Coordination to RMg^+ and RZn^+ Cations[1]

Hui Tang,[†,1] Masood Parvez,*[,‡] and Herman G. Richey, Jr.*[,†]

Departments of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802, and University of Calgary, Calgary, Alberta, Canada T2N 1N4

Received May 19, 2000

Addition of a second coordinating agent (coord*) to a solution of $RM(coord)^+A^-$ (R = ethyl or neopentyl, M = Zn or Mg, A^- = 1,2,3,4-tetraphenylcyclopentadienyl) can provide equilibrium mixtures of these compounds, coord, and $RM(coord^*)^+A^-$. This exchange with $RMg(coord)^+$ requires the addition of a small amount of R_2Mg, but added R_2Zn is not necessary for exchanges with $RZn(coord)^+$. The equilibrium constants provide information about the relative abilities of different coordinating agents to coordinate to RM^+ and reveal significant differences between coordination to RMg^+ and RZn^+. Reactions of $RM(coord)^+$ with R'_2M (R = ethyl or neopentyl for $RMg(coord)^+$ and ethyl, isopropyl, *tert*-butyl, neopentyl, or *p*-methylphenyl for $RZn(coord)^+$) provide equilibrium mixtures of these components, R′M-$(coord)^+$, and R_2M. The equilibrium constants provide information about the effect of R on stability. An X-ray structure of *p*-methylphenylzinc(2,5,8,11-tetramethyl-2,5,8,11-tetraazadodecane)$^+$ shows that just three of the N atoms are coordinated to Zn. The effects of coord, R, and metal on $RM(coord)^+$ stability are discussed, and the abilities of coordinating agents to coordinate to RM^+, to slow allylic isomerization of $(CH_2{=}CMeCH_2)_2Zn$, and to convert R_2Zn to $RZn(coord)^+$ are compared.

Coordination plays a major role in organomagnesium and organozinc chemistry. Because of a strong propensity to form additional bonds, the metal atoms of the compounds, usually written as RMgX, R_2Mg, RZnX, and R_2Zn (X a halogen, R alkyl or aryl), generally coordinate to functions such as alkoxy or amino when these are present, often as part of the solvent.[3,4] Additional bonds also may result from bridging of groups between metal atoms. Formation of several strong bonds between O or N atoms of a macrocycle and the Mg of the cation must provide the driving force for reactions of some macrocycles with organomagnesium compounds to produce coordinated RMg^+ cations and organomagnesate anions, as exemplified in eq 1.[5−8] Because of such observations, we wanted to determine the abilities of coordinating

$$2\ R_2Mg + coord \rightarrow RMg(coord)^+ + R_3Mg^- \quad (1)$$

agents to coordinate to RMg^+. Disproportionations such as that in eq 1 are less favorable with organozinc compounds.[9−11] We also wanted to determine abilities to coordinate to RZn^+, permitting comparisons of coordination to Mg, a main-group metal, and to Zn, similar to Mg in some ways (e.g., size, absence of a partially filled d shell) but in the transition group and less electropositive. Guidance from the literature is limited, most data involving Mg^{2+} or Zn^{2+} being in water or methanol.[12] A communication[13] described preliminary results of a study of coordination to RMg^+ and RZn^+. This paper provides additional data on the relative abilities of coordinating agents to coordinate to RM^+ (M = Mg or Zn), a comparison of abilities to coordinate to RM^+ and convert R_2M to form $RM(coord)^+$ and ate anions, a relevant $RZn(coord)^+$ X-ray structure, and information about the mechanisms of exchange of coord of $RM(coord)^+$ with external coord.

[†] The Pennsylvania State University.
[‡] University of Calgary.

(1) Most of the work in this paper is taken from ref 2.

(2) Tang, H. Ph.D. Dissertation, The Pennsylvania State University, l997.

(3) For information and references concerning organomagnesium compounds: Lindsell, W. E. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, l982; Chapter 4. Lindsell, W. E. In *Comprehensive Organometallic Chemistry*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, l995; Vol. 1, Chapter 3.

(4) For information and references concerning organozinc compounds: Boersma, J. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, l982; Chapter 16. O'Brien, P. In *Comprehensive Organometallic Chemistry*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, l995; Vol. 3, Chapter 4.

(5) Squiller, E. P.; Whittle, R. R.; Richey, H. G., Jr. *J. Am. Chem. Soc.* **l985**, *107*, 432.

(6) Richey, H. G., Jr.; Kushlan, D. M. *J. Am. Chem. Soc.* **1987**, *109*, 2510.

(7) Pajerski, A. D.; Parvez, M.; Richey, H. G., Jr. *J. Am. Chem. Soc.* **l988**, *110*, 2660.

(8) Fabicon, R. M.; Pajerski, A. D.; Richey, H. G., Jr. *J. Am. Chem. Soc.* **1993**, *115*, 9333. Pajerski, A. D.; Chubb, J. E.; Fabicon, R. M.; Richey, H. G., Jr. *J. Org. Chem.* **2000**, *65*, 2231.

(9) Fabicon, R. M.; Pajerski, A. D.; Richey, H. G., Jr. *J. Am. Chem. Soc.* **l991**, *113*, 6680.

(10) Fabicon, R. M.; Parvez, M.; Richey, H. G., Jr. *Organometallics* **l999**, *18*, 5163.

(11) Fabicon, R. M. Ph.D. Dissertation, The Pennsylvania State University, l991.

(12) Many equilibrium data are available for coordination to Mg^{2+} and Zn^{2+} in water and methanol. Coordination to macrocycles: Izatt, R. M.; Bradshaw, J. S.; Nielsen, S. A.; Lamb, J. D.; Christensen, J. J.; Sen, D. *Chem. Rev.* **1985**, *85*, 271. Izatt, R. M.; Pawlak, K.; Bradshaw, J. S.; Bruening, R. L. *Chem. Rev.* **l991**, *91*, 1721. Coordination to macrocyclic and acyclic coordinating agents: Christensen, J. J.; Izatt, R. M. *Handbook of Metal Ligand Heats and Related Thermodynamic Quantities*, 3rd ed.; Dekker: New York, l983. Smith, R. M.; Martell, A. E. *Critical Stability Constants*; Plenum: New York, Vol. 2 (l975), Vol. 5 (l982), Vol. 6 (l989).

(13) Tang, H.; Richey. H. G., Jr. *Organometallics* **l996**, *15*, 4891.

10.1021/om000427e CCC: $19.00
Publication on Web 10/07/2000

Results

With most coordinating agents, the position of the equilibrium in eq 2 lies immeasurably far to the right.

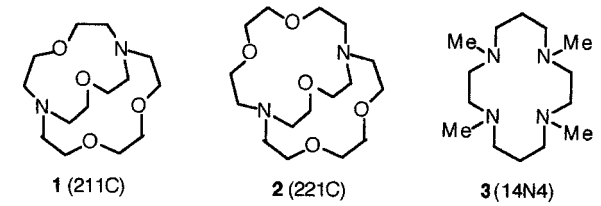
$$RM^+ + \text{coord} \rightleftharpoons RM(\text{coord})^+ \quad (2)$$

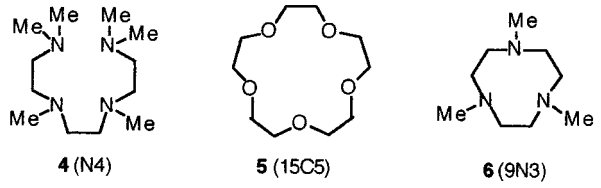
Relative coordinating abilities, however, can be determined by competition experiments.[14] If exchange (eq 3) occurs when a second coordinating agent (coord*) is added to a solution containing a $RM(coord)^+$ cation, then

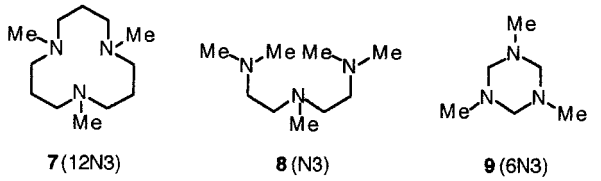
$$RM(\text{coord})^+ + \text{coord}^* \rightleftharpoons RM(\text{coord}^*)^+ + \text{coord} \quad (3)$$

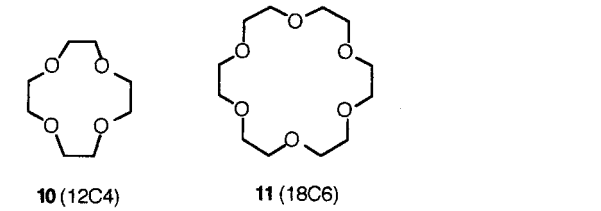
the composition of the solution after equilibrium is reached provides the relative abilities of coord and coord* to coordinate to RM^+. To minimize influences on the *relative* values of the equilibrium constants, specific interactions between $RM(coord)^+$ and the accompanying anion (A^-) should be minimal. A noncoordinating solvent, benzene, was chosen for the work described in this paper.

Experiments with EtZnCp. This compound, readily prepared and purified, was used for the first experiments. Reactions with 14N4 (**3**) or N3 (**8**) resulted in two liquid phases, the lower much smaller than the upper. A lower liquid phase containing much of the



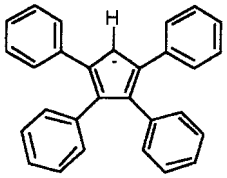






solute is often observed when organometallic ions form in aromatic solvents.[15] The ^1H NMR spectrum (Figure 1) of the lower phase of the preparation with 14N4 had two sets of Et absorptions and one Cp absorption. The upfield set of Et absorptions and the 14N4 absorptions have intensities that indicate the groups responsible for them to be 1:1 and positions similar to those previously observed for $EtZn(14N4)^+$ in the presence of other anions.[9,11] The Cp absorption and the other Et absorptions indicate that the groups responsible for them are ~2:1. The cation therefore is $EtZn(14N4)^+$, but anions such as $EtZnCp_2^-$ are present instead of Cp^-. The Cp and Et absorptions in ^1H NMR spectra of EtZnCp solutions were somewhat shifted by an equimolar amount of DMSO, HMPA, or TMEDA; these additives therefore must coordinate significantly to the Zn of EtZnCp but without leading to ion formation. The ^1H NMR absorptions of solutions prepared from EtZnCp with 12C4 (**10**), 15C5 (**5**), or 18C6 (**11**) were little changed from those of the components when alone, suggesting little coordination.

Preparation of $RZn(coord)^+$ and $RMg(coord)^+$ Solutions. The next efforts used reactions of R_2Zn and hydrocarbons (HA) to prepare RZnA compounds having an A more likely than Cp to form A^- rather than anions such as $RZnA_2^-$. Hydrocarbons included indene, fluorene, and particularly 1,2,3,4-tetraphenylcyclopentadiene, the precursor of a bulky anion (**12**) with a highly



12

dispersed charge (1,2,3,4,5-pentaphenylcyclopentadiene, an attractive possibility, was quite insoluble in benzene). No reactions took place between equimolar amounts of Et_2Zn and these hydrocarbons in benzene or in some more polar solvents (including DMSO), even after heating (75 °C) for as long as 2 weeks. Similar reactions of indene or fluorene in benzene at 95 °C (sealed tube) were tried with 1 equiv of a coordinating agent also present. No significant reactions with N3, N4 (**4**) or 211C (**1**), and only a slow reaction with 14N4, were observed after 2 weeks. No significant reaction was observed with tetraphenylcyclopentadiene when the coordinating agent was 12C4, 15C5, 18C6, 6N3 (**9**), TMEDA, HMPA, or DMSO. With N3, N4, 12N3 (**7**), 9N3 (**6**), 14N4, and 211C, however, several features of ^1H NMR spectra (evident in the example in Figure 2) of solutions obtained in less than 4 h using temperatures in the range 25−70 °C indicate the quantitative formation of $EtZn(coord)^+Ph_4C_5H^-$ (eq 4, M = Zn). (1) The

$$R_2M + Ph_4C_5H_2 + \text{coord} \rightarrow RM(\text{coord})^+ + Ph_4C_5H^- + RH \quad (4)$$

intensities of the principal absorptions—for an Et, coord, and $Ph_4C_5H^-$—show that the groups responsible for them are 1:1:1. An additional set of either Et or coord absorptions is seen if Et_2Zn or coord had initially been in excess. (2) When 14N4 or 211C is used, the Et and 14N4 or 211C absorptions are similar to those previously observed for $EtZn(14N4)^+$ or $EtZn(211C)^+$ with other anions.[9,11] The ethyl CH_2 absorption is consider-

(14) Wang, T.; Bradshaw, J. S.; Izatt, R. M. *J. Heterocycl. Chem.* **l994**, *31*, 1097.
(15) Atwood, J. L. In *Inclusion Compounds*; Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Eds.; Academic: London, l984; Vol. 1, Chapter 9.

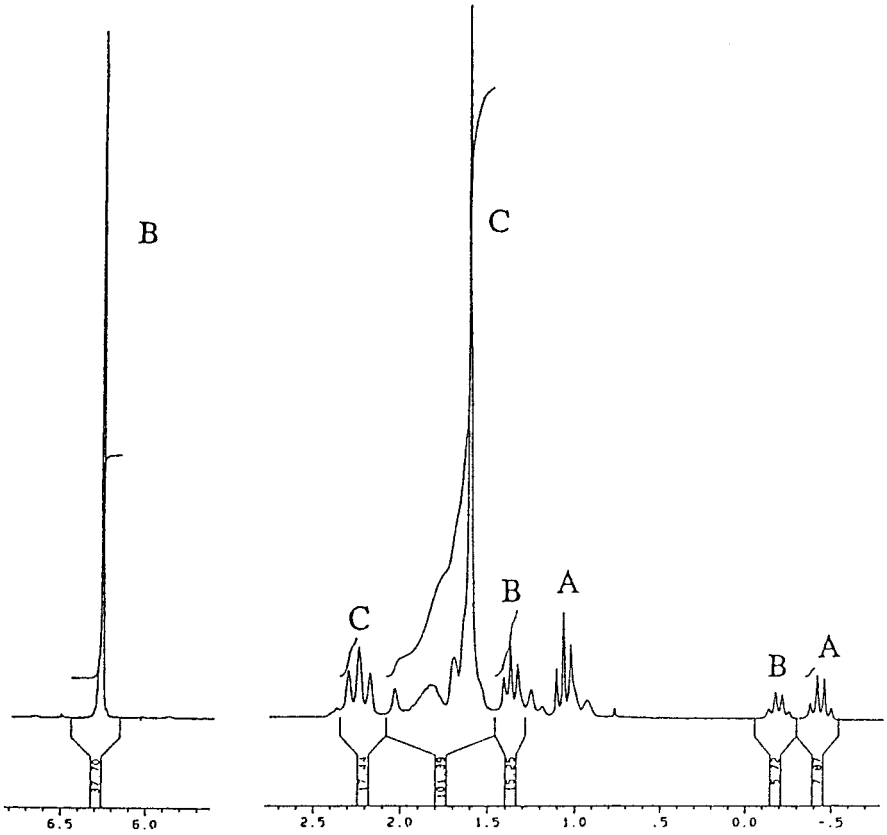


Figure 1. ^{1}H NMR spectrum (200 MHz) of the lower liquid phase containing $EtZn(14N4)^+EtZnCp_2^-$ that formed from dissolving equimolar amounts of EtZnCp and 14N4 in benzene-d_6. Et absorptions of $EtMg(14N4)^+$ are labeled A, and some of the 14N4 absorptions of this cation are labeled C. "$EtZnCp_2^-$" absorptions are labeled B.

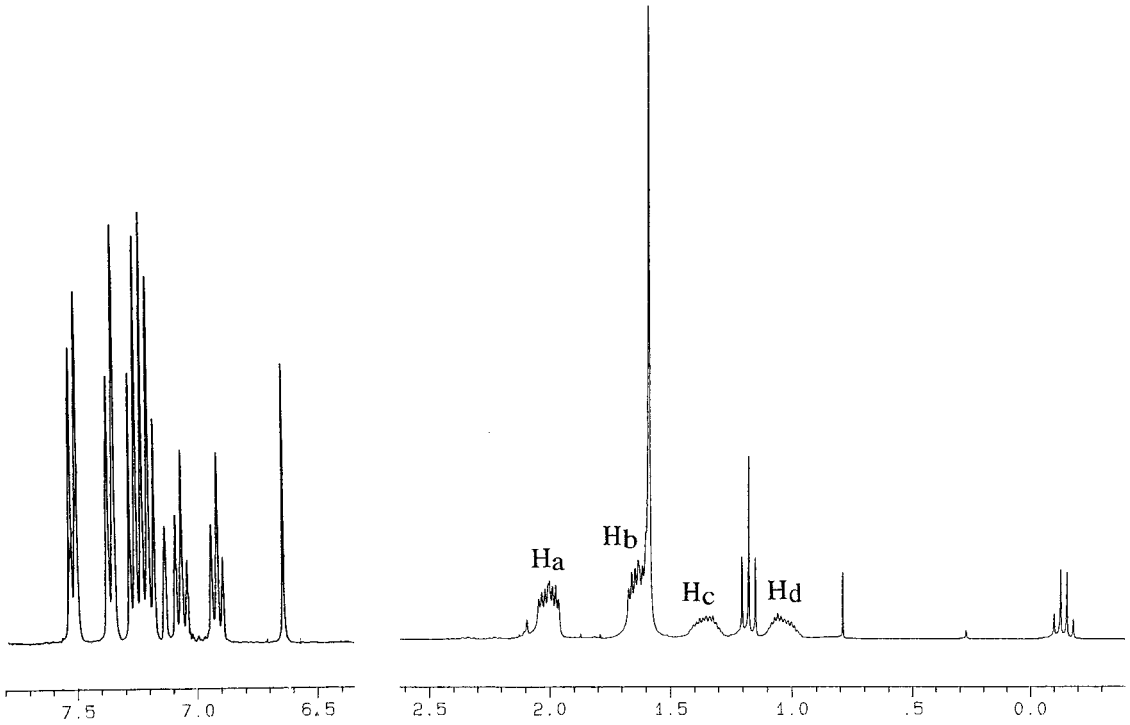


Figure 2. Portion of the ^{1}H NMR spectrum (300 MHz) of a benzene-d_6 solution (0.10 M) of $EtZn(12N3)^+Ph_4C_5H^-$. See **13** for labeling of H's of 12N3. Assignments for the $Ph_4C_5H^-$ absorptions (shown at a higher intensity) are given in the Experimental Section.

ably upfield from that of Et_2Zn, and the coord absorptions are shifted upfield from and generally are more numerous than those of free coord. (3) All solutions exhibit essentially identical $Ph_4C_5H^-$ absorptions.

^{1}H NMR observations showed that similar reactions using *i*-Pr_2Zn, *t*-Bu_2Zn, and Np_2Zn (Np = neopentyl (Me_3CCH_2)) also formed $RZn(coord)^+Ph_4C_5H^-$. Observations at different times indicated reactivities with 14N4

Table 1. Values of K[a] for the Equilibrium RM(coord)$^+$ + coord* ⇌ RM(coord*)$^+$ + coord in Benzene-d_6 at 22 °C[b]

coord*	NpMg(coord*)$^+$[c]	EtMg(coord*)$^+$	NpZn(coord*)$^+$[c]	EtZn(coord*)$^+$
211C (**1**)	66 000 000		(1) [0.025]	(1)
221C (**2**)	440 000			
14N4 (**3**)	370 000 [8500]	45 000	40 [1.0]	390
N4 (**4**)	500 [11]	72	82 [2.1]	9.3
15C5 (**5**)	240 [5.6]	12		
9N3 (**6**)	40 [0.92]	(1)	1 100 000 [28 000]	26 000
12N3 (**7**)	2.1		88 [2.2]	21
N3 (**8**)	(1)		142 [3.6]	3.0
6N3 (**9**)	<0.001			

[a] K = [RM(coord*)$^+$][coord]/[RM(coord)$^+$][coord*]. [b] The "coord" in each column is the coordinating agent to which a value of (1) is assigned. [c] Values in brackets were assigned as described in the text.

to be in the order Et_2Zn > i-Pr_2Zn ≫ t-Bu_2Zn (because of its low thermal stability, reactions with t-Bu_2Zn were carried out at ambient temperature).

The increased rate of metalation of tetraphenylcyclopentadiene when certain coordinating agents are added probably is due to small amounts of organozincates (e.g., R_3Zn^-). Metalations by dialkylmagnesium compounds were already known to be speeded by addition of macrocyclic compounds that form organomagnesates.[16,17] In fact, the NpMg(coord)$^+$ and EtMg(coord)$^+$ ions listed in Table 1 (insoluble solids formed in reactions of Np_2-Mg with 12C4 and 18C6 and of Et_2Mg with 211C, 221C, 12N3, N3, and 6N3) were prepared from reactions of Et_2Mg or Np_2Mg with tetraphenylcyclopentadiene and a coordinating agent using shorter times and lower temperatures than needed with Et_2Zn or Np_2Zn and using coordinating agents ineffective with the R_2Zn compounds. Formation of RMg(coord)$^+Ph_4C_5H^-$ solutions was indicated by ^{1}H NMR spectra that had features similar to those found for the organozinc preparations and by RMg(coord)$^+$ absorptions similar to those of the cations that had already been prepared with other anions.[5,7,8,17] The identical $Ph_4C_5H^-$ absorptions of all RZn(coord)$^+$ and RMg(coord)$^+$ solutions confirm the absence of significant cation−anion interactions. All of the RM(coord)$^+$ solutions appeared to be stable over the periods (several days to several weeks) that they were used.

RM(coord)$^+$ + coord* Equilibrium Results. Addition of a second coordinating agent (coord*) to a RM(coord)$^+$ (R = Et or Np) solution in some instances led to exchange to form RM(coord*)$^+$. Essentially identical results obtained by studying each system starting with RM(coord)$^+$ or RM(coord*)$^+$ verified that equilibrium had been achieved. At least one discrete ^{1}H NMR absorption could be seen for each component in eq 3, and the absorption intensities permitted assigning relative concentrations. The equation K = [RM(coord*)$^+$][coord]/[RM(coord)$^+$][coord*] should describe the equilibria;[18] for the case in which R = Et, M = Zn, and coord and coord* = N3 and N4, it was verified that different reactant concentrations led to the same value of K.

Each column of Table 1 gives the values of K determined for equilibria (eq 3) of coord* and NpMg(coord)$^+$, EtMg(coord)$^+$, NpZn(coord)$^+$, or EtZn(coord)$^+$, where coord is the coordinating agent to which a value of 1 is assigned in that column. Data reported in the table were obtained in a stepwise fashion using pairs of coordinating agents that in their column were closest in coordinating ability.[19] In the EtZn(coord)$^+$ series, for example, 211C, the poorest coordinating agent, was studied with N3, which in turn was studied with N4, and so on. Other combinations (see Experimental Section) were investigated, however, and led to similar values of K. Only a limiting value can be assigned to 6N3 in the NpMg(coord)$^+$ column, since NpMg(6N3)$^+$ absorptions were not detected at equilibrium.

NpZn(N3)$^+$ absorptions were not detected when comparing N3 and 9N3 in the NpZn(coord)$^+$ series, indicating that K for 9N3 is >10^3 that for N3. That abilities of $NpZn^+$ and $EtZn^+$ to coordinate to different coordinating agents are not exactly parallel, however, permits an indirect determination of this K. The equilibrium constant for the reaction in eq 5, K_{Np-Et} = [EtZn(9N3)$^+$]-

$$EtZn(N3)^+ + NpZn(9N3)^+ \rightleftharpoons EtZn(9N3)^+ + NpZn(N3)^+ \quad (5)$$

[NpZn(N3)$^+$]/[EtZn(N3)$^+$][NpZn(9N3)$^+$], also equals K_{Et}/K_{Np}, where K_{Et} and K_{Np} involve only Et and Np groups, respectively. K_{Np-Et} was found experimentally to be 1.1; using the value of K_{Et} (Table 1) then permitted assigning the value listed in Table 1 for K_{Np}.

RM(coord)$^+$ + R′$_2$M Equilibrium Results. Reactions of RM(coord)$^+$ and R′$_2$M led to solutions also containing R′M(coord)$^+$ and R_2M (eq 6). At least one

$$2\ RM(coord)^+ + R'_2M \rightleftharpoons 2\ R'M(coord)^+ + R_2M \quad (6)$$

discrete ^{1}H NMR absorption was seen for each component in eq 6, permitting determination of the values of K = [R′M(coord)$^+$]^2[R_2M]/[RM(coord)$^+$]^2[R′$_2$M] listed in Table 2.[20] Note (for coord = N3) that the value for t-Bu and Et obtained directly is essentially the same as that obtained by combining the comparison of i-Pr and Et with that of t-Bu and i-Pr. Solutions of R_2M and R′$_2$M must also contain RR′M; in some instances, absorptions

(16) Richey, H. G., Jr.; King, B. A. *J. Am. Chem. Soc.* **1982**, *104*, 4672.

(17) Pajerski, A. D. Ph.D. Dissertation, The Pennsylvania State University, 1990.

(18) Absolute concentrations are known from the amounts of reagents used to prepare the solutions. To the extent that the equilibrium expression for eq 3 is valid, however, K is dependent on ratios of the species but independent of their absolute concentrations.

(19) The value for NpMg(211C)$^+$ in Table 1 was determined by comparison with NpMg(14N4)$^+$ because significant overlapping of ^{1}H NMR absorptions of coordinated 211C and 221C made accurate integration impossible.

(20) For the Np_2Mg−Et_2Mg−14N4 case, only one broad absorption was observed for Np_2Mg and Et_2Mg, presumably due to rapid exchange of Np and Et groups. NpMg(14N4)$^+$ and EtMg(14N4)$^+$ absorptions were available, however, and [Et_2Mg]/[Np_2Mg] could be calculated from the amounts of reagents used to prepare the solutions.

Table 2. Values of K^a for the Equilibrium 2 RM(coord)$^+$ + R′$_2$M ⇌ 2 R′M(coord)$^+$ + R$_2$M (Eq 6) in Benzene-d_6 at 22 °C

M	coord	R	R′	*K*
Zn	14N4	*i*-Pr	Et	>10^4 [b]
Zn	14N4	*t*-Bu	*i*-Pr	>10^4 [c]
Zn	N3	*i*-Pr	Et	1.2
Zn	N3	*t*-Bu	*i*-Pr	2.0
Zn	N3	*t*-Bu	Et	2.5
Zn	N3	Et	Np	1.4
Mg	14N4	Et	Np	0.036

[a] K = [R′M(coord)$^+$]^2[R$_2$M]/[RM(coord)$^+$]^2[R′$_2$M]. [b] *i*-Pr(14N4)$^+$ absorptions not seen. [c] *t*-Bu(14N4)$^+$ absorptions not seen.

of RR′Zn could be distinguished from those of R$_2$Zn and R′$_2$Zn. The difference in stability of R in R$_2$Zn or R′RZn is small,[21] however, and in calculating *K*, all R and R′ groups were treated as being in R$_2$M and R′$_2$M.

The numbers in different columns of Table 1 are not on the same scale. Coordination by a strong coordinating agent in one column may be stronger or weaker than by a weak coordinating agent in another column. The positions of the equilibria in eq 6, however, provide an approach to putting the data for different R's (except the same metal) on the same scale. The value of the equilibrium constant (K = [NpZn(N3)$^+$]^2[Et$_2$Zn]/[EtZn(N3)$^+$]^2[Np$_2$Zn]) for the equilibrium in eq 7 is 1.45. If

$$2\ \mathrm{EtZn(N3)^+} + \mathrm{Np_2Zn} \rightleftharpoons 2\ \mathrm{NpZn(N3)^+} + \mathrm{Et_2Zn} \quad (7)$$

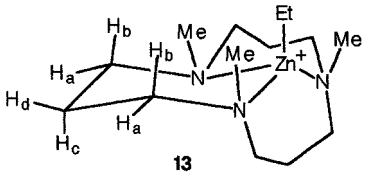
we assume that the effects of R and R′ are exerted principally on the ions (instead of on R$_2$Zn and R′$_2$Zn), then a factor of (1.45)$^{1/2}$ can be used to transform the NpZn(N3)$^+$ value into a value [in brackets] more related to the EtZn(N3)$^+$ value; the other NpZn(coord)$^+$ values can then be scaled to the bracketed NpZn(N3)$^+$ value. The corresponding equilibrium constant is 0.036 when the metal is Mg and the coordinating agent is 14N4; a factor of (0.036)$^{1/2}$ is used to transform the NpMg(14N4)$^+$ value to the bracketed value, and the other NpMg(coord)$^+$ values are scaled to this bracketed NpMg(14N4)$^+$ value.

RZn(coord)$^+$ and RMg(coord)$^+$ results could not in a similar manner be placed on the same scale. An attempt (eq 8) to connect the scales using 9N3, the best coordinating agent for RZn$^+$ and one of the poorest for RMg$^+$, led to the 9N3 being associated solely with Mg, a result that illustrates the much stronger tendency of Mg than of Zn to coordinate to donor atoms.

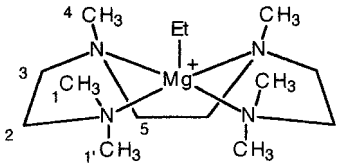
$$2\ \mathrm{NpZn(9N3)^+} + \mathrm{Np_2Mg} \rightarrow 2\ \mathrm{NpMg(9N3)^+} + \mathrm{Np_2Zn} \quad (8)$$

Structural Information from NMR Spectra. Different ^{1}H NMR absorptions for the two H's of CH$_2$ groups of monocyclic coordinating agents (14N4, 9N3, 12N3, 6N3) in RZn(coord)$^+$ and RMg(coord)$^+$ verify that the two sides of the coordinating agents are different, as expected for RM(coord)$^+$. Well-resolved peaks are seen for H$_a$, H$_b$, H$_c$, and H$_d$ (see **13** for labeling) of EtZn(12N3)$^+$. The structure probably resembles that in **13**.[22]

The ^{1}H NMR absorptions of a coordinating agent in RMg(coord)$^+$ and RZn(coord)$^+$ generally were similar, but N4 was an exception. The overlapping N4 absorptions of EtMg(N4)$^+$ were sharp. The ^{1}H−^{13}C COSY spectrum revealed three sets of CH$_a$H$_b$ absorptions (the connectivity of each H$_a$−H$_b$ pair established by ^{1}H−^{1}H COSY experiments), having characteristic geminal coupling (J_{AB} = 12 Hz), and the ^{1}H and ^{13}C NMR spectra had three CH$_3$N absorptions. A ^{1}H NOESY experiment revealed effects between CH$_2$Mg and two kinds of CH$_3$N groups (C$_1$ and C$_4$ in **14**). The N4 conformation, probably resembling that in **14**, is fixed relative to the NMR time scale. The ^{1}H NMR absorptions of N4 in NpMg(N4)$^+$



13



14

and EtMg(N4)$^+$ are so similar that these ions must have similar structures. By contrast, the ^{1}H NMR spectrum of EtZn(N4)$^+$ exhibited only two CH$_3$N absorptions (2:1) and one broad CH$_2$ absorption. Some exchange involving the N atoms must be sufficiently rapid to influence the NMR spectrum; perhaps just three of the N atoms are simultaneously coordinated to the Zn atom, as found (next section) in the crystal structure of a related ion. Spectra taken at lower temperatures (toluene-d_8 solutions) in an effort to slow exchange were not definitive: increased broadness was seen, but of all absorptions equally.

X-ray Structure of TolZn(N$_4$)$^+$Ph$_4$C$_5$H$^-$. Crystals suitable for X-ray diffraction analysis were obtained from a benzene solution of Tol$_2$Zn (Tol is *p*-methylphenyl), N4, and Ph$_4$C$_5$H$_2$. The ORTEP drawing of the cation (Figure 3) indicates that only three of the four N atoms are bonded to the Zn atom. Selected bond lengths and bond angles are listed in Table 3. The Zn−C bond distance is longer than typical[23] (1.946−1.988 Å) in neutral compounds. The Zn−N bond distances fall in the range[23] customary for Zn−N dative[24] bonds.

Discussion of the Effect of Coord, R, and Metal on RM(coord)$^+$ Stability. For NpMg$^+$, 211C is the most effective coordinating agent, consonant with its geometry, which permits bonds of relatively normal lengths to Mg from all of its O and N atoms.[5] 221C, which has a larger "cavity", is much less effective. 15C5, with five donor O atoms, is less effective than 14N4, with four donor N atoms, even though it is known that Mg sometimes bonds to all five O atoms of 15C5.[7] 14N4

(21) Mynott, R.; Gabour B.; Lehmkuhl, H. Döring, I. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 335.

(22) A similar structure was determined by X-ray diffraction for Zn(OH)(12N3′)$^+$ (12N3′ has NH rather than NMe): Kimura, E.; Shiota, T.; Koike, T.; Shiro, M.; Kodama, M. *J. Am. Chem. Soc.* **1990**, *112*, 5805.

(23) Melnik, M.; Skoršepa, J.; Györyová, K.; Holloway, C. E. *J. Organomet. Chem.* **1995**, *503*, 1.

(24) For the use here of "covalent" and "dative" bonds, see: Haaland, A. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 992.

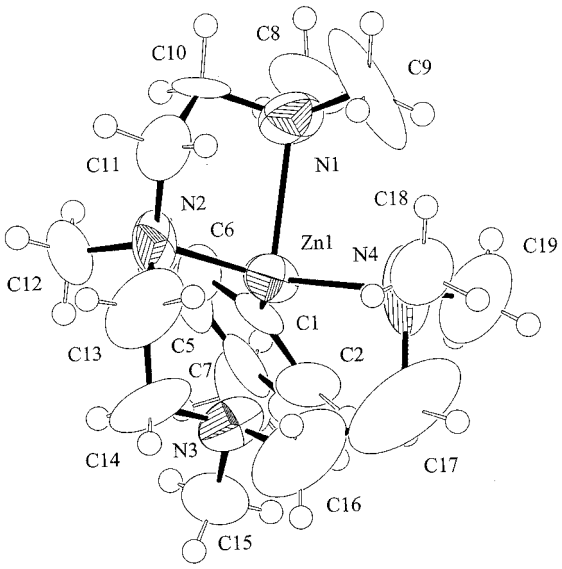


Figure 3. ORTEP drawing of the cation unit in the crystal of TolZn(N4)$^+$Ph$_4$C$_5$H$^-$. Atoms are shown with 50% probability ellipsoids.

Table 3. Selected Bond Distances (Å) and Angles (deg) (esd's in Parentheses) of the Cation of TolZn(N4)$^+$Ph$_4$C$_5$H$^-$

Bond Distances			
Zn−C(1)	2.01 (1)	Zn−N(1)	2.35 (1)
Zn−N(2)	2.13 (1)	Zn−N(4)	2.17 (1)
Bond Angles			
N(1)−Zn−N(2)	80.2(5)	N(1)−Zn−N(4)	87.7(5)
N(1)−Zn−C(1)	107.9(5)	N(2)−Zn−N(4)	121.6(5)
N(2)−Zn−C(1)	121.6(5)	N(4)−Zn(1)−C(1)	116.6(5)

is more effective[25] than acyclic N4, which in turn is more effective than the coordinating agents having only three N atoms. The results with EtMg$^+$ parallel those with NpMg$^+$, although low solubilities of some EtMg(coord)$^+$ salts precluded studies with some coordinating agents used in the NpMg(coord)$^+$ series. Particularly when R is the small Et group and coord has only three donor atoms, RMg(coord)$^+$ conceivably might exist significantly as a dimer.[26] The results in the Et and Np series are so similar, however, that it is unlikely that significant amounts of dimeric structures were present.

Results with RZn$^+$ differ significantly from those with RMg$^+$. 9N3 is by far the strongest coordinating agent, and all coordinating agents having three and four N atoms have similar coordinating abilities. 15C5 did not sufficiently promote the reaction of tetraphenylcyclopentadiene and R$_2$Zn for RZn(15C5)$^+$ to be formed and probably is a particularly poor coordinating agent for RZn$^+$. Because lengths of bonds to Mg and Zn are similar,[27] 211C, an excellent coordinating agent for RMg$^+$, might be expected to be a strong coordinating agent for RZn$^+$. Its relatively poor coordinating ability probably is due to tendencies of RZn$^+$ to coordinate with O considerably less effectively[29] than with N (211C has only two N's) and with fewer atoms than does RMg$^+$ (crystallographic data for organomagnesium[28] and organozinc[23] compounds indicate a tendency for fewer bonds to zinc).[30] Note (Table 1) the similar coordinating abilities of N3 and N4 and also the strong ability of 9N3, which without much distortion can provide a near-tetrahedral geometry for RZn(9N3)$^+$. RMg$^+$, by contrast, can utilize four and even more coordinating atoms.[31]

The results in Table 1 indicate that 211C and 14N4 coordinate much more strongly to EtZn$^+$ than to NpZn$^+$; this probably results much more from influences of R on RZn(coord)$^+$ than on R$_2$Zn. The results in Table 2 for Et, *i*-Pr, and *t*-Bu also indicate that increasing size of R is unfavorable for RZn(14N4)$^+$ but has little effect on RZn(N3)$^+$. If RZn(14N4)$^+$ ions have the same structure as RMg(14N4)$^+$ ions[32]—the metal atom bonded to all N's, the N−Me groups and R on the same side of the ring—then steric interactions with the N−Me groups may be responsible.

RM(coord)$^+$ + coord* Rate Experiments. It had been observed[17] that *i*-BuMg(14N4)$^+$ and 211C form *i*-BuMg(211C)$^+$ only if some *i*-Bu$_2$Mg is added. We studied several NpMg(coord)$^+$ + coord* systems (12N3−N3, 9N3−12N3, N4−14N4, N3−N4, and 14N4−211C) and also found no exchange in either direction, even after many weeks, in the absence of Np$_2$Mg. Equilibrium was achieved within 24 h, however, when some Np$_2$Mg was added. In the equilibrium experiments reported in Table 1, therefore, some R$_2$Mg (0.04 equiv) was included with the RMg(coord)$^+$ and coord*. This R$_2$Mg and the coord* will form some organomagnesate anion (eq 1). The crucial step may be transfer of R from this anion to RMg(coord)$^+$ (eq 9). The R$_2$Mg(coord) that is produced

$$\mathrm{RMg(coord)^+ + R_3Mg^- \rightleftharpoons R_2Mg(coord) + R_2Mg} \quad (9)$$

will be in equilibrium with coord and R$_2$Mg, making the latter available to form more RMg(coord*)$^+$.[33]

Exchanges of RZn(coord)$^+$ and coord*, by contrast, proceeded readily without added R$_2$Zn; the half-times for exchange (a few minutes to a few hours when RZn(coord)$^+$ and coord* were about 0.1 M) were not reduced if some (≤0.1 equiv) R$_2$Zn was present. For the relatively slow exchange in eq 10, the rate of appearance of EtZn(N3)$^+$ was independent of the initial N3 concentration.

(25) This may be a reflection of the "macrocyclic effect". Martell, A. E.; Hancock, R. D.; Motekaitis, R. J. *Coord. Chem. Rev.* **1994**, *133*, 39.

(26) The cation in crystalline MeMg(N3)$^+$ fluorenide$^-$ is a dimer, the Mg atoms connected by bridging Me groups: Viebrock, H.; Abeln, D.; Weiss, E. *Z. Nauturforsch. B* **1994**, *49*, 89. Also see: Viebrock, H.; Behrens, U.; Weiss, E. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1257.

(27) Data[23,28] from X-ray structures shows that covalent[24] C−Zn, N−Zn, and O−Zn bonds usually are slightly shorter and dative[24] N−Zn and O−Zn bonds often are slightly longer than the corresponding bonds involving Mg. Also see: Gruter, G.-J. M.; van Klink, G. P. M.; Akkerman, O. S.; Bickelhaupt, F. *Chem. Rev.* **1995**, *95*, 2405.

(28) Reviews of crystal structures of organomagnesium compounds: Markies, P. R.; Akkerman, O. S.; Bickelhaupt, F.; Smeets, W. J. J.; Spek, A. L. *Adv. Organomet. Chem.* **1991**, *32*, 147. Holloway, C. E.; Melnik, M. *J. Organomet. Chem.* **1994**, *465*, 1. Bickelhaupt, F. In *Grignard Reagents: New Developments*; Richey, H. G., Jr., Ed.; Wiley: Chichester, 2000; Chapter 9.

(29) Data obtained with aqueous and MeOH solutions often show that an additional N atom in the coordinating agent increases the equilibrium constant much more for coordination to Zn^{2+} than to Mg^{2+}.[12]

(30) For one recent discussion, see: Bock, C. W.; Katz, A. K.; Glusker, J. P. *J. Am. Chem. Soc.* **1995**, *117*, 3754. Also see: Markies, P. R.; Schat, G.; Akkerman, O. S.; Bickelhaupt, F.; Smeets, W. J. J.; Spek, A. L. *Organometallics* **1991**, *10*, 3538.

(31) Six bonds in NpMg(211C)$^+$, for example.[5]

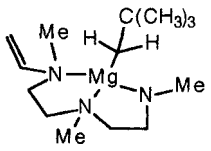
(32) Such a structure is seen for crystalline ZnCl(14N4)$^+$ though the dominant structure in solution may be different. Alcock, N. W.; Herron, N.; Moore, P. *J. Chem. Soc., Dalton Trans.* **1978**, 1282.

(33) The R$_2$Mg(coord) could have a rotaxane structure [Richey, H. G., Jr. In *Comprehensive Supramolecular Chemistry*; Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Vögtle, F., Eds.; Pergamon: Oxford, l996; Vol. 1 (G. W. Gokel, Ed.), Chapter 21] or alternatively a routine structure having only two or so O's coordinated to the Mg.

$$EtZn(211C)^+ + N3 \rightleftharpoons EtZn(N3)^+ + 211C \quad (10)$$

Decoordination of 211C from $EtZn(211C)^+$, not necessarily complete but at least sufficient to permit intrusion of N3, may initiate the exchange. $RZn(coord)^+ + coord^*$ exchanges merit further study to determine if the results for the system studied are typical.

R_2M and Coordinating Agents. The ^1H NMR spectra of solutions prepared from Np_2Mg and 9N3 revealed the formation of **15** by a cleavage of the 9N3



15

ring that is complete within 4 h at ambient temperature.[34] The spectra have characteristic $>NCH{=}CH_2$ absorptions. The Mg is a chiral center, and separate absorptions that therefore are possible for the two CH_2-Mg H's (if racemization by cleavage of Mg−N bonds, rotation around single bonds, and reformation of Mg−N bonds is slow relative to the NMR time scale) are seen. Cleavage probably results from abstraction of a hydrogen of 9N3 or of $NpMg(9N3)^+$ by a magnesate ion.[35]

In contrast with reactions of Np_2Mg with 211C or 14N4 that quantitatively produce $NpMg(coord)^+$ and Np_3Mg^-,[5,17] ^1H NMR spectra of solutions of Np_2Mg and N4 or 12N3 are similar to those of the reactants; small shifts of absorptions are consistent with formation only of rapidly exchanging peripheral complexes, having only two or so N atoms coordinated to the Mg. ^1H NMR absorptions of solutions of Et_2Zn and 9N3 or 211C and of solutions of Tol_2Zn and N3 or N4 (as observed[10] for these organozinc compounds with 221C) also were shifted only slightly from those of the reactants. Tol_2Zn and 211C or 9N3, however, formed $TolZn(211C)^+Tol_3Zn^-$[10] or $TolZn(9N3)^+Tol_3Zn^-$ (^1H NMR spectrum in Figure 4) quantitatively. Tol_2Zn and 12N3 or 14N4 formed precipitates; since little remained in solution when the ratio of Tol_2Zn to coordinating agent was 2, these precipitates also may be $TolZn(coord)^+Tol_3Zn^-$.

The ^1H NMR spectrum of a solution prepared from $EtZn(9N3)^+Ph_4C_5H^-$ and Tol_2Zn (2:1) showed that $K \cong 3$ for the equilibrium in eq 11.[36] The equilibrium in eq

$$2\ EtZn(9N3)^+ + Tol_2Zn \rightleftharpoons 2\ TolZn(9N3)^+ + Et_2Zn \quad (11)$$

$$2\ Et_3Znk + 3\ Tol_2Zn \rightleftharpoons 2\ Tol_3Znk + 3\ Et_2Zn \quad (12)$$

12 lies substantially to the right, however; the ^1H NMR spectrum of a solution prepared from Et_3ZnK and Tol_2Zn (2:3) had Et absorptions characteristic of Et_2Zn and an *o*-H absorption shifted considerably downfield, as observed for Tol_3Zn^- in the presence of other cations. Taken together, these results indicate that the greater

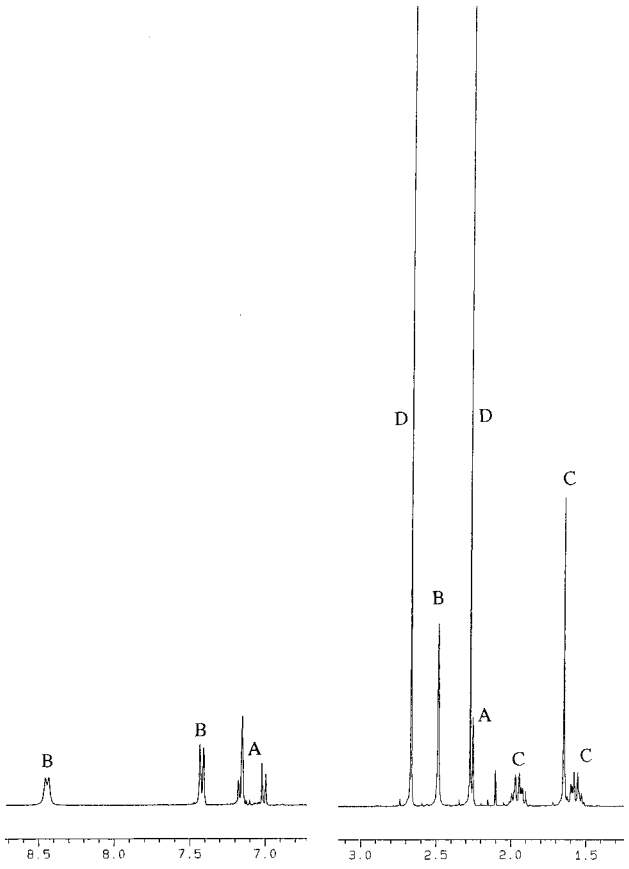


Figure 4. ^1H NMR spectrum (300 MHz) of a benzene-d_6 solution (0.1 M) of $TolZn(9N3)^+Tol_3Zn^-$ also containing free 9N3. Tol absorptions of the cation are labeled A, and those of the anion are labeled B. Absorptions of 9N3 of the cation are labeled C, and those of free 9N3 are labeled D.

tendency of Tol_2Zn than of Et_2Zn to form $RZn(coord)^+R_3Zn^-$ is due more to greater stabilization of an anion by Tol than by Et than it is to different strengths of coordination to 9N3 in $EtZn(9N3)^+$ and $TolZn(9N3)^+$. Disproportionation of R_2Zn requires both a coordinating agent particularly effective for RZn^+ and an R particularly effective at stabilizing R_3Zn^-.

Comparison of Abilities to Coordinate to RZn^+ and to Convert R_2Zn to $RZn(coord)^+R_3Zn^-$. Abilities to coordinate to RZn^+, measured by the equilibrium in eq 3, and to convert R_2Zn to $RZn(coord)^+$ and R_3Zn^- (eq 1) are not parallel. For example, 211C but not N3 or N4 can disproportionate Tol_2Zn, but (at least with Et and Np) N3 and N4 coordinate to RZn^+ more effectively than does 211C. These differences must arise because coordination *is possible both to R_2Zn and to RZn^+*. Formation of $RZn(coord)^+$ is reduced by the competing formation of $R_2Zn(coord)$. Due to its shape, 211C does not coordinate particularly effectively with an R_2Zn compound: its cavity cannot envelop RZnR but can accept RZn^+. By contrast, N atoms of N3 and N4 can readily surround the Zn atoms of both R_2Zn and RZn^+.

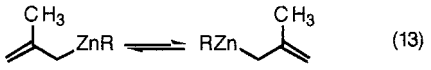
^1H NMR spectra of $(CH_2{=}CMeCH_2)_2Zn$ provide confirming information about abilities to coordinate to R_2Zn. At ambient temperature, only two singlets ordinarily are observed, one for CH_3 and one representing both $=CH_2$ and CH_2Zn. Discrete CH_2Zn and cis and trans $=CH_2$ absorptions have been seen only at low

(34) Formation of **15** was not significant in the exchange experiments in which $NpMg(9N3)^+Ph_4C_5H^-$ was a component.

(35) A similar though slower cleavage of 211C by Np_2Mg has been reported. Squiller, E. P.; Whittle, R. R.; Richey, H. G., Jr. *Organometallics* **1985**, *4*, 1154.

(36) TolZnEt also must be present, but we assume that the stability of Tol (Et) in this species is not very different than in Tol_2Zn (Et_2Zn).

temperatures[37] that slow the allylic isomerization (eq 13) that at ambient temperature is rapid relative



(13)

to the NMR time scale. We found, however, that solutions with N3, N4, or 14N4 exhibit at ambient temperature the absorptions expected for nonisomerizing $(CH_2{=}CMeCH_2)_2Zn$ (although with 14N4, absorptions are broad); solutions with 9N3, 12N3, or 211C have only one broad absorption for the allylic CH_2 groups. Coordination of the Zn by N3 and N4 must be more effective than by the cyclic coordinating agents.[38,39]

Experimental Section

Procedures involving organometallic compounds were performed under a nitrogen atmosphere using Schlenk techniques, a glovebox, and a vacuum line. Nitrogen was purified by passing through columns of manganese oxide oxygen scavenger and molecular sieves (4 Å). Glassware was dried in an oven at 200 °C for at least 4 h prior to use. Benzene-d_6 (Cambridge Isotope Laboratories) was stored over molecular sieves (4 Å). Benzene (isotopically normal), pentane, dioxane, and organic halides were distilled from CaH_2; dioxane was stored over molecular sieves (4 Å) under a nitrogen atmosphere. Diethyl ether and tetrahydrofuran were distilled from sodium benzophenone ketyl immediately prior to use. TMEDA, DMSO, and HMPA were distilled from CaH_2 at reduced pressure. Mg was "99.95%" (Aldrich Chemical Co.). Et_2Hg (Strem Chemicals) and all other chemicals (Aldrich Chemical Co.) were used as received. NMR spectra were taken in benzene-d_6. ^1H absorptions are reported relative to internal C_6D_5H (taken as δ 7.15 ppm) using the following notations: s, singlet; d, doublet; t, triplet; q, quartet; m, a more complex multiplet; c, complex overlapping absorptions; b, broad. ^{13}C absorptions are reported relative to internal C_6D_6 (taken as δ 128.0). Solutions for NMR analysis were prepared in the glovebox and transferred into NMR tubes, to which an extension of routine glass tubing had been added to facilitate sealing with a flame. The NMR tube was capped temporarily with a rubber septum, removed from the glovebox, immersed in liquid nitrogen, and sealed at the extension.

Reactions of EtZnCp with Coordinating Agents. Solutions were prepared in benzene-d_6 having equal concentrations (listed for each preparation) of EtZnCp and a coordinating agent. The ^1H NMR spectrum of EtZnCp is given for purposes of comparison: (200 MHz) δ 0.26 (q, J = 8.1 Hz, 2, CH_2), 1.40 (t, J = 8.0 Hz, 3, CH_3), 6.03 (s, 5, CH).

14N4: Preparation of $EtZn(14N4)^+EtZnCp_2^-$. Components were initially 0.6 M, but phase separation occurred. ^1H NMR (360 MHz, lower phase): δ −0.44 (q, J = 8.2 Hz, 2, CH_2Zn^+), −0.20 (q, J = 7.9 Hz, 2, CH_2Zn^-), 0.90−2.00 (c, 16, most CH_2's of $14N4^+$), 1.06 (t, J = 8.2 Hz, 3, $CH_3CH_2Zn^+$), 1.34 (t, J = 8.1 Hz, 3, $CH_3CH_2Zn^-$), 1.59 (s, 12, CH_3N), 2.24 (bt, 4, $CHHCH_2CHH$), 6.25 (s, 10, CH).

TMEDA. ^1H NMR (0.4 M, 200 MHz): δ −0.15 (q, J = 8.0 Hz, 2, CH_2Zn), 1.39 (t, J = 8.0 Hz, 3, CH_3CH_2), 1.52 (s, 4, CH_2N), 1.78 (s, 12, CH_3N), 6.49 (s, 5, CH).

DMSO. ^1H NMR (0.3 M, 300 MHz): δ 0.28 (q, J = 8.0 Hz, 2, CH_2Zn), 1.27 (t, J = 8.0 Hz, 3, CH_3CH_2), 1.71 (s, 6, CH_3S), 6.26 (s, 5, CH).

HMPA. ^1H NMR (0.3 M, 200 MHz): δ 0.29 (q, J = 8.0 Hz, 2, CH_2Zn), 1.38 (t, J = 8.0 Hz, 3, CH_3CH_2), 2.20 (d, J = 9.5 Hz, 9, CH_3N), 6.53 (s, 5, CH).

Preparation of $RM(Coord)^+Ph_4C_5H^-$ Solutions. In a typical preparation of $RZn(coord)^+$, an R_2Zn compound (0.050 mmol) and $Ph_4C_5H_2$ (18 mg, 0.050 mmol) were weighed into a container, and a benzene-d_6 solution of the coordinating agent (0.50 mL, 0.10 M, 0.050 mmol) was added. The preparation was stirred (stirring bar) for a few minutes, and the resulting green solution was sealed into an NMR tube. The NMR tube was heated at 70 °C for 2 h and then examined by ^1H NMR spectroscopy to verify that reaction was complete. The $Ph_4C_5H^-$ absorptions in ^1H NMR spectra, essentially identical for all solutions, were assigned with the aid of NOE and decoupling experiments. The absorption at δ 6.77, which because of its position and because it is a singlet must be due to H_1, has a NOE effect with the doublet at δ 7.61 but not the doublet at δ 7.47. Therefore, the δ 7.61 doublet is assigned to the *o*-H of the α-phenyl and the δ 7.47 doublet to the *o*-H of the β-phenyl. Decoupling experiments that show connectivities to these H's then permitted assigning the other absorptions: (300 MHz) δ 6.77 (s, 1, $Ph_4C_5H^-$), 6.94 (t, J = 7.2 Hz, 2, *p*-H of α-Ph), 7.09 (t, J = 7.3 Hz, 2, *p*-H of β-Ph), 7.23 (t, J = 7.6 Hz, 4, *m*-H of α-Ph), 7.29 (t, J = 7.5 Hz, 4, *m*-H of β-Ph), 7.47 (d, J = 7.2 Hz, 4, *o*-H of β-Ph), 7.61 (d, J = 7.5 Hz, 4, *o*-H of α-Ph). The preparations of $RMg(coord)^+$ solutions followed the same procedure except that the NMR tube was heated at no more than 50 °C for no longer than 20−30 min before examination by ^1H NMR spectroscopy to verify that reaction was complete.

Exchange of $RZn(coord)^+$ with coord*. The general procedure is illustrated using N3 and N4 as the coordinating agents. A benzene-d_6 solution of N3 (0.50 mL, 0.10 M, 0.050 mmol) and the contents of an NMR tube containing a benzene-d_6 solution of $RZn(N4)^+Ph_4C_5H^-$ (0.50 mL, 0.10 M, 0.050 mmol) were added to a vial. Similar amounts of solutions of N4 and of $RZn(N3)^+Ph_4C_5H^-$ were added to another vial. The resulting solutions were stirred for a few minutes (stirring bar), each was then placed into an NMR tube, and the NMR tubes were sealed. When $K = [RZn(coord)^+][coord^*]/[RZn(coord^*)^+][coord]$ exceeded 100, an excess (ca. 5-fold) of coord was used to make small absorptions of $RMg(coord)^+$ and coord* larger and integration more accurate. The NMR tubes were maintained at 22 ± 1 °C. ^1H NMR data were recorded when (depending on the system, several hours to 2 days) it was evident that the NMR spectra of the two solutions no longer were changing. For K's of 100 or so, more than 100 scans were taken to obtain good signal-to-noise ratios for the smaller absorptions. Values of K (in parentheses) obtained from $RZn(coord)^+$ with coord*: $EtZn(211C)^+$ with N3* (3.5); $EtZn(N_3)^+$ with 211C* (1/3.7), N4* (3.0), 12N3* (7.5), 14N4* (180); $EtZn(N4)^+$ with N3* (1/3.1), 12N3* (2.2), 14N4* (48); $EtZn(12N3)^+$ with N3* (1/7.3), N4* (1/2.3) 14N4* (18); $EtZn(14N4)^+$ with N3* (1/155), N4* (1/43), 12N3* (1/19), 9N3* (68); $EtZn(9N3)^+$ with 14N4* (1/64); $NpZn(211C)^+$ with 14N4* (50), N3* (171); $NpZn(14N4)^+$ with 211C* (1/54), N4* (2.1), 12N3* (2.2), N3* (4.6); $NpZn(N4)^+$ with 14N4* (1/2.0), 12N3* (1.1), N3* (1.7); $NpZn(12N3)^+$ with 14N4* (1/2.4), N4* (1.0), N3* (1.7); $NpZn(N3)^+$ with 211C* (1/156), 14N4* (1/4.8), N4* (1/1.8), 12N3* (1/1.6). The values of K obtained from a pair of solutions ($RZn(coord)^+$ + coord* and RZn(coord*) + coord) always were very similar. In studies of $NpZn(9N3)^+$ with N3, 14N4, or N4, absorptions of $NpZn(N3)^+$, $NpZn(14N4)^+$, and $NpZn(N4)^+$ were not detected at equilibrium.

Exchange of $RMg(coord)^+$ with coord*. The solutions were prepared as for $RZn(coord)^+$ exchange except that an R_2Mg solution (20 mg, 0.10 M, 0.0020 mmol) was weighed into the vial. ^1H NMR absorptions generally were evident for the Np_2Mg, although their positions were somewhat altered by

(37) Benn, R.; Hoffmann, E. G.; Lehmkuhl, H.; Nehl, H. *J. Organomet. Chem.* **1978**, *146*, 103. Also see: Benn, R.; Grondey, H.; Lehmkuhl, H.; Nehl, H.; Angermund, K.; Krüger, C. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1279.

(38) Coordination by 18C6 effectively reduces allylic isomerization, but that is the consequence of forming a rotaxane structure.[10]

(39) Although solutions of $(CH_2{=}CMeCH_2)_2Zn$ in nonpolar solvents at ambient temperature are prone to decompose, solutions containing N3 and N4 seemed to be indefinitely stable and solutions containing 14N4 decomposed only slowly.

interaction with the coordinating agents in the solutions. After 4 h, it was evident that the NMR spectra of the two solutions no longer were changing, and ^{1}H NMR data were recorded. Values of K: $EtMg(14N4)^+$ with N4* (1/590); $EtMg(N4)^+$ with 14N4* (670), 15C5* (1/6.0), 9N3* (1/75); $EtMg(15C5)^+$ with N4* (6.1), 9N3* (1/11); $EtMg(9N3)^+$ with N4* (72), 15C5* (12); $NpMg(211C)^+$ with 14N4* (1/200); $NpMg(221C)^+$ with 14N4* (1/1.15); $NpMg(14N4)^+$ with 211C* (165), 221C* (1.24), N4* (1/790); $NpMg(N4)^+$ with 14N4* (670), 15C5* (1/2.2), 9N3* (1/12), 12N3* (1/260); $NpMg(15C5)^+$ with N4* (2.1), 9N3* (1/6.1); $NpMg(9N3)^+$ with N4* (11), 15C5* (6.4), 12N3* (1/18); $NpMg(12N3)^+$ with N4* (240), 9N3* (20), N3* (1/2.0); $NpMg(N3)^+$ with 12N3* (2.1). In a study of $NpMg(6N3)^+$ with N3, $NpMg(6N3)^+$ absorptions were not detected at equilibrium.

RZn(211C)$^+$ + N3 Kinetic Experiments. A benzene-d_6 solution of $EtZn(211C)^+Ph_4C_5H^-$ (0.046 M, a small excess of $Ph_4C_5H_2$ was used in its preparation to ensure that no Et_2Zn remained) was injected rapidly using a syringe, and the mixture was monitored by ^{1}H NMR spectroscopy at 22 ± 1 °C. Initial N3 concentrations ($[N3]_0$) were determined by integration of N3 absorptions relative to the $Ph_4C_5H^-$ absorption. For solutions prepared with different $[N3]_0/[EtZn(211C)^+]_0$ ratios (1.4−10.1), plots against time of $[CH_3CH_2Zn(N3)^+]/[Ph_4C_5H^-]$ (determined by integration of the indicated absorptions) using values < 0.10−0.15 gave straight lines (R^2 = 0.97−0.99) with similar (variation <±1%) slopes.

Exchange of EtZn(N3)$^+$ and NpZn(9N3)$^+$. Benzene-d_6 solutions of $EtZn(N3)^+Ph_4C_5H^-$ and $NpZn(9N3)^+Ph_4C_5H^-$ (each 0.10 M) were combined. Similar solutions of $EtZn(9N3)^+Ph_4C_5H^-$ and $NpZn(N3)^+Ph_4C_5H^-$ were combined. Each new solution was sealed into an NMR tube. The ^{1}H NMR spectra of the two solutions recorded after 1 day, when no further change was apparent, were essentially identical. Relative concentrations of each component in eq 5 were determined using the absorptions already indicated. Values of 1.06 and 1.08 were calculated for K_{Np-Et}.

Exchange of NpMg(14N4)$^+$ and Et$_2$Mg. Et_2Mg (2.0 mg, 0.025 mmol) was weighed into a vial, and a benzene-d_6 solution of $NpMg(14N4)^+C_5Ph_4H^-$ (0.50 mL, 0.10 M, 0.050 mmol) was added. Np_2Mg (4.0 mg, 0.025 mmol) and a similar solution of $EtMg(14N4)^+Ph_4C_5H^-$) were placed in another vial. Each resulting solution was sealed in an NMR tube. The ^{1}H NMR spectra no longer were changing when examined after 4−5 h; spectra of the two solutions recorded after 1 day were virtually identical. Discrete absorptions were seen for $CH_3CH_2Mg(14N4)^+$ and $(CH_3)_3CCH_2Mg(14N4)^+$. However, the ^{1}H NMR absorptions of Et and Np groups in Np_2Mg and Et_2Mg (and probably also NpMgEt) were too broad (presumably due to exchanges with half-times not very long relative to the NMR time scale) to permit distinguishing Et and Np absorptions. The ratios of $[EtMg(14N4)^+]/[NpMg(14N4)^+]$ obtained from the two solutions were 2.6 and 3.5. From the average of these values and the amounts of reagents used to prepare the solutions, $K = [NpMg(14N4)^+][Et_2Mg]^{1/2}/[EtMg(14N4)^+][Np_2Mg]^{1/2}$ was calculated to be 0.19.

RZn(coord)$^+$ + R′$_2$Zn Exchange Experiments. The general procedure is described for the case in which R and R′ = Et and *i*-Pr and coord = N3. Et_2Zn (6.2 mg, 0.025 mmol) was weighed into a vial to which then was added a benzene-d_6 solution of i-PrZn(coord)$^+Ph_4C_5H^-$ (0.50 mL, 0.10 M, 0.050 mmol). i-Pr_2Zn (7.6 mg. 0.025 mmol) and a similar solution of $EtZn(coord)^+Ph_4C_5H^-$ were placed in another vial. Each new solution was sealed into an NMR tube. ^{1}H NMR spectra of the solutions, recorded after 1 day, at which time the spectra no longer were changing, were essentially identical. To help identify ^{1}H NMR absorptions of diorganozinc compounds, RZnR′, expected to be present, spectra of solutions prepared from R_2Zn and R′$_2$Zn were examined. Discrete RZnR′ absorptions were detected when R and R′ were Et and *t*-Bu or were *i*-Pr and *t*-Bu. When R and R′ were Et and *i*-Pr or were Et and Np, R and R′ absorptions were broad, presumably a consequence of fast exchanges. The relative concentrations of the organozinc cations and diorganozinc compounds were determined from intensities of absorptions of hydrogens α to zinc. In calculating $K = [R'Zn(coord)^+]^2[R_2Zn]/[RZn)coord)^+]^2[R'_2Zn]$, all R (R′) absorptions were treated as being due to R_2Zn (R′$_2$Zn), even when discrete NMR absorptions are seen for RZnR′.

Reaction of Np$_2$Mg and 9N3: Formation of 15. A homogeneous solution resulted from combining Np_2Mg (25 mg, 0.15 mmol) and 9N3 (12 mg, 0.07 mmol) in benzene-d_6 (0.5 mL). The following ^{1}H NMR (200 MHz) spectrum was taken after 4 h: δ −0.11 (d, 2, J = 11 Hz, C*H*HMg), 0.15 (d, 2, J = 11 Hz, CH*H*Mg), 1.36 (s, 9, (CH_3)C), 1.83 (s, 3, CH_3NMg), 1.9−3.6 (c, 8, CH_2N), 2.26 (s, 3, another CH_3N), 2.60 (s, 3, another CH_3N), 3.73 (d, 1, J = 15 Hz, C*H*H═), 3.85 (d, 1, J = 9 Hz, CH*H*═), 6.01 (d of d, 1, J = 9 and 15 Hz, NCH═). Besides the absorptions above ascribed to **15**, large absorptions of neopentane and Np_2Mg were present.

Reactions of Tol$_2$Zn and coord to Form TolZn(coord)$^+$-Tol$_3$Zn$^-$. TolZn(9N3)$^+$Tol$_3$Zn$^-$. Tol_2Zn (20 mg, 0.08 mmol), 9N3 (14 mg, 0.08 mmol), and benzene-d_6 (0.5 mL) gave a homogeneous solution. ^{1}H NMR (300 MHz): δ 1.57 (m, 6, C*H*H of $9N3^+$), 1.64 (s, 9, CH_3 of $9N3^+$), 1.96 (m, H, CH*H* of $9N3^+$), 2.25 (s, 3, CH_3 of $TolZn^+$), 2.49 (s, 9, CH_3 of Tol_3Zn^-), 2.27 (s, 9, CH_3 of 9N3), 2.67 (s, 12, CH_2 of 9N3), 7.01 (d, J = 7.8 Hz, 2, *o*- or *m*-H's of $TolZn^+$), 7.16 (d, J = 7.7 Hz, 2, *o*- or *m*-H's of $TolZn^+$), 7.42 (d, J = 7.2 Hz, 6, *m*-H of Tol_3Zn^-), 8.44 (d, J = 6.8 Hz, 6, *o*-H of Tol_3Zn^-).

TolZn(211C)$^+$Tol$_3$Zn$^-$. Tol_2Zn (12 mg, 0.05 mmol), 211C (7 mg, 0.025 mmol), and benzene-d_6 (0.5 mL) gave a homogeneous solution. ^{1}H NMR (200 MHz): δ 1.16−3.10 (c, 28, 211C), 2.32 (s, 3, CH_3 of $TolZn^+$), 2.37 (s, 9, CH_3 of Tol_3Zn^-), 7.28 (c, 10, overlapping of *o*- and *m*-H's of $TolZn^+$ and *m*-H's of Tol_3Zn^-), 8.14 (d, J = 7.0 Hz, 6, *o*-H's of Tol_3Zn^-).

Reaction of Et$_3$ZnK and Tol$_2$Zn: Preparation of Tol$_3$ZnK. Et_3ZnK[40] (10.8 mg, 0.060 mmol) and Tol_2Zn (22.5 mg, 0.090 mmol) were weighed into a vial, and benzene-d_6 (0.5 mL) was added. The resulting solution was placed into an NMR tube; equilibrium was achieved rapidly and ^{1}H NMR data were recorded after 2 h. ^{1}H NMR (360 MHz): δ 0.12 (q, J = 8.2 Hz, 4, CH_2Zn), 1.13 (t, J = 8.2 Hz, 6, CH_3CH_2), 2.20 (s, 9, CH_3 of Tol), 7.06 (d, J = 7.4 Hz, 6, *m*-H), 7.62 (d, J = 6.9 Hz, 6, *o*-H).

Single-Crystal X-ray Diffraction Analysis of TolZn(N4)$^+$-Ph$_4$C$_5$H$^-$. Tol_2Zn (24.4 mg, 0.10 mmol), N4 (24.0 mg, 0.10 mmol), $Ph_4C_5H_2$ (37.6 mg, 0.10 mmol), and benzene (1 mL) were combined. This mixture was heated to 90 °C for 1 h to dissolve all solid and then slowly cooled over a day. Large crystals formed. A yellow prismatic crystal having dimensions of 0.55 × 0.40 × 0.35 mm was mounted in an X-ray diffraction capillary. Diffraction data for this crystal ($C_{48}H_{58}N_4Zn$, mol wt = 756.39) were collected at −73 ± 1 °C with a Rigaku AFC6S diffractometer using graphite monochromated Mo Kα (λ = 0.71069 Å) radiation. Lattice constants obtained by least-squares refinement of the setting angles of 13 carefully centered reflections in the range 18.84° < 2θ < 20.87° corresponded to a primitive monoclinc cell: a = 12.363 (4) Å, b = 19.347 (3) Å, c = 18.156 (4) Å, β = 105.86 (2)°, V = 4177-(1) Å^3, Z = 4, D_{cacld} = 1.203 g cm^{-3}, F_{000} = 1616.00. Systematic absences uniquely determined the space group to be $P2_1/c$ (#14). Intensity data were collected using the ω−2θ technique to a maximum 2θ of 50.1°. Of the 7927 reflections that were collected, 7555 were unique. The intensities of three representative reflections decreased by 2.2% over the course of the data collection; a linear correction factor was applied to the data to correct for this decay. An empirical absorption correction based on azimuthal scans of several reflections was applied, which resulted in transmission factors ranging from 0.95 to 1.00. The data were corrected for Lorentz and polariza-

(40) Musser, C. A.; Richey, H. G., Jr. *J. Org Chem.*, in press.

tion effects. The structure was solved by and expanded using Fourier techniques. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included at geometrically idealized positions with C−H = 0.95 Å and were not refined. The final cycle of full-matrix least-squares refinement, based on 1997 reflections ($I > 3.00\sigma(I)$) and 478 parameters, converged with $R = 0.064$ and $R_w = 0.061$. In the final difference map, the maximum peak was 0.85 e^- $Å^{-3}$, and the minimum peak was −0.35 e^- $Å^{-3}$.

Acknowledgment. We thank the National Science Foundation for supporting this research. We are grateful to Alan Benesi for help with NMR experiments. H.G.R. acknowledges a NATO Collaborative Research Grant that made possible valuable discussions with Professor Friedrich Bickelhaupt and co-workers at the Free University in Amsterdam.

Supporting Information Available: Preparations of EtZnCp, diorganozinc compounds, and diorganomagnesium compounds; ^1H NMR spectra of $RMg(coord)^+Ph_4C_5H^-$ solutions, $RZn(coord)^+Ph_4C_5H^-$ solutions, coordinating agents, solutions of $RZn(coord)^+Ph_4C_5H^-$ and diorganozinc compounds, and solutions of coordinating agents and diorganozinc or diorganomagnesium compounds; 2D NMR experiments with $EtMg(N4)^+Ph_4C_5H^-$; study of effects of concentration on exchange of $EtZn(N3)^+$ and N4; and details of the X-ray structure determination of $TolZn(N4)^+$ $Ph_4C_5H^-$. This material is available free of charge via the Internet at http://pubs.acs.org.

OM000427E