Reactions of Diorganocadmium Compounds with Other Dialkylmetal Compounds and Macrocycles: Synthesis of Organocadmate Anions[1]

Hui Tang and Herman G. Richey, Jr.*

Department of Chemistry, The Pennsylvania State University,
University Park, Pennsylvania 16802

Received November 27, 2000

Combining R_2Cd (R an alkyl or Ph group), the corresponding R_2Mg compound, and 1,4,8,11-tetramethyl-1,4,8,11-tetraazatetradecane, 2,1,1-cryptand, or 2,2,1-cryptand in solution quantitatively produces R_3Cd^- and $RMg(macrocycle)^+$ ions. Solutions obtained by combining the same macrocycles with R_2Cd alone or with R_2Cd plus the corresponding R_2Zn compound do not contain significant amounts of ions; rapid exchange of R groups in these solutions, however, may be due to formation of trace amounts of R_3Cd^- ions.

Combining a polar organometallic compound and a coordinating agent can generate ate[2] anions by transfer of an organic group to an organometallic acceptor. Syntheses of organomagnesate anions and coordinated RMg^+ cations (e.g., eq 1) are examples.[3,4] The driving

$$2\ R_2Mg + \text{macrocycle} \rightarrow R_3Mg^- + RMg(\text{macrocycle})^+ \quad (1)$$

force is extensive coordination between O and N atoms of a macrocycle and the metal of the resulting cation. This potent ability to transfer "R^-" provides an attractive way of generating new organoate species. We set out to use this approach to synthesize triorganocadmate anions (R_3Cd^-). The closest analogues that had been studied by X-ray diffraction were some halogen-containing organocadmate anions shown to have polymeric structures with bridging halogens.[5,6] The only observations of solutions were of $(CF_3)_3Cd^-$,[6] an anion favored by extremely electron-withdrawing groups. NMR studies of solutions prepared from RLi and R_2Cd had suggested formation of mixed species (1:1, 2:1, and 3:1),[7] but these solutions certainly do not contain true organocadmate anions free of specific bonding to lithium. An earlier report[8] gave the X-ray structure of a solid having Me_3Cd^- and $MeMg(14N4)^+$ (14N4 = 1,4,8,11-tetramethyl-1,4,8,11-tetraazatetradecane) ions and NMR information indicating the presence of several R_3Cd^- $RMg(14N4)^+$ species in solutions. In such salts, the metal of the cation is so enveloped by the macrocycle that it cannot form specific bonding interactions with the anion. This note provides further information about $R_3Cd^-RMg(14N4)^+$ species, describes additional reactions that might synthesize R_3Cd^- anions, and provides information about exchange of R groups in some solutions.

Results and Discussion

Benzene was the solvent except where noted. It has been useful for studies of organometalate species since (1) they usually are stable in it, (2) they often are equally or more soluble in it than in solvents, such as diethyl ether or THF, often used for polar organometallic compounds, and (3) the deuterated version needed for ^1H NMR studies is relatively inexpensive.

R_2Cd and Macrocycles. ^1H NMR absorptions of solutions prepared using different ratios of Et_2Cd and 14N4 are almost the same (within <0.1 ppm) as those of Et_2Cd and 14N4 when each is the only solute. However, the effects of coupling of ^{111}Cd (13% natural abundance, spin 1/2) and ^{113}Cd (12%, 1/2) with the CH_2 and CH_3 H's, striking in spectra of Et_2Cd alone (both *J*'s ca. 50−60 Hz), are absent; only a slightly broadened quartet and triplet are seen for the CH_2 and CH_3. Therefore, the ethyl groups exchange rapidly relative to the NMR time scale. Although the equilibrium in eq 2 lies substantially to the left, formation of a trace

$$2\ R_2Cd + \text{macrocycle} \rightleftharpoons R_3Cd^- + RCd(\text{macrocycle})^+ \quad (2)$$

amount of $Et_3Cd^-EtCd(14N4)^+$ may be responsible for the rapid exchange, which would result if formation of these ions and their reversion to Et_2Cd and 14N4 is very rapid or, alternatively, if exchange of ethyl between Et_2Cd and Et_3Cd^- is very much more rapid than between Et_2Cd and Et_2Cd. Increased rates of methyl exchange

---

* To whom correspondence should be addressed. E-mail: hgr@chem.psu.edu.

[1] Much of this work is taken from: Tang, H. Ph.D. Dissertation, The Pennsylvania State University, 1997.

[2] Wittig, G. *Angew. Chem.* **1958**, *70*, 65.

[3] Squiller, E. P.; Whittle, R. R.; Richey, H. G., Jr. *J. Am. Chem. Soc.* **1985**, *107*, 432.

[4] 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.

[5] Osman, A.; Tuck, D. G. *J. Organomet. Chem.* **1979**, *169*, 255. Buttrus, N. H.; Eaborn, C.; El-Kheli, M. N. A.; Hitchcock, P. B.; Smith, J. D.; Sullivan, A. C.; Tavakkoli, K. *J. Chem. Soc., Dalton Trans.* **1988**, 381. Al-Juaid, S. S.; Buttrus, N. H.; Eaborn, C.; Hitchcock, P. B.; Smith, J. D., Tavakkoli, K. *J. Chem. Soc., Chem. Commun.* **1988**, 1389.

[6] Naumann, D.; Tyra, W. *J. Organomet. Chem.* **1989**, *368*, 131.

[7] Toppet, S.; Slinckx, G.; Smets, G. *J. Organomet. Chem.* **1967**, *9*, 205. Seitz, L. M.; Little, B. F. *J. Organomet. Chem.* **1969**, *18*, 227.

[8] Tang, H.; Parvez, M.; Richey, H. G., Jr. *Organometallics* **1996**, *15*, 5281.

10.1021/om001020c CCC: $20.00

in Me_2Cd and in Me_2Cd-Me_2Zn solutions caused by donor solvents have been attributed to more facile bridging by the methyl groups when the metal is coordinated to a solvent heteroatom.[9] Such coordinated species (e.g., $R_2Cd^{-}-{}^{+}OR'_2$) have ate character.

R_2Cd, R_2Mg, and Macrocycles. Another synthetic approach[10] to organocadmate anions is to use an organometallic compound that in combination with a macrocycle is a stronger "R^-" donor than R_2Cd. R_2Mg is a likely candidate (eq 3).

$$R_2Cd + R_2Mg + \text{macrocycle} \rightarrow R_3Cd^- + RMg(\text{macrocycle})^+ \quad (3)$$

In the absence of a macrocycle, ^1H NMR spectra of solutions of Et_2Cd and Et_2Mg have only one broad triplet and one broad quartet, and effects of coupling of ^{111}Cd and ^{113}Cd are absent. In equimolar solutions, these absorptions lie midway between the corresponding absorptions of Et_2Cd and Et_2Mg. The species in solution therefore are Et_2Cd and Et_2Mg, but all ethyl groups exchange rapidly relative to the NMR time scale (although not quite rapidly enough to lead to extremely sharp absorptions).

Preparations using equimolar amounts of Et_2Cd, Et_2Mg and 14N4 are good examples to introduce the experiments with macrocycles. For these preparations (and for others in this note), results were essentially identical when different initial concentrations (in the range 0.1−0.8 M) were used. Et_2Cd-Et_2Mg-14N4 preparations had two liquid phases, as is often seen when organometallic ions form in aromatic solvents.[11] When equimolar amounts of the reactants were used, ^1H NMR spectra showed that the upper phases contain little solute.[12] Many features of NMR spectra of a lower phase indicate that Et_3Cd^- and $EtMg(14N4)^+$ (e.g., eq 3) are its principal components. The ^1H NMR spectra (Figure 1) exhibit two sets of ethyl absorptions in 3:1 ratio. The 14N4 absorptions and the smaller set of ethyl absorptions have intensities indicating that the groups responsible for them are 1:1 and positions similar[13] to those previously observed[14−16] for $EtMg(14N4)^+$ in the presence of other anions (including a CH_2Mg absorption ~0.9 ppm *upfield* from that of Et_2Mg and all 14N4 absorptions *upfield* from those of free 14N4). The CH_2 absorption of the larger ethyl set is ~0.2 ppm downfield from that of Et_2Cd, just as α-H absorptions of R_3Zn^- [10] and R_3Mg^- [3,15] are downfield from those of the corresponding R_2Zn and R_2Mg compounds. The ^{13}C NMR spectrum of the lower phase also has two sets of ethyl absorptions and one set of 14N4 absorptions. The single ^{113}Cd NMR absorption of the lower phase is 298 ppm downfield from the ^{113}Cd absorption of a solution of Et_2Cd alone, a shift similar to that[6] between the ^{113}Cd absorptions of $(CF_3)_2Cd$ and $(CF_3)_3Cd^-$ Cs^+. Ethyl groups of Et_3Cd^- exchange rapidly since effects of coupling of ^{111}Cd and ^{113}Cd with the α-H's, β-H's, and α-C, prominent in ^1H and ^{13}C NMR spectra of Et_2Cd alone, are absent. Exchange conceivably could be between R_3Cd^- ions but more likely is between R_3Cd^- and small amounts of R_2Cd ($R_3Cd^- + R_2Cd^* \rightleftarrows R_2Cd + R_3Cd^{*-}$). ^1H NMR spectra were taken at lower temperatures (in toluene-d_8) in an effort to slow the exchange but, except for significant broadness of *all* absorptions at the lowest temperatures (−40 and −60 °C), are similar to those in ambient temperature spectra.

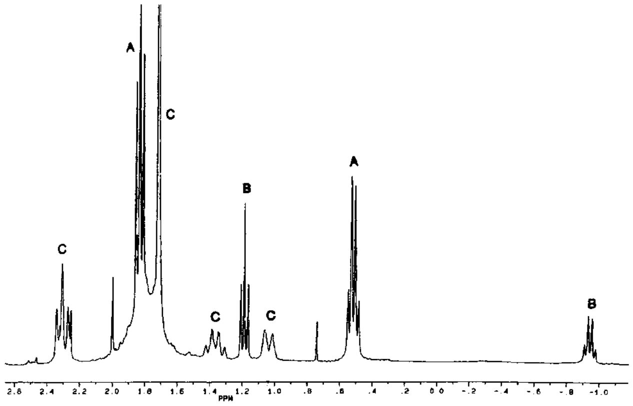

Figure 1. ^1H NMR spectrum (360 MHz) of the lower liquid phase containing $Et_3Cd^-EtMg(14N4)^+$ that separated when equimolar amounts of Et_2Cd, Et_2Mg, and 14N4 were added to benzene-d_6. Absorptions of Et_3Cd^- are labeled A, of Et of $EtMg(14N4)^+$ are labeled B, and of 14N4 of $EtMg(14N4)^+$ are labeled C.

Et_2Mg-Et_2Cd-14N4 preparations using an ether as the solvent also formed $Et_3Cd^-EtMg(14N4)^+$. Two liquid phases were present when dioxane or diethyl ether was used. Enough solute remained in the upper phases to be observed in ^1H NMR spectra, and the spectra of the upper and lower phases are similar. Homogeneous solutions were obtained when THF or DME was the solvent. All spectra exhibit two sets of ethyl absorptions (3:1) and 14N4 absorptions characteristic of $Et_3Cd^-EtMg(14N4)^+$.

Some R_2Mg-R_2Cd-14N4 reactions used bulkier R groups. All experiments using isobutyl, neopentyl (Np $= Me_3CCH_2$), and Me_3SiCH_2 groups resulted in two liquid phases, the lower containing most of the solute. ^1H NMR spectra of the lower phases are those expected for $R_3Cd^-RMg(14N4)^+$. As with the ethyl preparations, effects of coupling of ^{111}Cd and ^{113}Cd with α- and β-H's are absent, even at lower temperatures. With neopentyl and Me_3SiCH_2, phase separation was slow, apparently a result of slow $R_3Cd^-RMg(14N4)^+$ formation. With neopentyl, for example, phase separation did not begin until several hours after preparation; ^1H NMR spectra taken soon after preparation showed broad absorptions that must be principally of Np_2Mg, Np_2Cd, and 14N4,

---

[9] Oliver, J. P. *Adv. Organomet. Chem.* **l970**, *8*, 167. Henold, K.; Soulati, J.; Oliver, J. P. *J. Am. Chem. Soc.* **1969**, *91*, 3171.

[10] Fabicon, R. M.; Pajerski, A. D.; Richey, H. G., Jr. *J. Am. Chem. Soc.* **1991**, *113*, 6680.

[11] Atwood, J. L. In *Inclusion Compounds*; Atwood, J. L., Davies, J. E. D., Macnicol, D. D., Eds.; Academic: London, 1984; Vol. 1, Chapter 9.

[12] Equimolar amounts of Et_2Cd, Et_2Mg, and 14N4 generally were used. When more 14N4 was used, the excess 14N4 was principally in the upper phase. Where investigated in other reactions that produced two liquid phases, excess macrocycle also was mainly in the upper phase.

[13] Only the position of the most downfield ^1H NMR absorption of 14N4 of $RMg(14N4)^+$ cations is very dependent on the anion.[14,15] The four H's (NC*H*HCH$_2$C*H*HN) responsible for this absorption lie above one face of the 14N4, projecting into the solution at a location providing the least hindered approach to the center of positive charge.

[14] Pajerski, A. D.; Chubb, J. E.; Fabicon, R. M.; Richey, H. G., Jr. *J. Org. Chem.* **2000**, *65*, 2231.

[15] Pajerski, A. D. Ph.D. Dissertation, The Pennsylvania State University, 1990.

[16] Tang, H.; Parvez, M.; Richey, H. G., Jr. *J. Organomet. Chem.* **2000**, *19*, 4810.

but with positions somewhat altered by routine[17] coordination of 14N4 to Mg and Cd. After the lower phase is no longer growing (ca. 1 day), the upper phase has weak ^{1}H NMR absorptions attributable to $Np_3Cd^-NpMg(14N4)^+$, in fact, identical to those of a dilute solution formed by dissolving crystals of $Np_3Cd^-NpMg(14N4)^+$ (that precipitated slowly after hexane was layered over a benzene solution prepared from Np_2Cd, Np_2Cd, and 14N4).

A white crystalline solid precipitated rapidly when Me_2Mg, Me_2Cd, and 14N4 were mixed in benzene-d_6. This solid is virtually insoluble in benzene at ambient temperature, but two liquid phases were seen when it was heated in benzene at 70 °C. The ^{1}H NMR spectrum of the upper phase has weak absorptions expected for $Me_3Cd^-MeMg(14N4)^+$ (precipitation occurred before NMR spectra could be taken of the smaller lower phase).

Crystals formed slowly when equimolar amounts of Ph_2Mg, Ph_2Cd, and 14N4 were dissolved in THF and then a small layer of benzene and a larger layer of hexane were added. Although Ph_2Mg is virtually insoluble in benzene, these crystals were somewhat soluble (ca. 0.05 M) at 70 °C; precipitation was slow when a heated solution was cooled, permitting NMR spectra of this single phase to be taken at ambient temperature. ^{1}H NMR spectra indicate the solute to be $Ph_3Cd^-PhMg(14N4)^+$.[8,18,19]

Cryptands were used for some reactions. With 211C (2,1,1-cryptand) or 221C (2,2,1-cryptand), R_2Mg and R_2Cd ($R = Et$, Np, or Me_3SiCH_2) formed two liquid phases. ^{1}H NMR spectra of the lower phases exhibit the features observed with 14N4, including two sets of alkyl absorptions (3:1), and therefore contain $R_3Cd^-RMg(cryptand)^+$. Effects of coupling of ^{111}Cd and ^{113}Cd are absent, even in spectra of $NpMg(211C)^+Np_3Cd^-$ preparations to which TMEDA was added (TMEDA might slow exchange by coordinating with Np_3Cd^- and any excess Np_2Cd or Np_2Mg).

With 222C (2,2,2-cryptand), Np_2Mg and Np_2Cd produced a solution whose ^{1}H NMR spectrum has two sets of neopentyl absorptions. The positions of one set are shifted somewhat from those of Np_2Mg alone, as expected for routine coordination[17] of 222C to Np_2Mg. The positions of the other set are identical to those of Np_2Cd alone, but effects of coupling of ^{111}Cd and ^{113}Cd are absent. Coordination of $NpMg^+$ to 222C is sufficiently weaker than to 211C or 221C to preclude formation of observable amounts of $Np_3Cd^-NpMg(222C)^+$. The absence of coupling with Cd shows that the neopentyl groups of Np_2Cd exchange rapidly, but the independent absorptions for Np_2Mg and Np_2Cd indicate that *this exchange does not significantly involve* Np_2Mg. Therefore it is likely that a trace amount of $Np_3Cd^-NpMg(222C)^+$ is responsible for the exchange.[20] The observation of discrete Np_2Mg absorptions, however, indicates that the interconversion $Np_2Cd + Np_2Mg + 222C \rightleftarrows Np_3Cd^-NpMg(222C)^+$ is too slow to rapidly interchange the neopentyl groups of Np_2Cd (a conclusion in accord with the observation that formation of $Np_3Cd^-NpMg(14N4)^+$ is slow). *Therefore, by default, the principal exchange pathway is most likely between* Np_2Cd *and small amounts of* Np_3Cd^-.

R_2Cd, R_2Zn, and Macrocycles. The ^{1}H NMR spectrum of a solution prepared from equimolar amounts of Et_2Zn and Et_2Cd has two sets of ethyl absorptions (1:1) with positions identical to those of the components when alone. Coupling of ^{111}Cd and ^{113}Cd with the α- and β-hydrogens of Et_2Cd is observed, so any exchange involving the ethyl groups of Et_2Cd is slow. Addition of 221C provided a solution whose ^{1}H NMR spectrum has two sets (1:1) of broad ethyl absorptions. The positions of one set are identical to those of Et_2Cd; effects of ^{111}Cd and ^{113}Cd coupling are observable, although the satellite absorptions are less sharp than in the system without 221C. The positions of the other ethyl set are shifted slightly (0.1−0.2 ppm) from those of Et_2Zn, as expected for routine coordination[17] of 221C to Et_2Zn. 221C therefore does not cause significant ion formation and facilitates ethyl group exchange only to a very limited extent. In contrast to RMg^+, neither RZn^+ nor RCd^+ binds strongly enough with 221C to form sufficient ate anion to lead to an R group exchange that is rapid relative to the NMR time scale. ^{1}H NMR spectra of $Et_2Zn-Et_2Cd-14N4$ solutions, however, show only one broad set of ethyl absorptions and no effects of Cd coupling, both features indicating a faster exchange of ethyl groups. 14N4 binds more effectively than 221C to RZn^+,[16] and a trace of $Et_3Cd^-Et(14N4)^+$ may be responsible for the rapid exchange of ethyl groups. The Et_3Cd^- concentration must be low, however; the single absorption in the ^{113}Cd NMR spectrum is the same (within 0.1 ppm) as that of a solution of Et_2Cd alone, in contrast to the ^{113}Cd absorption of $Et_3Cd^-EtMg(14N4)^+$, which is 298 ppm downfield.

Summary. R_2Cd compounds do not form observable amounts of $R_3Cd^-RCd(macrocycle)^+$ with the macrocycles that were tried, but rapid R exchange may be due to formation of trace amounts of these ions. The failure to form significant amounts of ions is not surprising since organocadmium compounds[22] coordinate more feebly than organozinc compounds to O and N donor atoms and even conversion of R_2Zn to $R_3Zn^-RZn(macrocycle)^+$ requires both a macrocycle particularly effective for RZn^+ and an organic group particularly effective at stabilizing R_3Zn^-.[16] R_3Cd^- ions can be synthesized from R_2Cd compounds, however, by providing a stronger "R^-" donor. Combinations of R_2Mg and R_2Cd with 14N4, 211C, or 221C are effective. Similar

---

[17] "Routine" is used here to refer to coordination of one or two heteroatoms of the macrocycle to the metal atom, coordination similar to that by acyclic ethers and amines. Such coordinate bonds generally form and break rapidly relative to the NMR time scale.

[18] One THF per salt unit also is in the crystal; its absorptions are seen in the NMR spectra.

[19] A crystal obtained by a slightly different crystallization procedure was subjected to X-ray diffraction structural analysis.[1] The asymmetric unit is composed of two independent Ph_3Cd^- units, two independent $PhMg(14N4)^+$ units, and two THF molecules not involved in any specific bonding. Discrepancy indices ($R = 0.134$, $R_w = 0.144$) in the final refinement were high, but the results are adequate to show the principal structural features; in fact, the geometry determined for $PhMg(14N4)^+$ is very similar to that previously found for this cation[15] with a different anion and for $MeMg(14N4)^+$.[8] Ph_3Cd^- has an essentially trigonal planar geometry, as found for Me_3Cd^-.[8]

[20] The preparations of R_2Mg compounds, by precipitation of MgX_2 from RMgX solutions using dioxane,[21] generally leaves traces of halide, which might have a role in the exchanges. Np_2Mg was sublimed, however, and so residual halide is particularly low.

[21] Wakefield, B. J. *Organomagnesium Methods in Organic Synthesis*; Academic: London, l995; Section 3.4.1.

[22] 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 II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, 1995; Vol. 3, Chapter 4.

combinations with R_2Zn in place of R_2Mg do not produce observable amounts of $R_3Cd^{-}RZn(macrocycle)^{+}$, but trace amounts may be responsible for rapid exchange of R's of R_2Cd.

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. 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. An NMR tube was capped temporarily with a rubber septum, removed from the glovebox, immersed in liquid nitrogen, and sealed at the extension. Except where noted, NMR spectra were taken at ambient temperature. ^1H NMR absorptions are reported relative to internal C_6D_5H (δ 7.15 ppm) for solutions in benzene-d_6 and to internal tetramethylsilane (δ 0.00) for solutions in other solvents. ^{13}C NMR absorptions are reported relative to internal C_6D_6 (δ 128.0 ppm) and ^{113}Cd NMR absorptions relative to external Et_2Cd (0.4 M in benzene-d_6). The following notations are used: s, singlet; d, doublet; t, triplet; q, quartet; m, a more complex multiplet; c, complex overlapping absorptions; b, broad. An * is placed on those ^1H and ^{13}C NMR absorptions that have clearly evident satellite absorptions due to coupling to ^{111}Cd and ^{113}Cd. Benzene-d_6 (Cambridge Isotope Laboratories) was stored over molecular sieves (4 Å). Other hydrocarbon solvents and dioxane were distilled from CaH_2 and stored over molecular sieves (4 Å) under a nitrogen atmosphere. Immediately prior to use, diethyl ether and tetrahydrofuran were distilled from sodium benzophenone ketyl, and dimethoxyethane (DME) and tetramethylethylenediamine (TMEDA) were distilled under vacuum from CaH_2. All macrocyclic compounds, Et_2Zn, and Mg (99.95%) (Aldrich Chemical Co.) were used as received. Me_2Cd (Organometallics, Inc.) was purified by vacuum transfer prior to use.

Preparation of Diorganomagnesium Compounds. The following is a typical procedure. A solution of the alkyl halide (distilled from CaH_2 under nitrogen, 0.10 mol) in Et_2O (40 mL) was added dropwise over 2 h to a stirred mixture of Mg (3.0 g, 0.125 mol) in Et_2O (40 mL). Alkyl bromides were used for all preparations except that of bis(trimethylsilylmethyl)magnesium, for which the chloride was used. After addition was complete, the reaction mixture was allowed to stir for 12 h. The concentration of the Grignard reagent solution was determined by hydrolyzing an aliquot, adding an excess of a standard HNO_3 solution (0.10 M), and titrating with a standard NaOH solution (0.10 M) to a phenolphthalein red endpoint. Halide was also determined by titration;[23] to the above solution was added 2 drops of a 5% K_2CrO_4 solution followed by titration with a standard $AgNO_3$ solution (0.10 M) to a brick red endpoint. The diorganomagnesium compound was prepared by the dioxane precipitation method.[21] A solution of dioxane (8.8 g, 0.10 mol) in Et_2O (40 mL) was added dropwise over 2 h to the stirred Grignard reagent solution (0.10 mol). The resulting slurry was stirred for 12 h and then centrifuged. The clear supernatant liquid was transferred and the solvent removed at reduced pressure, leaving a solid, which was heated (50 °C) under vacuum (10^{-3} Torr) for an additional 5 h to remove residual Et_2O. All diorganomagnesium compounds had R/X ratios (determined by titration analysis) $>$ 20. Dineopentylmagnesium was further purified by sublimation (85 °C, 10^{-3} Torr). The following ^1H NMR spectra are of ca. 0.1 M solutions in benzene-d_6 (2 equiv of THF were used with dimethylmagnesium and diphenylmagnesium to make them sufficiently soluble).

Dimethylmagnesium (200 MHz): δ −0.95 (s).

Diethylmagnesium (200 MHz): δ −0.03 (q, $J = 8.0$ Hz, 2, CH_2), 1.66 (t, $J = 7.9$ Hz, 3, CH_3).

Diisobutylmagnesium (200 MHz): δ −0.11 (d, $J = 6.5$ Hz, 2, CH_2), 1.31 (d, $J = 6.1$ Hz, 6, CH_3), 2.24 (m, 1, CH).

Dineopentylmagnesium (200 MHz): δ 0.22 (s, 2, CH_2), 1.27 (s, 9, CH_3).

Bis(trimethylsilylmethyl)magnesium (200 MHz): δ −1.31 (s, 2, CH_2), 0.33 (s, 9, CH_3).

Diphenylmagnesium (300 MHz): δ 7.41 (t, $J = 7.2$ Hz, 1, *p*-H), 7.53 (t, $J = 6.6$ Hz, 2, *m*-H), 8.12 (d, $J = 7.4$ Hz, 2, *o*-H).

Preparation of Diorganocadmium Compounds. The following is a typical procedure. A Et_2O solution of a Grignard reagent (0.10 M, 80 mL) was added dropwise over a period of 2 h to a stirred suspension of $CdCl_2$ (6.4 g, 0.035 mol) in Et_2O (40 mL) in a reaction vessel protected from light with aluminum foil. After addition was complete, the reaction mixture was allowed to stir for 12 h. Most of the Et_2O was removed at reduced pressure. Then all of the volatile contents were transferred from the reaction mixture at low pressure. The resulting material was pumped on carefully (0 °C) to remove most residual diethyl ether. Then the remaining material was subjected to a second vacuum transfer. The following ^1H NMR spectra are of ca. 0.1 M solutions (benzene-d_6).

Dimethylcadmium: ^1H NMR (200 MHz) δ 0.59* (s, CH_3).

Diethylcadmium: ^1H NMR (200 MHz) δ 0.29* (q, $J = 8.0$ Hz, 2, CH_2), 1.26* (t, $J = 8.1$ Hz, 3, CH_3); ^{13}C NMR (90 MHz) δ 12.8* (both C's).[24]

Diisobutylcadmium: ^1H NMR (200 MHz) δ 0.62* (d, $J = 6.0$ Hz, 2, CH_2), 0.98 (d, $J = 7.1$ Hz, 6, CH_3), 2.29 (bm, 1, CH).

Dineopentylcadmium: ^1H NMR (200 MHz) δ 0.64* (s, 2, CH_2), 1.06 (s, 9, CH_3).

Bis(trimethylsilylmethyl)cadmium: ^1H NMR (200 MHz) δ 0.58* (s, 2, CH_2), 0.11 (s, 9, CH_3).

Diphenylcadmium: ^1H NMR (300 MHz) δ 7.15−7.35 (c, all H's).

Preparation of NMR Solutions. In the glovebox, the diorganocadmium compound, the corresponding diorganomagnesium or diorganozinc compound, and the macrocycle were weighed into a vial (in some preparations only two of these reactants were used), and the solvent (ordinarily 0.5 mL) was added. If a homogeneous solution was present after the preparation had been stirred (magnetic stirrer) for a few minutes, it was transferred into an NMR tube. When the preparation was opaque (indicating phase separation), it was allowed to stand unstirred until phase separation was complete. To obtain enough of a lower phase to permit taking routine NMR spectra, it was necessary to do a preparation on a larger scale (generally using 1.2 mL of solvent). For the representative spectra that are listed below, equimolar amounts of all reactants were used; the concentration listed for a spectrum is the concentration that each reactant would have if no reaction took place (and if no phase separation occurred). To allow comparison with spectra of other solutions, the spectra of 14N4 and Et_2Zn also are listed.

14N4 (benzene-*d*$_6$). ^1H NMR (0.2 M, 200 MHz): δ 1.55 (quintet, $J = 6.5$ Hz, 1, $CH_2CH_2CH_2$), 2.13 (s, 3, CH_3), 2.40 (s, 2, NCH_2CH_2N), 2.48 (t, $J = 6.4$ Hz, 2, $CH_2CH_2CH_2$).

Et_2Zn (benzene-*d*$_6$). ^1H NMR (0.1 M, 200 MHz): δ 0.12 (q, $J = 7.9$ Hz, 2, CH_2), 1.11 (t, $J = 7.8$ Hz, 3, CH_3).

Et_2Cd and 14N4 (benzene-*d*$_6$). ^1H NMR (0.1 M, 200 MHz): δ 0.37 (bq, $J = 8.1$ Hz, 2, CH_2Cd), 1.33 (bt, $J = 8.2$ Hz, 3, CH_3C), 1.49 (bm, 4, $CH_2CH_2CH_2$), 2.08 (s, 12, CH_3N), 2.34 (s, 8, NCH_2CH_2N), 2.42 (bt, 8, $CH_2CH_2CH_2$).

---

[23] Day, R. A., Jr.; Underwood, A. L. *Quantitative Analysis*, 6th ed.; Prentice Hall: Englewood Cliffs, NJ, l991; Chapter 22.

[24] The coincidence of the absorptions of the two C's has been noted before: Müller, H.; Rösch, L.; Erb, W.; Zeisberg, R. *J. Organomet. Chem.* **l977**, *140*, C17. We did a $^1H-^{13}C$ COSY NMR experiment and found the expected couplings of the CH_2 H's and the CH_3 H's, but to the same ^{13}C absorption position (δ 12.8).

Et$_2$Mg and Et$_2$Cd (benzene-d_6). ^{1}H NMR (0.6 M, 200 MHz): δ 0.17 (b, 2, CH$_2$), 1.41 (b, 3, CH$_3$), 3.30 (s, dioxane[25]).

Et$_2$Mg, Et$_2$Cd, and 14N4 (benzene-d_6); Preparation of EtMg(14N4)$^+$Et$_3$Cd$^-$. ^{1}H NMR (0.6 M, lower phase, 200 MHz): δ −0.95 (q, J = 8.3 Hz, 2, CH$_2$Mg), 0.51 (q, J = 7.9 Hz, 6, CH$_2$Cd), 1.19 (t, J = 8.2 Hz, 3, CH$_3$CMg), 1.83 (t, J = 8.1 Hz, 9, CH$_3$CCd), 0.90−2.10 (c, 16, most CH$_2$'s of 14N4), 1.69 (s, 12, CH$_3$N), 2.32 (bt, 4, C*H*HCH$_2$C*H*H). ^{13}C NMR (0.6 M, lower phase, 50 MHz): δ 59.7 (NCCN), 56.1 (N*C*CCN), 43.3 (NCH$_3$), 21.4 (NC*C*CN), 17.1 (*C*CCd), 14.9 (*C*CMg), 10.4 (CCd), −0.7 (CMg); ^{113}Cd NMR (0.6 M, lower phase, 67 MHz) δ 297.9.

Et$_2$Mg, Et$_2$Cd, and 14N4 (DME); Preparation of EtMg(14N4)$^+$Et$_3$Cd$^-$. ^{1}H NMR (1.0 M, 200 MHz): δ −0.69 (q, J = 8.3 Hz, 2, CH$_2$Mg), 0.10 (q, J = 7.8 Hz, 6, CH$_2$Cd), 1.27 (t, J = 8.1 Hz, 3, CH$_3$CMg), 1.44 (t, J = 8.3 Hz, 9, CH$_3$CCd), 1.50−2.80 (c, 16, most CH$_2$'s of 14N4), 2.36 (s, 12, CH$_3$N), 3.12 (bt, 4, C*H*HCH$_2$C*H*H), 3.28 (s, CH$_3$ of DME), 3.44 (s, CH$_2$ of DME).

Et$_2$Mg, Et$_2$Cd, and 14N4 (THF); Preparation of EtMg(14N4)$^+$Et$_3$Cd$^-$. ^{1}H NMR (1.0 M, 200 MHz): δ −0.71 (q, J = 8.5 Hz, 2, CH$_2$Mg), 0.16 (q, J = 7.9 Hz, 6, CH$_2$Cd), 1.20 (t, J = 7.8 Hz, 3, CH$_3$CMg), 1.30 (t, J = 8.1 Hz, 9, CH$_3$CCd), 1.50−2.80 (c, 16, most CH$_2$'s of 14N4), 2.42 (s, 12, CH$_3$N), 3.09 (bt, 4, C*H*HCH$_2$C*H*H), 1.76 (m, CH$_2$CO of THF), 3.62 (m, CH$_2$O of THF).

Et$_2$Mg, Et$_2$Cd, and 14N4 (dioxane); Preparation of EtMg(14N4)$^+$Et$_3$Cd$^-$. ^{1}H NMR (1.2 M, lower phase, 200 MHz): δ −0.78 (q, J = 8.2 Hz, 2, CH$_2$Mg), 0.50 (q, J = 8.0 Hz, 6, CH$_2$Cd), 1.17 (t, J = 8.3 Hz, 3, CH$_3$CMg), 1.27 (t, J = 8.1 Hz, 9, CH$_3$CCd), 1.40−2.72 (c, 32, most CH$_2$'s of 14N4$^+$), 2.38 (s, 12, CH$_3$N), 2.97 (bt, 4, C*H*HCH$_2$C*H*H), 3.57 (s, dioxane).

Et$_2$Mg, Et$_2$Cd, and 14N4 (Et$_2$O); Preparation of EtMg(14N4)$^+$Et$_3$Cd$^-$. ^{1}H NMR (1.0 M, lower phase, 200 MHz): δ −0.40 (b, 2, CH$_2$Mg), 0.38 (b, 6, CH$_2$Cd), 0.82 (b, 3, CH$_3$CMg), 1.21 (b, 9, CH$_3$CCd), 1.40−2.70 (c, 32, most CH$_2$'s of 14N4$^+$), 2.40 (s, 12, CH$_3$N), 2.90 (bt, 4, C*H*HCH$_2$C*H*H), 1.08 (t, CH$_3$ of Et$_2$O), 3.35 (q, CH$_2$ of Et$_2$O).

***i*-Bu$_2$Mg, *i*-Bu$_2$Cd, and 14N4 (benzene-d_6); Preparation of *i*-BuMg(14N4)$^+$*i*-Bu$_3$Cd$^-$.** ^{1}H NMR (0.4 M, lower phase, 200 MHz): δ −0.86 (d, J = 6.7 Hz, 2, CH$_2$Mg), 0.72 (d, J = 5.7 Hz, 6, CH$_2$Cd), 1.10 (d, J = 6.0 Hz, 6, CH$_3$CMg), 1.25 (d, J = 6.8 Hz, 18, CH$_3$CCd), 2.60−2.80 (c, 4, CHMg and CHCd), 1.10−2.70 (c, 16, most CH$_2$'s of 14N4), 1.70 (s, 12, CH$_3$N), 2.50 (bt, 4, C*H*HCH$_2$C*H*H).

Np$_2$Mg, Np$_2$Cd, and 14N4 (benzene-d_6); Preparation of NpMg(14N4)$^+$Np$_3$Cd$^-$. Liquid phase separation was slow (about 12 h to complete). ^{1}H NMR (0.4 M, lower phase, 300 MHz): δ −0.64 (s, 2, CH$_2$Mg), 0.71 (s, 6, CH$_2$Cd), 1.04 (s, 9, CH$_3$CMg), 1.38 (s, 27, CH$_3$CCd), 1.10−2.10 (c, 16, most CH$_2$'s of 14N4$^+$), 1.78 (s, 12, CH$_3$N), 2.30 (bt, 4, C*H*HCH$_2$C*H*H).

Crystals of NpMg(14N4)$^+$Np$_3$Cd$^-$ were obtained by carefully layering hexane (1 mL) over a solution prepared from Np$_2$Mg (80 mg, 0.48 mmol), Np$_2$Cd (122 mg, 0.48 mmol), and 14N4 (123 mg, 0.48 mmol) in benzene (0.8 mL). A homogeneous solution resulted from dissolving the crystals (10 mg) in benzene-d_6 (0.5 mL). ^{1}H NMR (300 MHz): δ −0.64 (s, 2, CH$_2$Mg), 0.85 (s, 6, CH$_2$Cd), 1.11 (s, 9, CH$_3$CMg), 1.61 (s, 27, CH$_3$CCd), 1.15−2.10 (c, 16, most CH$_2$'s of 14N4$^+$), 1.62 (s, 12, CH$_3$N), 2.70 (bt, 4, C*H*HCH$_2$C*H*H).

(Me$_3$SiCH$_2$)$_2$Mg, (Me$_3$SiCH$_2$)$_2$Cd, and 14N4 (benzene-d_6); Preparation of Me$_3$SiCH$_2$Mg(14N4)$^+$(Me$_3$SiCH$_2$)$_3$Cd$^-$. Liquid phase separation was slow (about 10 h to complete). ^{1}H NMR (0.4 M, lower phase, 360 MHz): δ −2.20 (s, 2, CH$_2$Mg), −0.50 (s, 6, CH$_2$Cd), 0.15 (s, 9, CH$_3$SiCMg), 0.34 (s, 27, CH$_3$SiCCd), 1.10−1.90 (c, 16, most CH$_2$'s of 14N4$^+$), 1.60 (s, 12, CH$_3$N), 2.64 (bt, 4, C*H*HCH$_2$C*H*H).

Me$_2$Mg, Me$_2$Cd, and 14N4 (benzene-d_6); Preparation of MeMg(14N4)$^+$Me$_3$Cd$^-$. Immediate precipitation of white crystals was observed from a preparation that would have produced a 0.3 M solution. Two liquid layers formed upon gentle heating (70 °C). ^{1}H NMR (upper layer, 300 MHz): δ −1.61 (s, 3, CH$_3$Mg), −0.26 (s, 9, CH$_3$Cd, 0.90−3.00 (c, 20, CH$_2$'s of 14N4), 1.60 (s, 12, CH$_3$N). Precipitation occurred before NMR spectra could be taken of the small lower layer.

Ph$_2$Mg, Ph$_2$Cd, and 14N4 (benzene-d_6); Preparation of PhMg(14N4)$^+$Ph$_3$Cd$^-$. Besides amounts of the reagents that would have produced a 0.2 M solution, 1 equiv of THF (to help dissolve the Ph$_2$Mg) also was weighed in before adding the solvent. A large amount of precipitate was present. The ^{1}H NMR spectrum of the remaining solution showed it to contain little solute. A homogeneous solution (ca. 0.05 M) resulted from heating a portion of the precipitate in benzene to 70 °C; after the solution was cooled to ambient temperature, it was possible to take an NMR spectrum of the supersaturated solution before crystals formed. ^{1}H NMR (300 MHz): δ 0.82−1.80 (c, 16, most CH$_2$'s of 14N4$^+$), 1.42 (s, 12, CH$_3$N), 2.24 (c, 4, C*H*HCH$_2$C*H*H), 7.26 (bs, 5, all H's of PhMg), 7.33 (t, J = 7.3 Hz, 3, *p*-H of PhCd), 7.49 (t, J = 7.6 Hz, 6, *m*-H of PhCd), 8.47 (d, J = 7.5 Hz, 6, *o*-H of Ph$_3$Cd).

Et$_2$Mg, Et$_2$Cd, and 221C (benzene-d_6); Preparation of EtMg(221C)$^+$Et$_3$Cd$^-$. Liquid phase separation took place slowly. ^{1}H NMR (0.5 M, lower phase, 200 MHz): δ −0.88 (q, J = 8.2 Hz, 2, CH$_2$Mg), 0.44 (q, J = 7.9 Hz, 6, CH$_2$Cd), 1.18 (t, J = 8.4 Hz, 3, CH$_3$CMg), 1.89 (t, J = 7.9 Hz, 9, CH$_3$CCd), 1.80−3.50 (c, 32, all H's of 221C).

Np$_2$Mg, Np$_2$Cd, and 211C (benzene-d_6); Preparation of NpMg(211C)$^+$Np$_3$Cd$^-$. Liquid phase separation was slow (about 5 h to complete). ^{1}H NMR (0.2 M, lower phase, 300 MHz): δ −0.63 (s, 2, CH$_2$Mg), 0.76 (s, 6, CH$_2$Cd), 1.20 (s, 9, CH$_3$CMg), 1.35 (s, 27, CH$_3$Cd), 1.70−3.30 (c, 28, all H's of 211C).

Colorless crystals of NpMg(211C)$^+$Np$_3$Cd$^-$ were obtained by layering hexane (1 mL) over a solution prepared from Np$_2$Mg (42 mg, 0.25 mmol), Np$_2$Cd (64 mg,0.25 mmol), and 211C (72 mg, 0.25 mmol) in benzene (0.8 mL). A homogeneous solution resulted from dissolving the crystals (10 mg) in benzene-d_6 (0.5 mL). ^{1}H NMR (300 MHz): δ −0.63 (s, 2, CH$_2$Mg), 0.80 (s, 6, CH$_2$Cd), 1.21 (s, 9, CH$_3$CMg), 1.38 (s, 27, CH$_3$CCd), 1.70−3.30 (c, 28, all H's of 211C).

NpMg(211C)$^+$Np$_3$Cd$^-$ and TMEDA (benzene-d_6). Crystals of NpMg(2,1,1-C)$^+$Np$_3$Cd$^-$ (10 mg, 0.014 mmol) were dissolved in a benzene-d_6 solution of TMEDA (0.5 mL, 0.008 M, 0.004 mmol). ^{1}H NMR (360 MHz): δ −0.62 (s, 2, CH$_2$Mg), 0.80 (s, 6, CH$_2$Cd), 1.19 (s, 9, CH$_3$CMg), 1.38 (s, 27, CH$_3$CCd), 1.60−3.20 (c, all H's of 211C), 1.48 (s, CH$_2$ of TMEDA), 1.49 (s, CH$_3$ of TMEDA).[26]

Np$_2$Mg, Np$_2$Cd, and 222C (benzene-d_6). ^{1}H NMR (0.3 M, 360 MHz): δ 0.18 (s, 2, CH$_2$Mg), 0.65 (s, 2, CH$_2$Cd), 1.05 (s, 9, CH$_3$CCd), 1.51 (s, 9, CH$_3$CMg), 2.38 (b, 12, CH$_2$N), 3.37 (b, 12, NCH$_2$C*H$_2$O*, 3.54 (b, 12, OC*H$_2$*C*H$_2$*O).

(Me$_3$SiCH$_2$)$_2$Mg, (MeSiCH$_2$)$_2$Cd, and 221C (benzene-d_6); Preparation of Me$_3$SiCH$_2$Mg(221C)$^+$(Me$_3$SiCH$_2$)$_3$Cd$^-$. Liquid phase separation was slow. ^{1}H NMR (0.3 M, lower phase, 200 MHz): δ −2.02 (s, 2, CH$_2$Mg), −0.51 (s, 6, CH$_2$Cd), −0.01 (s, 9, CH$_3$SiCMg), 0.32 (s, 27, CH$_3$SiCCd), 1.60−3.40 (c, all H's of 221C).

Et$_2$Zn and Et$_2$Cd (benzene-d_6). ^{1}H NMR (0.4 M, 200 MHz): δ 0.11 (q, J = 8.0 Hz, 2, CH$_2$Zn), 0.30* (q, J = 8.0 Hz, 2, CH$_2$Cd), 1.12 (t, J = 8.1 Hz, 3, CH$_3$CZn), 1.26* (t, J = 7.9 Hz, 3, CH$_3$CCd).

Et$_2$Zn, Et$_2$Cd, and 14N4 (benzene-d_6). ^{1}H NMR (0.4 M, 200 MHz): δ 0.27 (b, 2, CH$_2$Zn and CH$_2$Cd), 1.41 (b, 3, CH$_3$CZn and CH$_3$CCd), 1.26 (bm, 1, CH$_2$C*H$_2$*CH$_2$), 1.99 (s, 3, CH$_3$N), 2.18 (s, 2, NC*H$_2$*C*H$_2$*N, 2.38 (bt, 2, C*H$_2$*CH$_2$C*H$_2$*). ^{113}Cd NMR (0.4 M, 67 MHz): δ −0.08 (s).

---

[25] Small amounts of dioxane occasionally remained in the R$_2$Mg preparations.

[26] The absorptions of TMEDA alone in benzene-d_6 are δ 2.20 (CH$_2$) and 2.36 (CH$_3$). The absorption positions observed here suggest that TMEDA is coordinated to a metal.

Et_2Zn, Et_2Cd, and 221C (benzene-d_6). ^{1}H NMR (0.5 M, 360 MHz): δ 0.24 (q, $J = 8.4$ Hz, 2, CH_2Zn), 0.32* (q, $J = 7.8$ Hz, 2, CH_2Cd), 1.27* (t, $J = 8.1$ Hz, 3, CH_3CCd), 1.31 (t, $J = 7.8$ Hz, 3, CH_3CZn), 2.45−2.64 (c, 6, CH_2N), 3.40−3.60 (c, 10, CH_2O).

Acknowledgment. We thank the National Science Foundation for supporting this research and an anonymous referee for helpful suggestions. 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.

OM001020C