(150–250 mesh) were able to bind Cu^{2+} when stirred for 3 h with an excess of $CuCl_2$ in methanol at 25.0 °C. Quantitative assessment of the metal complexation by two different methods (elemental analysis of the polymer and spectrophotometric analysis of the methanol solution) agreed with each other and showed that 51%, 76%, and 89% of the diamine groups in **1–3** were exposed at the surface and at interstices where Cu^{2+} could reach the nitrogens. Since the amount of external diamine dropped to only 0.6% in copolymers formed without surfactant-stabilized water pools but of the same mesh size, the strategy for synthesizing porous polystyrene bearing chemically active surfaces obviously succeeded. The methodology might also be advantageously applied to open cell foams prepared from high internal-phase emulsions recently described in detail by Williams, Gray, and Wilkerson.[6] Potential applications include the development of high-capacity chiral stationary phases, an area we are beginning to explore.

Low levels of copper-coated porous polymer (150–250 mesh) displayed a modest heterogeneous catalysis in the hydrolysis of *p*-nitrophenyl diphenyl phosphate (pH = 8.00, 25.0 °C). For example, 8.0 mg of polymer **1** (representing 2.5×10^{-5} M Cu^{2+} had the polymer been water-soluble) hydrolyzed 2.5×10^{-4} M phosphate ester with a half-life of 2.5 h and a yield of 93%.[7,8] Under the same conditions but without catalyst, the half-life was about 60 h. Since a 10-fold excess of substrate was completely hydrolyzed by the solid catalyst, turnover must have taken place. When the substrate and the "virtual" polymer concentration were reversed from that given above, the substrate was totally and immediately adsorbed from the buffer onto the polymer surface. All attempts to recover adsorbed ester from the polymer, including sonication over dry tetrahydrofuran, furnished only a hydrolysis product, *p*-nitrophenol.

Acknowledgment. This work was supported by the Army Research Office. We thank Dow Chemical Co. for a gift of vinylbenzyl chloride.

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(7) This represents a 2.5-fold improvement in half-life over the best of the nonporous copper polymers previously described in ref 3.

(8) For lead references on polymer-based catalysts and polymer–copper complexes, see: ref 1.

The First Square-Planar Complex of Cd(II): Cd(OAr)$_2$(THF)$_2$ Where OAr = 2,6-Di-*tert*-butylphenoxide. A Structure Governed by Two Strong Covalent and Two Weak Dative Bonds

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As a part of our studies of the alkoxides of divalent metals,[1] we have solved the crystal structure of the title compound **1**, $Cd(OAr)_2(THF)_2$ (OAr = 2,6-t-$Bu_2C_6H_3O$). The structure of **1** is novel and prompts us to suggest consolidation of a few empirical arguments to rationalize the structures of main-group compounds having datively bound ligands. They are (1) dative bonds to heavier element acceptors are often significantly weaker than the corresponding bonds to lighter congeners, (2) such *weak* dative bonds may be considered "secondary bonds",[2] and (3) secondary bonds do not affect the geometrical arrangement of primary bonds and lone pairs about a central atom.[3] These arguments derive from Alcock's discussion of secondary bonds[2] and Haaland's recent discussion of dative bonds.[4]

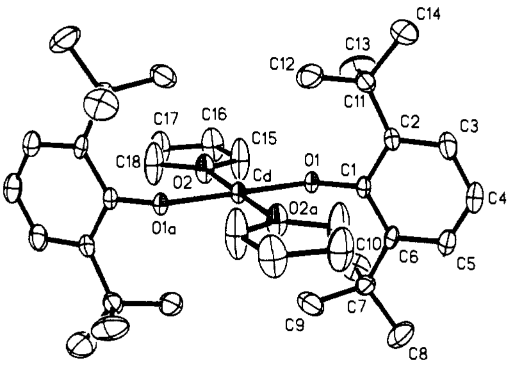

Figure 1. ORTEP of $Cd(OAr)_2(THF)_2$ (**1**, OAr = 2,6-t-$Bu_2C_6H_3O$). Hydrogen atoms were omitted for clarity. Cd resides on a crystallographic inversion center. Selected distances (Å): Cd–O(1), 2.058 (4); Cd–O(2), 2.498 (5); O(1)–C(1), 1.349 (7). Selected angles (deg): O(1)–Cd–O(2), 81.8 (2); O(1)–Cd–O(1A), 180.0 (1); O(2)–Cd–O(1A), 98.2 (2); O(2)–Cd–O(2A), 180.0 (1); Cd–O(1)–C(1), 127.6 (4).

Compound **1** was isolated as pale-yellow crystals from THF according to eq 1; a view of the molecular structure is shown in

$$Cd[N(SiMe_3)_2]_2 + 2ArOH \xrightarrow{THF} Cd(OAr)_2(THF)_2 + 2HN(SiMe_3)_2 \quad (1)$$

Figure 1.[5] Two distinctive features are evident: the crystallographically imposed square-planar geometry about Cd(II), which is unprecedented,[6] and the large difference (0.44 Å) between the Cd–O separations for the aryloxide ligand [$Cd–O_{aryloxide}$ = 2.058 (4) Å] and the THF ligand [$Cd–O_{THF}$ = 2.498 (5) Å]. The latter is consistent with a description of the $Cd–O_{aryloxide}$ vectors as normal covalent bonds, and the $Cd–O_{THF}$ vectors as dative bonds.[4] According to Haaland, dative bonds are generally less than half the strength of normal covalent bonds for a given atom pair and may be distinguished by significant differences in bond distances.[4]

The trans, square-planar geometry of **1** is not as readily justified. Square-planar geometries are typically enforced by $d^{8\pm1}$ configurations and strong ligand fields; on steric grounds, they are disfavored.[7] Ligand-field effects do not exist for main-group compounds, and a tetrahedral or distorted tetrahedral[4] arrangement for **1** is predicted by standard VSEPR arguments. Obviously, other influences must be responsible for the square-planar structure of **1**.

A useful comparison may be drawn to the structure of $Zn(OAr')_2(THF)_2$ (**2**, OAr′ = 2,4,6-t-$Bu_3C_6H_2O$), previously determined by Geerts, Huffman, and Caulton.[8] Compound **2** has the expected[4] distorted tetrahedral geometry, and the Zn–O distances involving the aryloxide [$Zr–O_{aryloxide}$ = 1.89 (1) Å] and THF [$Zn–O_{THF}$ = 2.08 (1) Å] ligands differ by only 0.19 Å.

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(3) Argument 3 is explicit in Alcock's discussion.[2]

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(5) Crystal data for **1**: $C_{36}H_{58}O_4Cd$, M_r = 667.2, monoclinic, $P2_1/n$, a = 9.621 (5) Å, b = 11.780 (4) Å, c = 16.032 (9) Å, β = 93.35 (5)°, V = 1813.9 (15) Å^3, T = 295 K, Z = 2, D_c = 1.222 g cm^{-3}, λ(Mo Kα) = 0.71073 Å. Of the 3208 unique intensities measured, 1848 with $F_o > 6.0\sigma(F_o)$ yielded $R(F)$ = 0.0393 and $R_w(F)$ = 0.0458.

(6) The coordination environment about cadmium is square pyramidal (CN 5) in (5,10,15,20-tetraphenylporphinato)cadmium(II) (Cd(TPP)),[6a] and z-out tetragonal (CN 6) in $Cd(TPP)(dioxane)_2$.[6b] A square-planar geometry was claimed in a Schiff-base chelate of Cd(II), but was not verified by a crystallographic determination.[6c] (a) Hazell, A. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1986**, *C42*, 296. (b) Rodesiler, P. F.; Griffeth, E. H.; Ellis, P. D.; Amma, E. L. *J. Chem. Soc., Chem. Commun.* **1980**, 492. (c) Blum, P. R.; Wei, R. M. C.; Cummings, S. C. *Inorg. Chem.* **1974**, *13*, 450.

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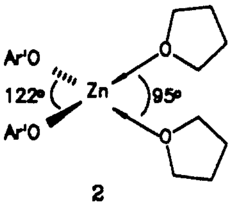

2

Clearly, the dative bonds in **2** are comparatively stronger than the dative bonds in **1**.

Dative bonds to main-group-element acceptors have sizable dipole moments and are very sensitive to inductive effects and formal charges on acceptor or donor atoms.[4] Thus, dative bonds involving main-group atoms probably have a substantial electrostatic component in general. Because Cd(II) is larger than Zn(II), it has a smaller charge-to-size ratio, a consequently weaker electrostatic interaction with THF, and thus a comparatively weaker dative bond. This electrostatic argument may apply fairly generally in such *main-group* comparisons. Exceptions are expected for extreme soft–soft interactions, and for cases with small acceptor atoms (such as boron) when dative bonds are destabilized by steric interactions between ligands.[4]

We propose that the square-planar geometry of **1** may be rationalized by identifying the Cd–O_{THF} interactions as secondary bonds. Secondary bonds were previously defined by Alcock as weak, "directed" interactions that form with 180 ± 15° angles to normal covalent bonds and are several tenths of an angstrom longer.[2] In Alcock's model, the primary bonds and lone pairs about a central atom determine the primary coordination geometry according to VSEPR, with secondary bonds forming in line with the primary bonds.[2] We submit that a distinction between the 180° interactions and other weak dative bonds is unnecessary and a more general definition is desirable; all weak interactions may serve as secondary bonds.

Thus, the geometry of **1** results from the two primary covalent bonds (aryloxide ligands) forming a linear arrangement as predicted by VSEPR for 2 coordination, and the secondary interactions (THF ligands) forming in the manner that least disrupts the primary coordination geometry. The best positions for the secondary interactions in this special case are in the clefts provided by the *t*-Bu groups, which give the observed square-planar structure. In **2**, the dative bonds are stronger and all four of the dative and covalent bonds about zinc are primary, geometry-determining bonds. Regardless of their specific natures, we suggest primary bonds be defined as those bonds that, along with the lone pairs about a central atom, dictate the primary coordination geometry, and secondary bonds as those that do not.

The principal conclusions are (1) Haaland's description of dative bonds[4] and Alcock's description of secondary bonds[2] are conceptually related and can be usefully united, (2) Alcock's definition of secondary bonds is unnecessarily restrictive, and (3) dative bonds to heavier element acceptors are comparatively weaker than dative bonds to lighter congeners when the electrostatic components of the dative interactions are dominant; the former may behave as secondary bonds and the latter as primary bonds.

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Supplementary Material Available: A description of experimental details and listings of the details of the data collection, final positional and equivalent isotropic thermal parameters, bond distances, bond angles, calculated hydrogen atom parameters, and anisotropic thermal parameters for **1** (8 pages); a listing of observed and calculated structure factors for **1** (12 pages). Ordering information is given on any current masthead page.

Conformational Enantiomers of 3,4,5,6-Tetramethylphenanthrene 9,10-Oxide. A Novel Axially Chiral Arene Oxide with Unusual Conformational Stability and Reactivity

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Recent investigations of the structure and conformational stability of 3,4,5,6-tetramethylphenanthrene (**1**)[1] and the corresponding 9,10-disubstituted-9,10-dihydrophenanthrenes[2] suggested that it should be possible to prepare the strained, axially chiral conformational enantiomers of 3,4,5,6-tetramethylphenanthrene 9,10-oxide, **2M** and **2P**. The severe nonbonded interaction between the methyl groups at the 4- and 5-positions was anticipated to (i) increase the solvolytic reactivity of the oxirane by distortion of the ground state toward the geometry of the carbocation intermediate,[3] (ii) prevent the mutarotational interconversion of the two possible diastereomeric carbocations,[4] and (iii) predispose each conformational enantiomer to nucleophilic attack at only one of the two diastereotopic oxirane carbons as illustrated in Scheme I. In this paper we report the synthesis and preliminary characterization of the conformational enantiomers of **2**.

Oxidation of racemic **1** with *m*-chloroperoxybenzoic acid in a two-phase system of benzene and aqueous $NaHCO_3$[5] followed by chromatography on DEAE-cellulose in a 1:1 v/v mixture of benzene/cyclohexane gave racemic **2** in 50% isolated yield. The structure of **2** was confirmed by IR, UV, high-resolution MS, ^{13}C and ^{1}H NMR spectroscopy where the chemical shifts and vicinal coupling constant of the diastereotopic oxirane protons [δ 4.36 (d, 1 H), 4.53 (d, 1 H), $^{3}J_{9,10}$ = 4.0 Hz] were particularly diagnostic.[6] Direct oxidation of **1M** and **1P** (≥90% enantiomeric purity)[1b] at 5 °C followed by workup at low temperature afforded **2M** and **2P**, respectively, with enantiomeric purities of ≥90%. Absolute configurations of the two antipodes were confirmed by the signs of the dissymmetry transitions at 230 nm in their circular dichroism spectra (Figure 1), which reflects the helical twist of the biphenyl chromophore.[2b] The axially chiral arene oxides exhibit a substantial conformational stability characterized by a rate constant for pseudorotation, $k_{inv} = 1.9 \times 10^{-4}\ s^{-1}$ at 25 °C in *n*-hexane [$\Delta G^{\ddagger}_{inv}$ = 22.5 kcal/mol, $t_{1/2}$(racemization) = 30 min]. Activation parameters obtained from the temperature dependence of k_{inv} are as follows: $\Delta H^{\ddagger} = 22.6 \pm 0.2$ kcal/mol and $\Delta S^{\ddagger} = 0.2 \pm 0.7$ eu at 25 °C. The rather low rate of pseudorotation of **2** clearly suggests that mutarotation of the two

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