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Comparison of Coordination to RMg^+ and RZn^+ Cations

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Summary: Addition of a second coordinating agent (coord) to a solution of $RM(coord)^+$ ($M = Zn$ or Mg) leads to equilibrium mixtures of $RM(coord)^+$ and $RM(coord*)^+$. The equilibrium constants provide information about the relative abilities of different coordinating agents to coordinate to RM^+. The results for RMg^+ and RZn^+ are significantly different.*

We earlier found that reactions, as in the example in eq 1, of an organomagnesium compound with an appropriate coordinating agent (coord), particularly some macrocyclic compounds, could form a magnesate anion and a RMg^+ cation in which the Mg is coordinated by the macrocycle.[1] Formation of several strong bonds

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

from oxygen and nitrogen atoms of the coordinating agent to the Mg of the cation must provide the driving force for this disproportionation. We have since used such reactions to form new organometallic cations and anions of magnesium and other metals[2] and as a consequence have wanted to know more about the abilities of different coordinating agents to coordinate to organometallic cations. For example, what is the position of the equilibrium in eq 2 for different coordinating agents and metals (M)?

$$RM^+ + coord \rightleftharpoons RM(coord)^+ \qquad (2)$$

Of course, if M is a polar metal, uncoordinated RM^+ will not exist significantly under any normal circumstances and, with any useful coordinating agent, the position of the equilibrium in eq 2 would lie immeasurably far to the right. *Relative* coordinating abilities, however, are potentially available by using a competitive[3] complexation procedure. To a solution containing a coordinated organometallic cation is added a different coordinating agent. If exchange (eq 3) occurs, then determining the composition of the solution after equilibrium is achieved will indicate the relative abilities of the two coordinating agents to coordinate to RM^+.[4]

$$RM(coord)^+A^- + coord^* \rightleftharpoons RM(coord^*)^+A^- + coord \qquad (3)$$

We chose 2,3,4,5-tetraphenylcyclopentadienyl as the anion (A^-). Because of its bulk and dispersed charge, this anion should have little specific interaction with the cation and, hence, no significant effect on the relative values of the equilibrium constants. Moreover, its salts with $RMg(coord)^+$ and $RZn(coord)^+$ often are soluble in benzene. Benzene was used as the solvent, since the deuterated version often needed for NMR studies is relatively inexpensive and the large organic

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[⊗] Abstract published in *Advance ACS Abstracts*, October 15, 1996.

[1] Squiller, E. P.; Whittle, R. R.; Richey, H. G., Jr. *J. Am. Chem. Soc.* **1985**, *107*, 432. Richey, H. G., Jr.; Kushlan, D. M. *J. Am. Chem. Soc.* **1987**, *109*, 2510. Pajerski, A. D.; Parvez, M.; Richey, H. G., Jr. *J. Am. Chem. Soc.* **1988**, *110*, 2660. Fabicon, R. M.; Pajerski, A. D.; Richey, H. G., Jr. *J. Am. Chem. Soc.* **1993**, *115*, 9333.

[2] Al: Richey, H. G., Jr.; BergStresser, G. L. *Organometallics* **1988**, *7*, 1459. Zn: Fabicon, R. M.; Pajerski, A. D.; Richey, H. G., Jr. *J. Am. Chem. Soc.* **1991**, *113*, 6680. Cd: Tang, H.; Parvez, M.; Richey, H. G., Jr. Submitted for publication in *Organometallics*.

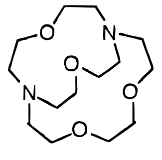
[3] Wang, T.; Bradshaw, J. S.; Izatt, R. M. *J. Heterocycl. Chem.* **1994**, *31*, 1097.

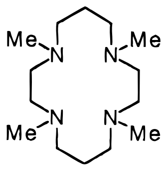
[4] Note that the coordinating ability measured by the equilibrium in eq 3 will not exactly parallel that in the equilibrium in eq 1, since formation of $RMg(coord)^+$ in eq 1 can be affected also by the ability of the coordinating agent to coordinate to R_2Mg.

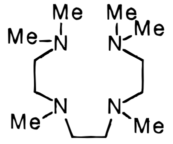
salts that we are concerned with often are equally or more soluble in benzene than in solvents, such as diethyl ether and THF, used more commonly for polar organometallic compounds.

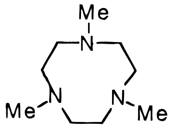
Salts were synthesized by reaction of R_2M with 1,2,3,4-tetraphenylcyclopentadiene in the presence of a coordinating agent (eq 4). Reactions with Et_2Zn or neo-Pe_2Zn (neo-Pe = neopentyl) at temperatures in the range 25−70 °C are complete within a few hours when the coordinating agent is 211C (**1**; 2,1,1-cryptand), 14N4 (**2**; 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane), N4 (**3**; 2,5,8,11-tetramethyl-2,5,8,11-tetraazadodecane), 9N3 (**4**; 1,4,7-trimethyl-1,4,7-triazacyclononane), 12N3 (**5**; 1,5,9-trimethyl-1,5,9-triazacyclododecane), or N3 (**6**; 2,5,8-trimethyl-2,5,8-triazanonane). No significant reaction occurs over many days, however, when the coordinating agent is 15-crown-5, 18-crown-6, 12-crown-4, or 6N3 (1,3,5-trimethyl-1,3,5-triazacyclohexane).[5] Reactions of neo-Pe_2Mg and the cyclopentadiene with all of these coordinating agents, however, are relatively ready.[5] The significant absorptions in ^1H NMR spectra of the resulting solutions can be assigned to RM(coord)$^+$$(Ph)_4C_5H^-$. For example, as is typical of RMg(coord)$^+$ and RZn(coord)$^+$ cations, the α-hydrogen absorptions of neopentyl or ethyl are considerably *upfield* from those in the R_2M reactant. The absorptions of the coordinating agent are shifted from and often more numerous than those of the free coordinating agent. In fact, the NMR spectra of the cations with M = Mg and coord = 211C, 14N4 are similar to those previously observed for these cations in the presence of other anions.[1,6] All solutions exhibit essentially identical $(Ph)_4C_5H^-$ absorptions.

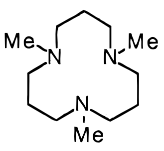
$$R_2M + (Ph)_4C_5H_2 + \text{coord} \rightarrow \text{RM(coord)}^+(Ph)_4C_5H^- + RH \quad (4)$$


1 (211C)


2 (14N4)


3 (N4)


4 (9N3)


5 (12N3)

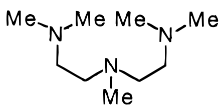

6 (N3)

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

coord*	neo-PeMg(coord*)$^+$	neo-PeZn(coord*)$^+$ [b]	EtZn(coord*)$^+$
1 (211C)	66 000 000	(1) [0.025]	(1)
2 (14N4)	370 000	40 [1.0]	390
3 (N4)	500	82 [2.1]	9.3
4 (9N3)	40	1 100 000 [28,000]	26 000
5 (12N3)	2.1	88 [2.2]	21
6 (N3)	(1)	142 [3.6]	3.0

[a] "coord" is the least coordinating ligand for the particular RM^{2+}. [b] The values in brackets were assigned as described in the text.

Addition of a second coordinating agent (coord*) to a solution of RM(coord)$^+$ in some instances leads to exchange to form RM(coord*)$^+$. Exchanges are slow on the NMR time scale, and discrete absorptions are seen for all four components in eq 3. Therefore, the relative concentration of each component can be determined by integration of the area of an appropriate ^1H NMR absorption.[7] To be certain that equilibrium was achieved, each exchange was studied in both directions. The expression K_R = [RM(coord*)$^+$][coord]/[RM(coord)$^+$][coord*] should describe the equilibria, and this was shown to be correct for the case in which R = Et, M = Zn, and coord, coord* = N3, N4.

A column of Table 1 gives the values of *K* for the equilibrium (eq 3) of coord* and neo-PeMg(coord)$^+$, neo-PeZn(coord)$^+$, or EtZn(coord)$^+$, where coord is the least effective coordinating agent in that column. Most data listed in the table were obtained in a stepwise fashion using pairs of coordinating agents which in that column were closest in coordinating ability. In the neo-PeZn(coord)$^+$ series, for example, 211C was the poorest coordinating agent and was studied with 14N4, which in turn was studied with N4, and so on. Some other combinations were studied, however, and led to very similar *K* values. The constant relating neo-PeZn(N3)$^+$ and neo-PeZn(9N3)$^+$ was too large to measure in this manner, and we could only conclude that *K* for 9N3 was ≥1000 times that for N3. This constant could be determined less directly, however, by a relay from the EtZn(coord)$^+$ system. The equilibrium constant ($K_{\text{Et-neo-Pe}}$ = [EtZn(9N3)$^+$][neo-PeZn(N3)$^+$]/[EtZn(N3)$^+$][neo-PeZn(9N3)$^+$]) for the mixed system in eq 5 is 1.1.

$$\text{EtZn(N3)}^+ + \text{neo-PeZn(9N3)}^+ \rightleftharpoons \text{EtZn(9N3)}^+ + \text{neo-PeZn(N3)}^+ \quad (5)$$

Note that $K_{\text{Et-neo-Pe}}$ equals $K_{\text{Et}}/K_{\text{neo-Pe}}$, where K_{Et} and $K_{\text{neo-Pe}}$ are the constants for equilibria in eq 3 which involve only ethyl or only neopentyl groups. K_{Et} has been determined for this pair of coordinating agents, permitting a value to be assigned to $K_{\text{neo-Pe}}$. The fact that the abilities of neo-PeZn$^+$ and EtZn$^+$ to cordinate to different coordinating agents are not exactly parallel permits this use of the mixed system to determine an equilibrium constant too large to measure directly.

The numbers in any column of Table 1 are not on the same scale as those in the other columns—coordination by the poorest coordinating agent in one column may be stronger than by the poorest coordinating agent in another. Determining the position of equilibria such as that in eq 6, however, provides an approach to putting the data in different columns on the same scale. The value of the equilibrium constant (*K* = [neo-PeZn(N3)$^+$]^2[Et_2Zn]/[EtZn(N3)$^+$]^2[neo-Pe_2Zn]) for this equa-

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(5) The species removing the proton from the cyclopentadiene probably is an ate ion (e.g., R_3M^-) (Richey, H. G., Jr.; King, B. A. *J. Am. Chem. Soc.* **1982**, *104*, 4672). The ease of the reaction, therefore, may be related to the degree of disproportionation of R_2M (e.g., eq 1) by the coordinating agent.

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

(7) Absolute concentrations are known from the amounts of reagents used to prepare the solutions. To the extent that the equilibrium expression for eq 2 is valid, however, the equilibrium constant depends on ratios of the species but is independent of their absolute concentrations.

$$2\mathrm{EtZn(N3)}^{+}\mathrm{A}^{-} + \text{neo-Pe}_2\mathrm{Zn} \rightleftharpoons 2\text{neo-PeZn(N3)}^{+}\mathrm{A}^{-} + \mathrm{Et}_2\mathrm{Zn} \quad (6)$$

tion is 1.45. In a related experiment using ethyl and isopropyl, the value of K was 1.20. If we assume that the effects of Et and neo-Pe are exerted principally on the ions (instead of on neo-Pe_2Zn and Et_2Zn),[8] then a factor of $(1.45)^{1/2}$ can be used to transform the values in the neo-PeZn(coord)$^+$ column into values (given in brackets) that should be related to those in the EtZn(coord)$^+$ column. The EtZn(coord)$^+$ and bracketed neo-PeZn(coord)$^+$ values show considerable similarity, except for a significantly reduced tendency in the neopentyl system for coordination to 211C and 14N4, reasonable because of adverse steric effects of the neopentyl group.

The results with neo-PeMg(coord)$^+$ are not surprising. The cryptand (**1**) is the most effective coordinating agent, followed by the four-nitrogen macrocycle **2** and then by the four-nitrogen acyclic compound **3**. The three-nitrogen coordinators are the least effective. Although zinc is in a transition group, in many respects it exhibits main-group behavior and often is thought of as a less polar magnesium. The results with neo-PeZn(coord)$^+$, however, show 9N3 to be most effective and the cryptand to be least effective. The differences between coordination to RZn^+ and RMg^+ must be due to a number of factors, including the lesser tendency of Zn generally to form dative[9] bonds, resulting in a tendency for fewer bonds to Zn,[10] and a greater preference of Zn than Mg for bonding to N instead of O donors.[13] Thus, the cryptand, having only two nitrogens, is not very effective for Zn compared to the donors having more nitrogens. Note that in the neo-PeMg(coord)$^+$ series N4 is considerably more effective than N3, but in the neo-PeZn(coord)$^+$ series, N4 and N3 are comparable. Probably all nitrogens of N4 are bonded to Mg, but only three are bonded to Zn. Steric factors due to small differences in lengths of bonds to Zn[11] and Mg[12] also could contribute to the differences between coordination to RMg(coord)$^+$ and RZn(coord)$^+$.[14]

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[8] Solutions of Et_2Zn and neo-Pe_2Zn in benzene must also contain EtZnneo-Pe, but the difference in stability of an alkyl group in a symmetrical or mixed species is small (Mynott, R.; Gabor, B.; Lehmkuhl, H.; Döring, I. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 335).

[9] For a discussion of the distinction between covalent and dative bonds, see: Haaland, A. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 992.

[10] The body of crystallographic data available for zinc[11] compounds and magnesium[12] compounds indicates a tendency for fewer bonds to zinc. 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.

[11] For references to X-ray structures of organozinc compounds, see: Boersma, J. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, U.K., 1982; Chapter 16. O'Brien, P. In *Comprehensive Organometallic Chemistry*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, U.K., 1995; Vol. 3, Chapter 4.

[12] For comprehensive reviews of crystal structures of magnesium compounds, see: 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.

[13] 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.* **1991**, *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, 1983. Smith, R. M.; Martell, A. E. *Critical Stability Constants*; Plenum: New York; Vol. 2 (1975), Vol. 5 (1982), Vol. 6 (1989). The absolute values, of course, are influenced by the large hydration energies of the ions in water and methanol. An additional nitrogen in the coordinating agent, however, generally increases the equilibrium constant much more for coordination to Zn^{2+} than to Mg^{2+}.

[14] Data[11,12] from X-ray structures shows covalent[9] C−Zn, N−Zn, and O−Zn bonds usually to be shorter than the corresponding bonds involving a magnesium. In contrast, dative[9] N−Zn and O−Zn bonds often are somewhat 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.