achieved by laser vaporization of the metal in the experiments of Fuke et al.<sup>17</sup> and Castleman et al.<sup>18</sup> It is conceivable, as already has been pointed out by Babcock et al.,<sup>7</sup> that a large fraction of the Mg<sup>+</sup> ions generated by laser vaporization is excited and that only excited Mg<sup>+</sup> adds to water. It is also interesting to note that a slow addition reaction of Mg<sup>+</sup> with O<sub>2</sub> has been observed to proceed in Ar buffer gas under operating conditions otherwise similar to ours with a three-body rate coefficient of ~2.5 × 10<sup>-30</sup> cm<sup>6</sup> molecule<sup>-2</sup> s<sup>-1</sup>.<sup>27</sup> Apparently, argon is more effective than helium in stabilizing the transient intermediate (MgO<sub>2</sub><sup>+</sup>)\*.

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

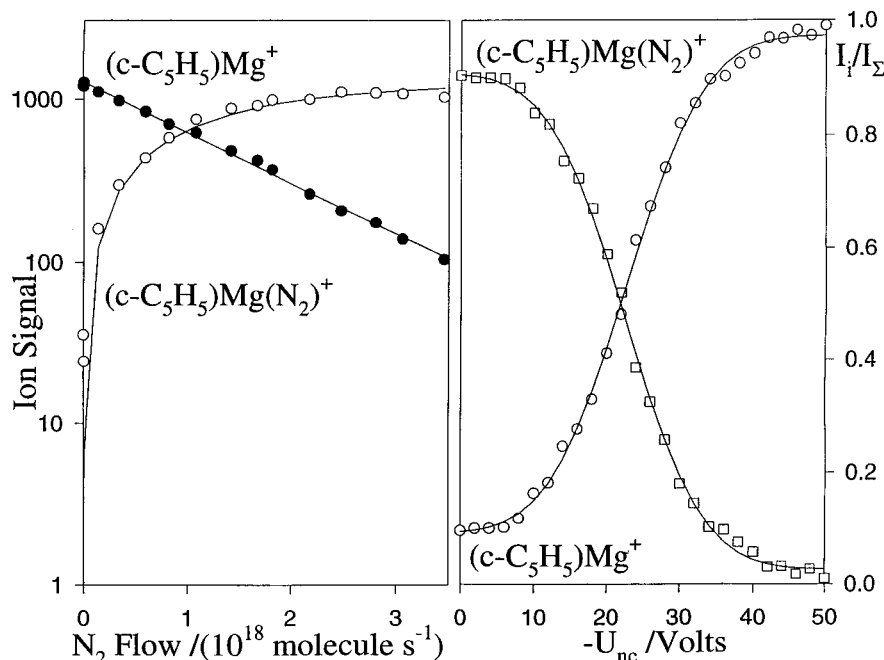


are endothermic by more than 80 and 170 kcal mol<sup>-1</sup>, respectively. We have used a method described previously<sup>28</sup> at the CCSD(T)(full)/6-311++G(2df,p)//MP2(full)/6-311++G(d,p) level of theory to calculate these endothermicities and found them to be 66 and 156 kcal mol<sup>-1</sup>, respectively, at 298 K. The standard enthalpy of formation at 298 K for the <sup>2</sup>Π ground state of MgO<sup>+</sup> was computed to be 219.7 kcal mol<sup>-1</sup>, which is lower than the experimental value of 238 ± 8 kcal mol<sup>-1</sup>.<sup>25</sup> 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<sup>29</sup> and the reported experimental value of 7.9 ± 0.1 eV, which was determined using Fourier transform mass spectrometry.<sup>30</sup> 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.<sup>31</sup>

A recent computation at MP2(FU)/6-311G\*\*//MP2(FU)/6-311G\*\* predicts an endothermicity for the hydrogenation reaction 8 of 220 kcal mol<sup>-1</sup>.<sup>32</sup>

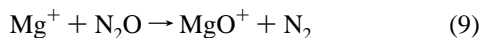


Insufficient thermochemical data are available for the standard enthalpy change for the analogous reaction between Mg<sup>+</sup> and N<sub>2</sub>. Oxidation reactions analogous to reaction 7 with H<sub>2</sub>O, CO, NO, CO<sub>2</sub>, N<sub>2</sub>O, or NO<sub>2</sub> and hydrogenation reactions analogous to reaction 8 with NH<sub>3</sub> and H<sub>2</sub>O are also endothermic according



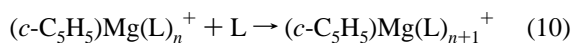
**Figure 1.** (Left) Experimental data for the reaction of  $(c\text{-C}_5\text{H}_5)\text{Mg}^+$  with  $\text{N}_2$ . The measurements were performed at  $294 \pm 3$  K and at a helium buffer gas pressure of  $0.35 \pm 0.01$  Torr.  $(c\text{-C}_5\text{H}_5)\text{Mg}^+$  was generated from pure  $(c\text{-C}_5\text{H}_5)_2\text{Mg}$  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  $(c\text{-C}_5\text{H}_5)\text{Mg}(\text{N}_2)^+$  in the laboratory energy scale and at a  $\text{N}_2$  flow of  $2.5 \times 10^{18}$  molecules  $\text{s}^{-1}$ .

to the available thermochemical data.<sup>25</sup> However, the oxidation reaction 9 with  $\text{N}_2\text{O}$ , which has a computed endothermicity of  $5 \pm 8$  kcal  $\text{mol}^{-1}$ ,<sup>25</sup> is a borderline case.



Failure to observe ligation with  $\text{Mg}^+$  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.<sup>19</sup> 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  $\text{Mg}^+$ . We have computed  $D_0(\text{Mg}^+ - \text{NH}_3) = 37.7$  kcal  $\text{mol}^{-1}$  (or  $D_{298} = 39.7$  kcal  $\text{mol}^{-1}$ ) at MP4SDTQ(fc)/6-311++G(2df,pp)/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  $\text{mol}^{-1}$  at MCP level using a TZ2P basis set<sup>11</sup> and an experimentally determined value of  $28.4 \pm 3.0$  kcal  $\text{mol}^{-1}$  at 0 K.<sup>33</sup>

**B.  $(c\text{-C}_5\text{H}_5)\text{Mg}^+$  Reactions.** In contrast to the chemistry of  $\text{Mg}^+$ ,  $(c\text{-C}_5\text{H}_5)\text{Mg}^+$  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  $(c\text{-C}_5\text{H}_5)\text{Mg}^+$  with  $\text{N}_2$ ,  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{N}_2\text{O}$ ,  $\text{NH}_3$ , and  $\text{H}_2\text{O}$  are summarized in Tables 1 and 2. All of the observed reactions were addition reactions of type 10:



There was no evidence for the oxidation of magnesium to form  $(c\text{-C}_5\text{H}_5)\text{MgO}^+$ .

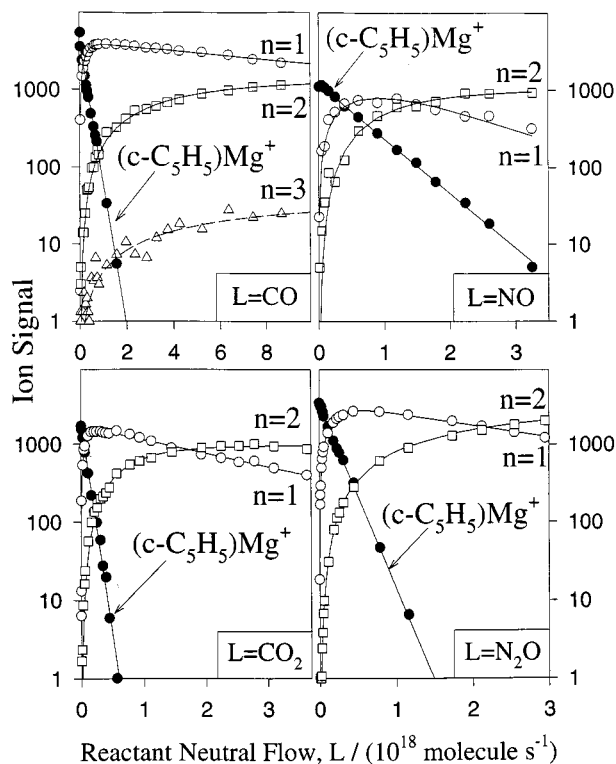
No reactions were observed with  $\text{H}_2$  ( $k < 5 \times 10^{-13}$   $\text{cm}^3$  molecules $^{-1}$   $\text{s}^{-1}$ ) and  $\text{O}_2$  ( $k < 10^{-13}$   $\text{cm}^3$  molecule $^{-1}$   $\text{s}^{-1}$ ).  $(c\text{-C}_5\text{H}_5)\text{Mg}^+$  was observed to react with  $\text{N}_2$  only slowly ( $k = 3.8$

$\times 10^{-11}$   $\text{cm}^3$  molecule $^{-1}$   $\text{s}^{-1}$ ), as indicated in Figure 1. A second addition was not observed in the flow range of the experiments. The experimental dissociation onset for  $(c\text{-C}_5\text{H}_5)\text{Mg}(\text{N}_2)^+$  in Figure 1 is 12 V (lab energy). This small value indicates that a weak bond is being fragmented,<sup>24</sup> and this is consistent with the rather low value for the effective bimolecular rate coefficient for ligation.

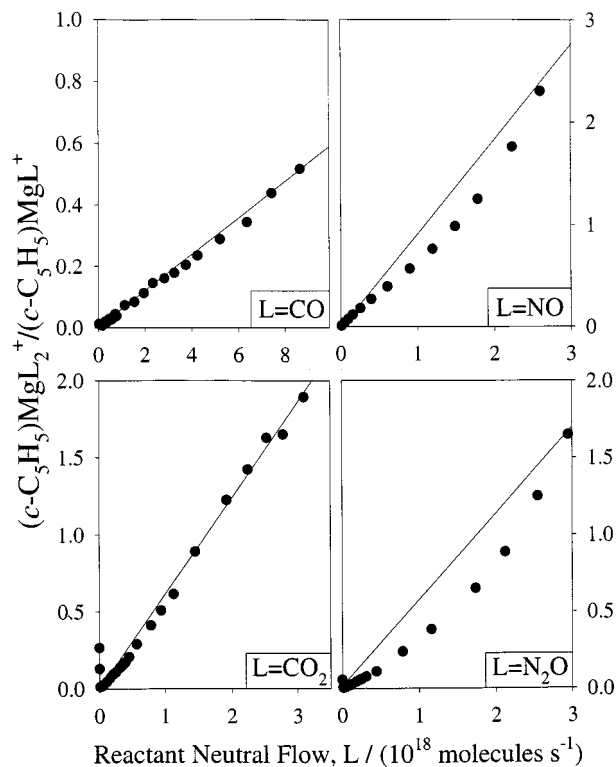
Figure 2 presents the observed reaction profiles for the reactions of  $(c\text{-C}_5\text{H}_5)\text{Mg}^+$  with  $\text{L} = \text{CO}$ ,  $\text{NO}$ ,  $\text{CO}_2$ ,  $\text{N}_2\text{O}$ . In each case two ligands were observed to add sequentially over the range of reactant flow employed, although there was also evidence for the addition of a third molecule of  $\text{CO}$ . 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  $\text{CO}$  and  $\text{CO}_2$  and the approach to equilibrium in the second ligation step with  $\text{NO}$  and  $\text{N}_2\text{O}$ . 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  $(c\text{-C}_5\text{H}_5)\text{Mg}(\text{NO})_2^+$  is unique in that it shows an inflection, which suggests the presence of two isomers of  $(c\text{-C}_5\text{H}_5)\text{Mg}(\text{NO})_2^+$ . 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  $\text{NO}_2$  add sequentially to  $(c\text{-C}_5\text{H}_5)\text{Mg}^+$  under our operating conditions, although the first addition is decidedly the fastest ( $k = 7.4 \times 10^{-10}$   $\text{cm}^3$





**Figure 2.** Experimental data for reaction 10 with L = CO, NO, CO<sub>2</sub>, and N<sub>2</sub>O. The measurements were performed at 294 ± 3 K and at a helium buffer gas pressure of 0.35 ± 0.01 Torr. (c-C<sub>5</sub>H<sub>5</sub>)Mg<sup>+</sup> was formed by electron-impact dissociative ionization of Mg(c-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub> 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.

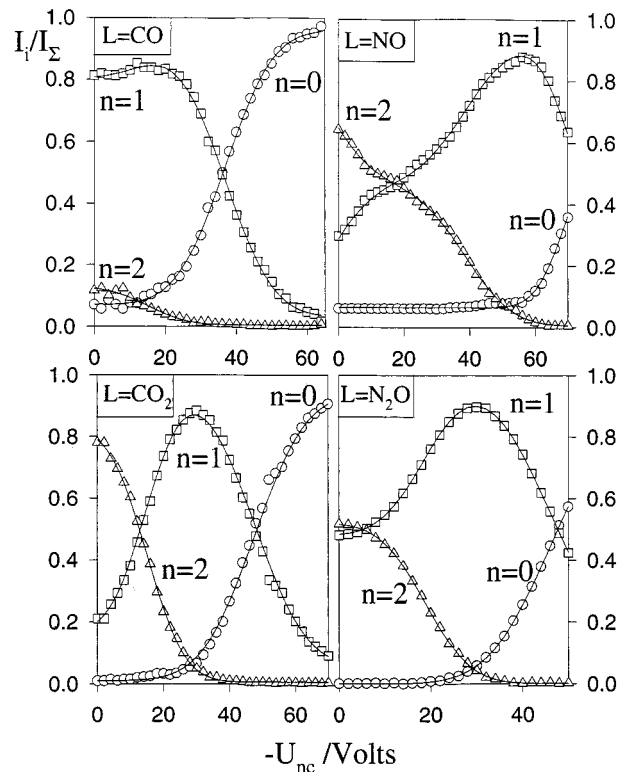


**Figure 3.** Ion-signal ratio plots showing the approach to, and attainment of, equilibrium for some of the data shown in Figure 2.

molecule<sup>-1</sup> s<sup>-1</sup>). The ligation reactions for the addition of the next two NO<sub>2</sub> molecules appeared to achieve equilibrium (see Table 3). The CID profiles indicate that the NO<sub>2</sub> ligands are

**TABLE 3: Room-Temperature Equilibrium Constants (Standard State = 1 atm) and Standard Free Energy Changes (in kcal mol<sup>-1</sup>) for Ligation Reactions (c-C<sub>5</sub>H<sub>5</sub>)Mg(L)<sub>n</sub><sup>+</sup> + L → (c-C<sub>5</sub>H<sub>5</sub>)Mg(L)<sub>n+1</sub><sup>+</sup>**

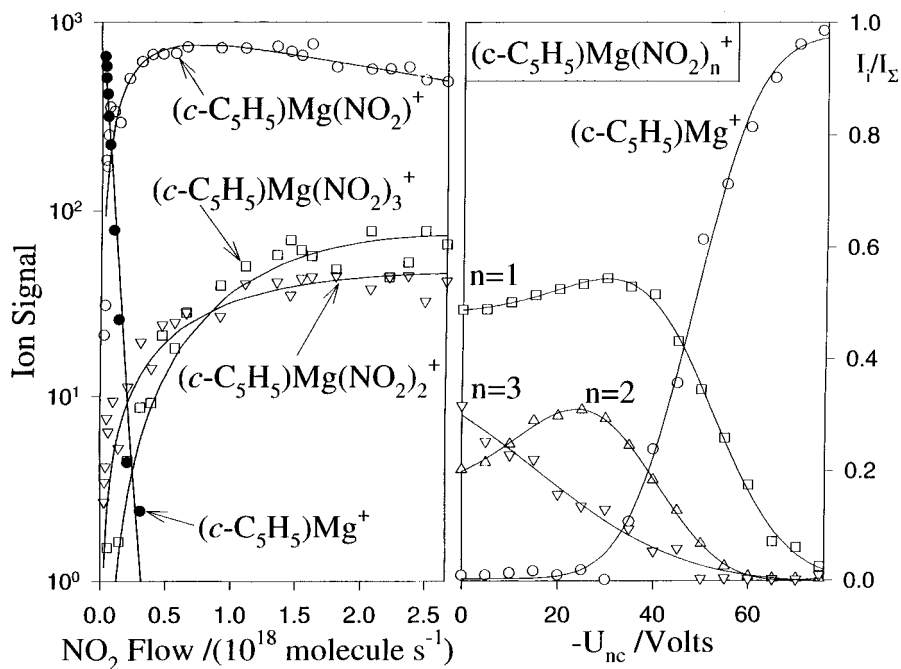
L	n	K <sub>eq</sub>	ΔG°
N <sub>2</sub>	0	≥ 2.1 × 10 <sup>7</sup>	-(≥10)
CO	1	4.6 × 10 <sup>5</sup>	-7.7
NO	1	≥ 6.4 × 10 <sup>6</sup>	-(≥9.3)
CO <sub>2</sub>	1	4.4 × 10 <sup>6</sup>	-9.1
N <sub>2</sub> O	1	≥ 4.1 × 10 <sup>6</sup>	-(≥9.0)
NO <sub>2</sub>	1	1.9 × 10 <sup>6</sup>	-8.5
	2	7.8 × 10 <sup>6</sup>	-9.4



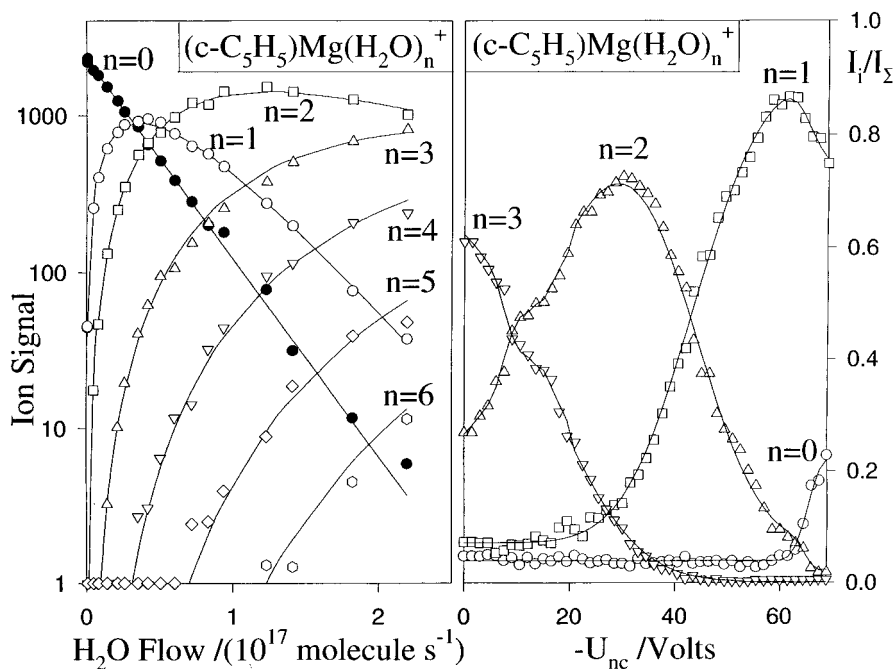
**Figure 4.** Multicollision CID results for (c-C<sub>5</sub>H<sub>5</sub>)Mg(L)<sub>n</sub><sup>+</sup> with L = CO, NO, CO<sub>2</sub>, and N<sub>2</sub>O in the laboratory energy scale. The measurements were performed with a helium buffer-collision gas at a total pressure of 0.35 ± 0.01 Torr. (c-C<sub>5</sub>H<sub>5</sub>)Mg<sup>+</sup> was generated from pure (c-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>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<sup>-1</sup>): CO at 2.0 × 10<sup>18</sup>, NO at 3.0 × 10<sup>18</sup>, CO<sub>2</sub> at 1.3 × 10<sup>18</sup>, and N<sub>2</sub>O at 2.5 × 10<sup>18</sup>.

removed sequentially and that the threshold for dissociation drops with increasing ligation.

The reaction profile of the ligation chemistry of (c-C<sub>5</sub>H<sub>5</sub>)Mg<sup>+</sup> with H<sub>2</sub>O 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<sub>5</sub>H<sub>5</sub>)Mg(H<sub>2</sub>O)<sub>3</sub><sup>+</sup> deserves further comment. The inflections in the dissociation curve of (c-C<sub>5</sub>H<sub>5</sub>)Mg(H<sub>2</sub>O)<sub>3</sub><sup>+</sup> and the concomitant



**Figure 5.** (Left) Experimental data for the reaction of  $(c\text{-C}_5\text{H}_5)\text{Mg}^+$  with  $\text{NO}_2$  in helium buffer gas at  $294 \pm 3$  K and  $0.35 \pm 0.01$  Torr.  $(c\text{-C}_5\text{H}_5)\text{Mg}^+$  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  $(c\text{-C}_5\text{H}_5)\text{Mg}(\text{NO}_2)_n^+$  in the laboratory energy scale and a flow of  $\text{NO}_2 = 2.5 \times 10^{18}$  molecules  $\text{s}^{-1}$ .

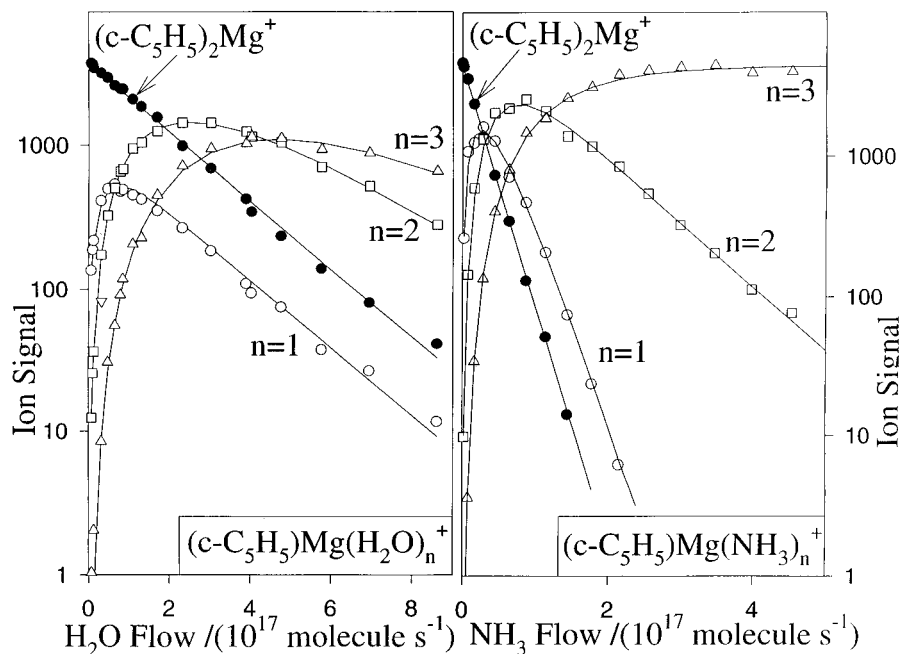


**Figure 6.** (Left) Experimental data for the reaction of  $(c\text{-C}_5\text{H}_5)\text{Mg}^+$  with  $\text{H}_2\text{O}$ . The measurements were performed at  $294 \pm 3$  K and at a helium buffer gas pressure of  $0.35 \pm 0.01$  Torr.  $(c\text{-C}_5\text{H}_5)\text{Mg}^+$  was formed initially by 25 eV electron-impact dissociative ionization of  $\text{Mg}(c\text{-C}_5\text{H}_5)_2$ . 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  $(c\text{-C}_5\text{H}_5)\text{Mg}(\text{H}_2\text{O})_n^+$  in the laboratory energy scale and a flow of  $\text{H}_2\text{O} = 2.5 \times 10^{17}$  molecules  $\text{s}^{-1}$ .

appearance curve of  $(c\text{-C}_5\text{H}_5)\text{Mg}(\text{H}_2\text{O})_2^+$  in Figure 6 indicate the presence of two states or isomers of  $(c\text{-C}_5\text{H}_5)\text{Mg}(\text{H}_2\text{O})_3^+$ . We interpret the data in terms of the presence of two isomers of  $(c\text{-C}_5\text{H}_5)\text{Mg}(\text{H}_2\text{O})_3^+$ , 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  $(c\text{-C}_5\text{H}_5)\text{Mg}(\text{H}_2\text{O})_3^+$  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  $\text{mol}^{-1}$  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  $1.2 \times 10^{-9}$ ,  $1.4 \times 10^{-9}$ , and  $3.7 \times 10^{-10}$   $\text{cm}^3$  molecule<sup>-1</sup> s<sup>-1</sup>.<sup>26</sup> 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-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Mg<sup>+</sup> with H<sub>2</sub>O (left) and NH<sub>3</sub> (right). The measurements were performed at 294 ± 3 K and at a helium buffer-gas pressure of 0.35 ± 0.01 Torr. (c-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Mg<sup>+</sup> was generated from pure (c-C<sub>5</sub>H<sub>5</sub>)Mg 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-C<sub>5</sub>H<sub>5</sub>)Mg(NH<sub>3</sub>)<sub>3</sub><sup>+</sup> by collisional dissociation.<sup>26</sup> Inflections were observed in the dissociation curve of (c-C<sub>5</sub>H<sub>5</sub>)Mg(NH<sub>3</sub>)<sub>3</sub><sup>+</sup> and the concomitant appearance curve of (c-C<sub>5</sub>H<sub>5</sub>)Mg(NH<sub>3</sub>)<sub>2</sub><sup>+</sup>, and these were interpreted in terms of the possible presence of two isomers of (c-C<sub>5</sub>H<sub>5</sub>)Mg(NH<sub>3</sub>)<sub>3</sub><sup>+</sup>, as is suggested here for (c-C<sub>5</sub>H<sub>5</sub>)Mg-(H<sub>2</sub>O)<sub>3</sub><sup>+</sup>. However, the fraction of what presumably again is a weaker bound hydrogen-bonded isomer is very low.

**C. (c-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Mg<sup>+</sup> Reactions.** The full-sandwich (c-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Mg<sup>+</sup> cation was observed to react only with NH<sub>3</sub> and H<sub>2</sub>O. The observed reactions with these two molecules correspond to ligand substitution or switching as in reaction 11.



Ligand switching was not observed with L = H<sub>2</sub>, N<sub>2</sub>, CO, NO, O<sub>2</sub>, CO<sub>2</sub>, N<sub>2</sub>O, and NO<sub>2</sub>, nor was simple addition. The measured upper limits to the rate coefficients for reactions of (c-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Mg<sup>+</sup> with these molecules were in the range between <10<sup>-14</sup> and <10<sup>-13</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>.

Figure 7 presents reaction profiles for the reactions of (c-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Mg<sup>+</sup> with NH<sub>3</sub> and H<sub>2</sub>O. The first step in the observed chemistry in both cases is a rapid ligand switching with one of the cyclopentadienyl rings in (c-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Mg<sup>+</sup>. The ligand substitution is followed by the sequential addition of two ligands in the case of NH<sub>3</sub> and more than two ligands in the case of H<sub>2</sub>O, in a manner similar to that observed for the higher-order reactions of the half-sandwich cation, and with similar rates.

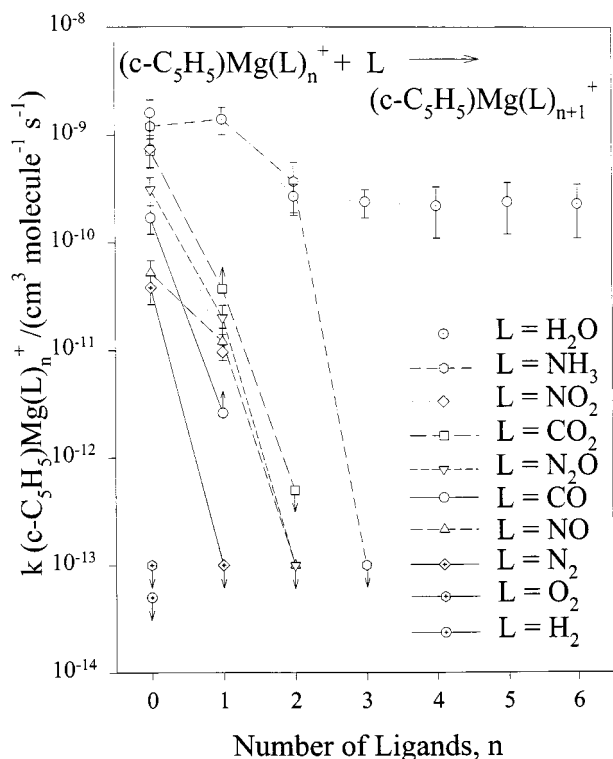
The switching reactions with NH<sub>3</sub> and H<sub>2</sub>O are not equally fast; the switching reaction with H<sub>2</sub>O is about 5 times slower than that with NH<sub>3</sub>, which reacts at close to the collision rate (see Table 1). The rapid occurrence of switching implies that these two molecules ligate more strongly to (c-C<sub>5</sub>H<sub>5</sub>)Mg<sup>+</sup> than c-C<sub>5</sub>H<sub>5</sub> itself, viz. that  $D_{298}((c-C_5H_5)Mg^+ - NH_3)$  and  $D_{298}((c-C_5H_5)Mg^+ - H_2O) > D_{298}((c-C_5H_5)Mg^+ - c-C_5H_5)$ . Conversely, the failure to observe switching with H<sub>2</sub>, N<sub>2</sub>, CO, NO, O<sub>2</sub>, CO<sub>2</sub>, N<sub>2</sub>O, and NO<sub>2</sub> implies that these molecules ligate less strongly.

**D. Variation in the Rate of Ligation with the Number of (c-C<sub>5</sub>H<sub>5</sub>) Ligands.** The results of the measurements reported here show a strong dependence of the rate of ligation with the number of (c-C<sub>5</sub>H<sub>5</sub>) ligands. We have seen that Mg<sup>+</sup> is unreactive except with ammonia, which ligates slowly ( $k = 4 \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>). Single ligation of Mg<sup>+</sup> with c-C<sub>5</sub>H<sub>5</sub> substantially enhances reactivity; the initial ligation of the “half-sandwich” (c-C<sub>5</sub>H<sub>5</sub>)Mg<sup>+</sup> cation is rapid ( $k > 5 \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>) with all ligands except H<sub>2</sub>, N<sub>2</sub>, and O<sub>2</sub>. Double ligation with c-C<sub>5</sub>H<sub>5</sub> 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<sub>3</sub> and H<sub>2</sub>O.

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 redistribution.

Mg<sup>+</sup> 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-C<sub>5</sub>H<sub>5</sub> 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<sup>+</sup> with a measurable rate coefficient and did so sequentially. We have discussed previously the trend in the observed kinetics of this sequential ligation.<sup>26</sup> 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<sub>3</sub>)<sub>3</sub><sup>+</sup> and Mg(NH<sub>3</sub>)<sub>4</sub><sup>+</sup> 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  $(c\text{-C}_5\text{H}_5)\text{Mg}^+$  by  $\text{H}_2$ ,  $\text{O}_2$ ,  $\text{N}_2$ ,  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{N}_2\text{O}$ ,  $\text{NH}_3$ , and  $\text{H}_2\text{O}$  with the number of ligands  $n$  added in the gas phase at  $294 \pm 3$  K and at a helium buffer gas pressure of  $0.35 \pm 0.01$  Torr.

The range in the rates of ligation of  $(c\text{-C}_5\text{H}_5)\text{Mg}^+$  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  $1.6 \times 10^{-9}$  to  $< 10^{-13}$   $\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ , and the number of ligands observed to add sequentially ranges from 1 to  $>7$ . Only hydrogen and oxygen were observed *not* to ligate to  $(c\text{-C}_5\text{H}_5)\text{Mg}^+$  under our chosen operating conditions.

The magnitude of the rate of ligation of  $(c\text{-C}_5\text{H}_5)\text{Mg}^+$  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  $(c\text{-C}_5\text{H}_5)\text{Mg}^+$  or  $(c\text{-C}_5\text{H}_5)\text{Mg}(\text{L})_n^+$ . 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.  $(c\text{-C}_5\text{H}_5)\text{Mg}^+ \text{--} \text{L}$  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.<sup>21</sup> 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  $(c\text{-C}_5\text{H}_5)\text{Mg}^+$  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.<sup>21</sup> 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  $(c\text{-C}_5\text{H}_5)\text{Mg}^+$ : 0 for  $\text{O}_2$  and  $\text{H}_2$ , 1 for  $\text{N}_2$ , 1 or 2 for  $\text{CO}$  and  $\text{NO}_2$ , and 2 for  $\text{NO}$ ,  $\text{N}_2\text{O}$ , and  $\text{CO}_2$ .

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  $\text{FeO}^+$  with water molecules.<sup>20</sup>

Our previously reported results for the ligation of  $(c\text{-C}_5\text{H}_5)\text{Mg}^+$  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.<sup>26</sup> 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  $(c\text{-C}_5\text{H}_5)\text{Mg}(\text{NH}_3)_3^+$  that is likely formed by hydrogen bonding. The sequential ligation of  $(c\text{-C}_5\text{H}_5)\text{Mg}^+$  with ammonia is therefore consistent with a primary coordination number of 3.

The break in the kinetics of ligation with  $\text{H}_2\text{O}$  observed at  $n = 2$  in Figure 8 suggests an apparent primary coordination number for  $\text{H}_2\text{O}$  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  $\text{Mg}^+$  ion; the fourth water molecule in  $\text{Mg}^+(\text{H}_2\text{O})_4$  is predicted to bond more strongly to the other water molecules by hydrogen bonding than to the metal itself.<sup>13,34</sup> However, threshold CID measurements of the bond dissociation of  $\text{Mg}(\text{H}_2\text{O})_n^+$  with  $n = 1\text{--}4$  reported by Dalleska et al.<sup>33</sup> 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  $\text{Mg}^+$  and to  $(c\text{-C}_5\text{H}_5)\text{Mg}^+$  are all removed *sequentially* by collision-induced dissociation. There was no evidence for the occurrence of intramolecular ligand–ligand interactions leading to bond redistribution in the ligated ions of the type we have reported previously for several hydrocarbon-ligated  $\text{Fe}^+$  ions.<sup>21</sup> Production of  $\text{MgL}^+$  was not observed over the available range in CID energy. Apparently, the  $(c\text{-C}_5\text{H}_5)\text{Mg}\text{--L}^+$  bond is the weakest bond in each case. Also, all the CID profiles reported here, with the exception of those for  $(c\text{-C}_5\text{H}_5)\text{Mg}(\text{NO}_2)_2^+$  and  $(c\text{-C}_5\text{H}_5)\text{Mg}(\text{H}_2\text{O})_3^+$ , 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  $(c\text{-C}_5\text{H}_5)\text{MgL}_n^+$  cations. Some *plausible* structures for these ions are presented in Figure 9. We have discussed previously, in detail, the structures and bonding of  $\text{Mg}(\text{NH}_3)_n^+$  ( $n = 1\text{--}4$ ).<sup>26</sup> Our experiments show that three molecules of



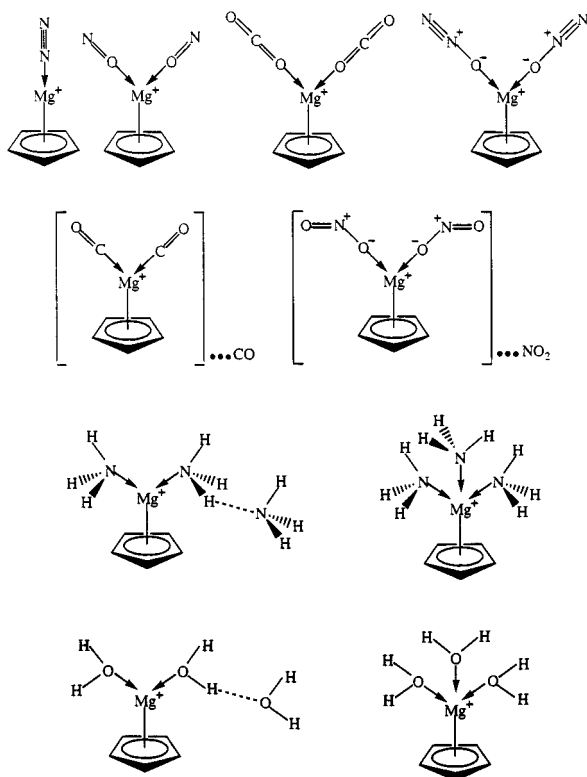


Figure 9. Proposed structures for several ligated (c-C<sub>5</sub>H<sub>5</sub>)Mg<sup>+</sup> cations.

NH<sub>3</sub> add sequentially to (c-C<sub>5</sub>H<sub>5</sub>)Mg<sup>+</sup> 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<sub>5</sub>H<sub>5</sub>)Mg(NH<sub>3</sub>)<sub>3</sub><sup>+</sup> for the formation of small amounts of the hydrogen-bonded isomer also shown in Figure 9.

The “end-on” structure of (c-C<sub>5</sub>H<sub>5</sub>)Mg(N<sub>2</sub>)<sup>+</sup> proposed in Figure 9 is based on what is known about CH<sub>3</sub>N<sub>2</sub><sup>+</sup>, HN<sub>2</sub><sup>+</sup>,<sup>35</sup> and Mg(N<sub>2</sub>)<sup>+</sup>. Results of a spectroscopic study of Mg(N<sub>2</sub>)<sup>+</sup> 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<sup>+</sup>←N≡N (C<sub>∞v</sub>, <sup>2</sup>Σ<sup>+</sup>).<sup>10</sup> Furthermore, Bauschlicher’s<sup>8</sup> theoretical studies and those of Tachikawa et al.<sup>36</sup> support this arrangement for the ground state with a small binding energy, D<sub>0</sub>(Mg<sup>+</sup>–N<sub>2</sub>) = 2.4 kcal mol<sup>−1</sup>. On the basis of these results, we propose that the half-sandwich ligated by N<sub>2</sub> 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<sup>10</sup> on Mg<sup>+</sup>–CO<sub>2</sub> systems determined that a linear ion–molecule complex is the result of the first addition of CO<sub>2</sub> to Mg<sup>+</sup> with the bonding dominated by charge–quadrupole interactions. The second ligation of Mg<sup>+</sup> by CO<sub>2</sub> 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<sub>5</sub>H<sub>5</sub>)Mg<sup>+</sup> with two CO<sub>2</sub> ligands is shown in Figure 9. CO–Mg<sup>+</sup> has also been examined by Bauschlicher’s group.<sup>9</sup> 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<sup>−1</sup> 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<sub>5</sub>H<sub>5</sub>)Mg(NO<sub>2</sub>)<sub>2</sub><sup>+</sup> 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<sup>2+</sup>. Addition to the nitrogen atom of NO is only slightly less exothermic. Two plausible isomers of (c-C<sub>5</sub>H<sub>5</sub>)Mg(H<sub>2</sub>O)<sub>3</sub><sup>+</sup> 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 ΔG° (ligation) summarized in Table 3 range from −7.7 to −(≥12.2) kcal mol<sup>−1</sup>. Values for ΔS° (ligation) are likely to be more negative than −25 cal K<sup>−1</sup> judging from available experimental values for entropy changes for ion–cluster dissociation.<sup>37</sup> A statistical thermodynamic assessment indicates values for ΔS°(translation) of −35.5 ± 0.5 cal K<sup>−1</sup>. ΔS° (rotation) is not known but will be much smaller, say less than ca. −5 cal K<sup>−1</sup>, and ΔS°(vibration) should be negligible. Thus, ΔH°(ligation), and also ΔE°(ligation), will be uniformly at least ca. 9 kcal mol<sup>−1</sup> more negative than ΔG°(ligation).

The low values of the free energies (and estimated enthalpies) for the second ligation of (c-C<sub>5</sub>H<sub>5</sub>)Mg<sup>+</sup> with CO and CO<sub>2</sub> and the higher values for the second ligation with NO and N<sub>2</sub>O 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<sub>5</sub>H<sub>5</sub>)Mg(CO)<sub>2</sub><sup>+</sup> and (c-C<sub>5</sub>H<sub>5</sub>)Mg(CO<sub>2</sub>)<sub>2</sub><sup>+</sup> and higher dissociation energies for the bulk of (c-C<sub>5</sub>H<sub>5</sub>)Mg(NO)<sub>2</sub><sup>+</sup> and (c-C<sub>5</sub>H<sub>5</sub>)Mg(N<sub>2</sub>O)<sub>2</sub><sup>+</sup>.

The standard free energies of ligation deduced from the measured equilibrium constants for reaction 10 with L = NO<sub>2</sub> are −8.5 and −9.4 kcal mol<sup>−1</sup> 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<sub>5</sub>H<sub>5</sub>)Mg(NO<sub>2</sub>)<sub>3</sub><sup>+</sup> exhibits a very early threshold for dissociation, while the early onset of (c-C<sub>5</sub>H<sub>5</sub>)Mg(NO<sub>2</sub>)<sub>2</sub><sup>+</sup> indicates an early threshold for the dissociation of (c-C<sub>5</sub>H<sub>5</sub>)Mg(NO<sub>2</sub>)<sub>2</sub><sup>+</sup>, which is present initially and is also produced by the dissociation of (c-C<sub>5</sub>H<sub>5</sub>)Mg(NO<sub>2</sub>)<sub>3</sub><sup>+</sup>.

**H. Circumstellar MgNH<sub>2</sub>.** 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.<sup>38,39</sup> 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*”.<sup>39</sup> We propose here, on the basis of the measured kinetics for the reaction of Mg<sup>+</sup> with ammonia, that ion–molecule reactions analogous to those proposed for the formation of MgNC<sup>37</sup> can lead to the formation of the MgNH<sub>2</sub> molecules in these environments. The proposed mechanism involves the initial ligation of Mg<sup>+</sup> with ammonia by radiative association, reaction 12, followed by dissociative recombination with electrons, reaction 13.



## Conclusions

The application of the SIFT technique has allowed an evaluation of the intrinsic kinetics of ligation of Mg<sup>+</sup>,

(*c*-C<sub>5</sub>H<sub>5</sub>)Mg<sup>+</sup>, and (*c*-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Mg<sup>+</sup> 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<sub>5</sub>H<sub>5</sub> and the nature and size of the inorganic ligand. Thermalized Mg<sup>+</sup> ions did not react with any of the inorganic ligands chosen for study, except NH<sub>3</sub>, 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<sup>+</sup> with *c*-C<sub>5</sub>H<sub>5</sub> substantially *enhances* the efficiency of ligation. Double ligation with *c*-C<sub>5</sub>H<sub>5</sub> 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<sub>3</sub> and H<sub>2</sub>O, indicating that these two molecules ligate more strongly to (*c*-C<sub>5</sub>H<sub>5</sub>)Mg<sup>+</sup> than does *c*-C<sub>5</sub>H<sub>5</sub> itself. Higher-order ligation reactions of (*c*-C<sub>5</sub>H<sub>5</sub>)Mg<sup>+</sup> with CO, NO, NH<sub>3</sub>, CO<sub>2</sub>, N<sub>2</sub>O, and NO<sub>2</sub> proceed with diminishing rates, adding up to at most three ligands. H<sub>2</sub>O is an exception; at least six H<sub>2</sub>O molecules were observed to add sequentially to (*c*-C<sub>5</sub>H<sub>5</sub>)Mg<sup>+</sup>. 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 redistribution after ligation.

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