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Synthesis of Trialkyl- and Triphenylcadmate Anions

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Summary: Single-crystal X-ray diffraction shows crystals isolated from a reaction of Me_2Cd, Me_2Mg, and 14N4 (1,4,7,11-tetramethyl-1,4,7,11-tetraazacyclotetradecane) in benzene to be $Me_3Cd^-MeMg(14N4)^+(C_6H_6)$. ^1H NMR observations indicate that solutions prepared from R_2Cd, the corresponding R_2Mg compound, and 14N4 (R = an alkyl group or Ph) also contain R_3Cd^- and RMg-$(14N4)^+$ ions.

We earlier reported that some combinations of organometallic compounds and coordinating agents can lead to formal transfer of an organic group as an anion "R^-" to another molecule.[1] An example is the quantitative synthesis of magnesate ions and accompanying RMg-$(coord)^+$ cations from diorganomagnesium compounds and suitable coordinating agents (coord), particularly some cryptands or crown ethers (eq 1).[1a−c] This potent

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

transfer ability might be used to synthesize other previously unreported species. Synthesis of triorganocadmate anions (R_3Cd^-) is an attractive objective. To our knowledge no X-ray structural data on such ions are available and the only observations in solution are of the special case where R is the strongly electron-withdrawing CF_3.[2−4] In this communication we report the synthesis of a salt of Me_3Cd^-, an X-ray structure determination of the solid, and the synthesis in solution of R_3Cd^- anions (R = an alkyl or Ph group).

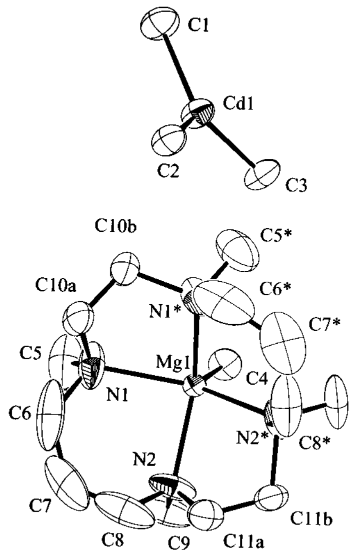

Figure 1. ORTEP drawings of Me_3Cd^- and $MeMg(14N4)^+$. Atoms are shown with 25% probability ellipsoids. The ions may be regarded as essentially independent units—the closest approach of cadmium to magnesium is 6.56 Å and to a nitrogen of 14N4 is 5.42 Å.

Colorless, prismatic crystals (mp 107−108 °C) deposited slowly but in good yield (85%) from a solution prepared by dissolving equimolar amounts of Me_2Cd, Me_2Mg, and 14N4 (1,4,7,11-tetramethyl-1,4,7,11-tetraazacyclotetradecane) in THF and then placing a layer of benzene on top. Single-crystal X-ray analysis[5] shows the crystal to consist of equal numbers of Me_3Cd^- and $MeMg(14N4)^+$ units, presumably having the indicated charges (eq 2).[6] One benzene per salt unit also is

$$Me_2Cd + Me_2Mg + 14N4 \rightarrow Me_3Cd^- + MeMg(14N4)^+ \qquad (2)$$

present but is remote from either metal. The cadmium anion has a trigonal planar bonding geometry (the C−Cd−C bond angles are 119.6(6), 120.0(7), and 120.1(7)°, and the Cd−C bond distances are 2.28(2), 2.25(2),

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[1] (a) Squiller, E. P.; Whittle, R. R.; Richey, H. G., Jr. *J. Am. Chem. Soc.* **1985**, *107*, 432. (b) Richey, H. G., Jr.; Kushlan, D. M. *J. Am. Chem. Soc.* **1987**, *109*, 2510. (c) Pajerski, A. D.; Parvez, M.; Richey, H. G., Jr. *J. Am. Chem. Soc.* **1988**, *110*, 2660. (d) Richey, H. G., Jr.; BergStresser, G. L. *Organometallics* **1988**, *7*, 1459. (e) Fabicon, R. M.; Pajerski, A. D.; Richey, H. G., Jr. *J. Am. Chem. Soc.* **1991**, *113*, 6680. (f) Fabicon, R. M.; Pajerski, A. D.; Richey, H. G., Jr. *J. Am. Chem. Soc.* **1993**, *115*, 9333.

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

[3] Some halogen-containing organocadmate anions have been prepared. X-ray structure determination shows solids to have polymeric structures with bridging halogens. See for example, the following and references cited therein: Reference 2. Osman, A.; Tuck, D. G. *J. Organomet. Chem.* **1988**, *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.

[4] NMR spectral studies of solutions prepared from RLi and R_2Cd suggest formation of 1:1, 2:1, and 3:1 species, but these are unlikely to contain true cadmate anions. Toppet, S.; Slinckx, G.; Smets, G. *J. Organomet. Chem.* **1967**, *9*, 205. Seitz, L. M.; Little, B. F. *J. Organomet. Chem.* **1969**, *18*, 227.

[5] Crystal data for $C_3H_9Cd{\cdot}C_{15}H_{35}N_4Mg{\cdot}C_6H_6$: orthorhombic, space group *Pnma* (No. 62), $a = 18.981(3)$ Å, $b = 9.621(5)$ Å, $c = 15.611(4)$ Å, $V = 2850(1)$ Å^3, $Z = 4$, $D_{calcd} = 1.238$ g/cm^3. A total of 2893 unique reflections were measured in the range $4.0 < 2\phi < 50.0°$ using graphite-monochromatized Mo Kα radiation at −73 °C. The structure was solved by direct methods. Non-hydrogen atoms were refined anisotropically; hydrogen atoms were included in the refinements at geometrically idealized positions with C−H = 0.95 Å. C10 and C11 lie across the mirror planes and were disordered over two sites (C10a, C10b and C11a, C11b, respectively). The final cycle of full-matrix, least-squares refinement was to $R = 0.0579$ and $R_w = 0.0655$ for 1001 reflections with $I > 3.00\sigma(I)$. The maximum and minimum peaks of the final difference Fourier map corresponded to 0.57 and −0.39 e/Å^3, respectively.

[6] The cation has been seen in another X-ray structure.[7]

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

[8] A distorted trigonal arrangement is seen in a case where two of the R groups also are bonded to a Li: Waggoner, K. M.; Power, P. P. *Organometallics* **1992**, *11*, 3209.

[9] Purdy, A. P.; George, C. F. *Organometallics* **1992**, *11*, 1955. Westerhausen, M.; Rademacher, B.; Schwarz, W.; Henkel, S. *Z. Naturforsch.* **1994**, *49b*, 199.

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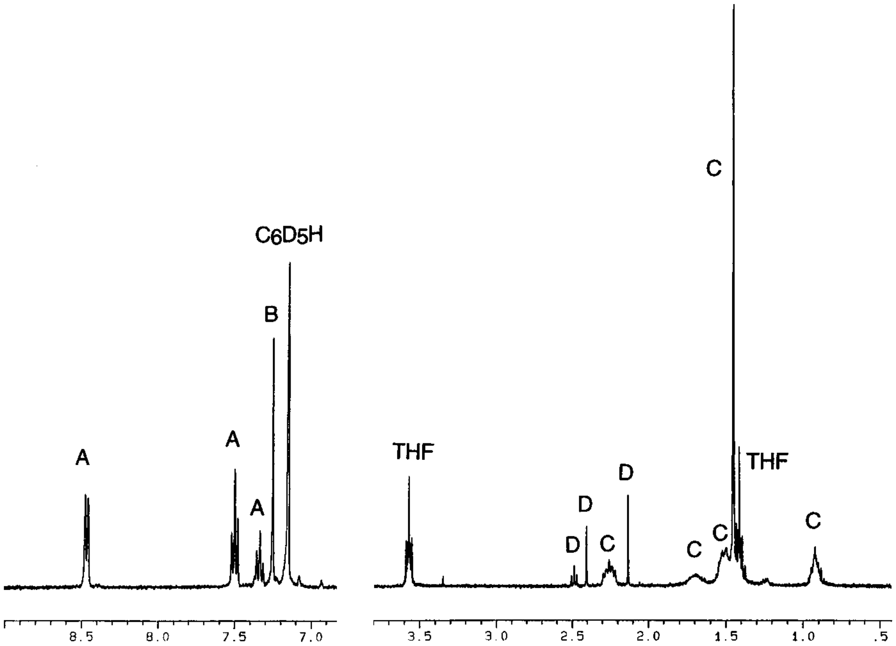

Figure 2. ^{1}H NMR spectrum (360 MHz) of a benzene-d_6 solution (ca. 0.05 M) prepared from crystalline $Ph_3Cd^-PhMg(14N4)^+(THF)$. Absorptions of the Ph of Ph_3Cd^- are labeled A and of the Ph of $PhMg(14N4)^+$ are labeled B. The absorptions labeled C are those of the 14N4 of $PhMg(14N4)^+$, and the weak absorptions labeled D are due to a trace of free 14N4 (probably arising from hydrolysis of the salt).

and 2.19(2) Å). A planar geometry has also been observed for triorganomagnesate[1a,8] and triorganozincate[9] ions.

Solutions of $R_3Cd^-RMg(14N4)^+$ salts also can be prepared. The ^{1}H NMR spectrum in Figure 2 is of a benzene solution of $Ph_3Cd^-PhMg(14N4)^+$. This supersaturated solution was obtained by heating in benzene crystals that had deposited slowly but in good yield (80%) from a solution prepared by dissolving equimolar amounts of Ph_2Cd, Ph_2Mg, and 14N4 in THF and then adding a small layer of benzene and a larger layer of hexane.[10] Note (1) the two sets of Ph absorptions in 3:1 ratio, (2) a particularly downfield position (δ 8.47) of the ortho hydrogen absorption in the larger absorption set, in accord with large downfield shifts[1b,e] seen for ortho hydrogen absorptions in benzene solutions of arylzincate and arylmagnesate ions, and (3) 14N4 absorptions more complex than those of free 14N4 but similar to those observed[7] for (aryl)Mg(14N4)$^+$ cations in the presence of magnesate anions.

^{1}H NMR spectra of solutions resulting from combining R_2Cd and R_2Mg (where R is ethyl, isobutyl, neopentyl, or (trimethylsilyl)methyl (Me_3SiCH_2-)) in benzene with 14N4 also indicate essentially quantitative formation of $R_3Cd^-RMg(14N4)^+$. These observations are often complicated by the appearance of a second dense liquid layer which contains substantial amounts of the solute, a behavior often noted when ionic species are formed in aromatic solvents.[11] When R is neopentyl or (trimethylsilyl)methyl, however, sufficient solute remains in the upper phase, even after phase equilibrium is reached, to provide good ^{1}H NMR spectra.[12] The ^{1}H NMR spectra of the dense lower phases and the upper phases are sufficiently similar that they must contain the same species. Among the observations indicating ion formation are two sets of R absorptions in 3:1 ratio and similarity of the smaller set and the 14N4 absorptions to the absorptions[1f,7,13] of $RMg(14N4)^+$ ions formed with other anions. Similar ion formation occurs when 2,1,1-cryptand or 2,2,1-cryptand is used in place of 14N4. The ethyl reagents and 14N4 also were studied in other solvents. Two phases are observed in dioxane and Et_2O, the ^{1}H NMR spectra of the lower phases exhibiting two sets of R absorptions in 3:1 ratio. No phase separation occurs when the solvent is DME or THF, but the ^{1}H NMR spectra again show two sets of R absorptions in 3:1 ratio, although some absorption positions differ significantly from those observed for preparations in benzene. The methyl salt whose structure is shown in Figure 1 is very insoluble in benzene but dissolves sufficiently on heating to provide a similar spectrum having two sets of Me absorptions.

Coupling of ^{111}Cd and ^{113}Cd with the α- and β-hydrogens of R is seen in ^{1}H NMR spectra of R_2Cd alone in benzene but not in the spectra of $R_3Cd^-RMg(14N4)^+$. Rapid exchange of organic groups between cadmate ions may be responsible for the failure to observe coupling. Coupling has not been observed even when employing expedients that might slow exchange—lowering the temperature, adjusting reagent concentrations to minimize traces of free R_2Cd or R_2Mg which might catalyze the exchange, and adding TMEDA which by coordinating with R_3Cd^-, R_2Cd, or R_2Mg might slow exchange.

When 14N4 is added to a benzene solution of Et_2Zn and Et_2Cd, no new phase forms and the 14N4 absorptions are essentially those of free 14N4 . What were independent absorptions for the EtZn and EtCd groups,

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(10) The solution also contains the THF that is in the crystal. Its ^{1}H NMR absorptions are similar to those of free THF.

(11) Atwood, J. L. In *Inclusion Compounds*; Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Eds.; Academic: London, l984; Vol. 1, Chapter 9.

(12) Phase separation in the neopentyl and (trimethylsilyl)methyl cases was slow, occurring over many hours at ambient temperature. Investigation of the neopentyl system showed that the reaction to form the ions in fact is slow.

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

however, become broad common absorptions at positions intermediate between those of the pure components (and coupling between Cd and the α- and β-H's that is evident in the absence of 14N4 no longer is seen). The chemical shift of ^{113}Cd is changed <0.1 ppm; by contrast the Cd absorption in $Et_3Cd^-EtMg(14N4)^+$ (lower phase) is 298 ppm to lower field than the absorption of Et_2Cd (benzene). These observations indicate that no significant amounts of Et_2Zn and Et_2Cd are converted to $Et_3Cd^-EtZn(14N4)^+$ but that the 14N4 does induce rapid ethyl exchange. Rapid and reversible formation of amounts of $Et_3Cd^-EtZn(14N4)^+$ too small to influence NMR chemical shifts probably is responsible for this exchange.[14] It is evident that Et_2Zn plus 14N4 is a much poorer "R^-" donor than Et_2Mg plus 14N4, presumably due to much weaker coordination by 14N4 to Zn than to Mg.

This work provides a general procedure for synthesizing cadmate ions and illustrates the use of the strong "R^-" donating ability of appropriate organometallic–coordinating agent systems to generate new organometallic species.

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Supporting Information Available: Text and a table giving details of the X-ray study, tables of atomic coordinates and *B* values, anisotropic displacement parameters, and bond distances and angles, and ORTEP diagrams (13 pages). Ordering information is given on any current masthead page.

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[14] Methyl exchange in Me_2Cd and in Me_2Cd-Me_2Zn solutions has been studied: Oliver, J. P. *Adv. Organomet. Chem.* **1970**, *8*, l67. Soulati, J.; Henold, K. L.: Oliver, J. P. *J. Am. Chem. Soc.* **l971**, *93*, 5694. It was suggested that increases in exchange rate by donor solvents are due to a more facile bridging by methyl groups when a solvent heteroatom is bonded to a metal.