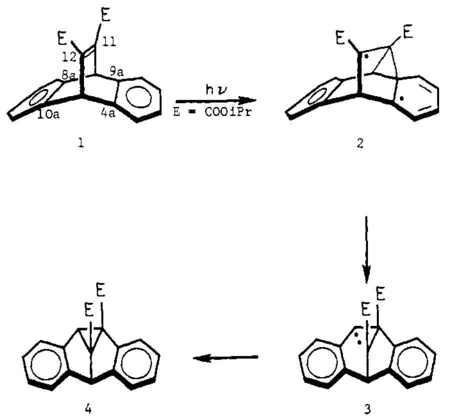
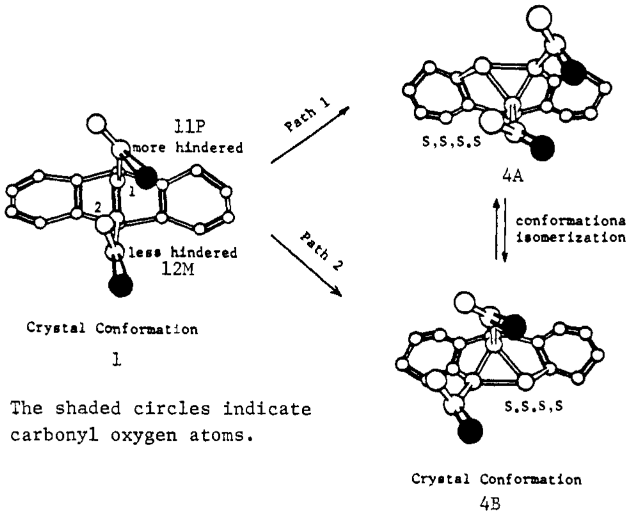
Scheme I



Path I: initial 9a-11 bonding
Path II: initial 10a-12 bonding
Path III: initial 4a-12 bonding
Path IV: initial 8a-11 bonding

Scheme II



The shaded circles indicate carbonyl oxygen atoms.

$P4_32_12$ for **4** at confidence levels of about 95%. Since this test may not be completely reliable in this situation,[4b] further comparisons were made by using the Bijvoet difference method.[3,4c,d] Among Friedel pairs with the largest expected intensity differences, 20 (out of 30) for **1** and 14 (out of 20) for **4** indicated the same absolute configurations as Hamilton's test. Hence, we are reasonably confident that the correct absolute configurations have been assigned. The crystal of **1** studied contained molecules with the 11P, 12M absolute configuration,[5] and its photoproduct had the *S,S,S,S*-(−) configuration. Ball and stick drawings of these absolute configurations are shown in Scheme II.

The first conclusion to be drawn from the results is that pathways I and/or II are followed; pathways III and/or IV would have given the *R,R,R,R*-(+) photoproduct. In terms of structure, the 11P, 12M conformation of **1** predicts that paths III and/or IV would involve severe clashing of the ester groups as they are forced toward each other during the initial stages of reaction. In contrast, paths I and/or II involve movement of the ester groups *away* from one another, thus providing a plausible rationale for the observed results. Two questions arise at this point: (a) with the data in hand, can we determine the relative importance of paths I and II and (b) can we identify the crystal forces that control the preferred pathway(s)? The answer to both questions is a qualified yes. Two pieces of evidence indicate that path II is favored over path I. First, the packing diagram shows that *the ester group 12M, which is attached to the vinyl carbon atom involved in path II, is in a much freer lattice environment than its path I counterpart.* Because the ester group attached to the reactive site is required to move most during the initial stages of the rearrangement, there is a clear prediction of a preference for path II. This qualitative conclusion is borne out quantitatively by packing potential energy calculations of the type previously reported,[6] which simulate the steric interactions developed between the host lattice and guest reactant during the early stages of rearrangement. Secondly, assuming a least motion (topochemical) process,[7] pathway II produces the photoproduct **4** *directly in its final crystal conformation 4B*; in contrast, topochemical reaction via path I would lead to the unobserved conformer 4A.[8]

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. Financial support by the Natural Sciences and Engineering Research Council of Canada is also gratefully acknowledged.

Supplementary Material Available: Stereodiagram of diester **1** showing the difference in local packing density around each of the ester groups and a table of Bijvoet measurements from which absolute configurations were determined (2 pages). Ordering information is given on any current masthead page.

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[4] (a) Hamilton, W. C. *Acta Crystallogr.* **1965**, *18*, 502. (b) Rogers, D. *Acta Crystallogr.* **1981**, A*37*, 734. (c) Hope, H.; de la Camp, U. *Acta Crystallogr.* **1972**, A*28*, 201. (d) Pennington, W. T.; Chakrabory, S.; Paul, I. C.; Curtin, D. Y. *J. Am. Chem. Soc.* **1988**, *110*, 6498.

[5] The designation 11P, 12M uses the conformational chirality formalism for describing absolute configuration. See: Cahn, R. S.; Ingold, C.; Prelog, V. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 385.

[6] Similar calculations account for the striking *regioselectivity* observed in the solid-state di-π-methane rearrangement of a series of unsymmetrically substituted dibenzobarrelene-11,12-diesters. See: Garcia-Garibay, M.; Scheffer, J. R.; Trotter, J.; Wireko, F. *Tetrahedron Lett.* **1988**, *29*, 2041. Scheffer, J. R.; Trotter, J.; Garcia-Garibay, M.; Wireko, F. *Mol. Cryst. Liq. Cryst. Inc. Nonlin. Opt.* **1988**, *156*, 63. We note that path I is slightly favored over path II by radical stability considerations (radical placement next to the more conjugated ester). However, the work referred to above has shown that radical stability arguments are *not* generally predictive for these systems.

[7] (a) Cohen, M. D.; Schmidt, G. M. J. *J. Chem. Soc.* **1964**, 1996. (b) Cohen, M. D. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 386.

[8] We cannot completely rule out the possibility that reaction occurs via path I followed by isomerization of the higher energy (MM2) conformer 4A to the lower energy conformer 4B during workup and recrystallization. This does not, however, affect the basic conclusion regarding the preference for pathways I and/or II over III and/or IV in the solid state.

Potential Precursors to Electronic Materials: Three-Coordinate Cd in $[MeCd(\mu\text{-}t\text{-}Bu_2P)]_3$, the First Cadmium Diorganophosphide

Brian L. Benac,[1a] Alan H. Cowley,*[1b] Richard A. Jones,*[1a] Christine M. Nunn,[1a] and Thomas C. Wright[1c]

Departments of Chemistry
The University of Texas at Austin
Austin, Texas 78712
Imperial College of Science, Technology and
Medicine, London SW7 2AY, England
The University of Texas at Arlington
Arlington, Texas 76019

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As part of a program focused on the design and synthesis of precursors for electronic materials we[2] and others[3] recently demonstrated the use of single source molecules for the growth of III/V

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[1] (a) The University of Texas at Austin. (b) Imperial College. (c) The University of Texas at Arlington.

[2] Cowley, A. H.; Benac, B. L.; Ekerdt, J. G.; Jones, R. A.; Kidd, K. B.; Lee, J. Y.; Miller, J. E. *J. Am. Chem. Soc.* **1988**, *110*, 6248.

[3] Bradley, D. C.; Faktor, M. M.; White, E. A. D.; Frigo, D. M. U.K. Patent No. 8703227. Andrews, D. A.; Davies, G. J.; Bradley, D. C.; Faktor, M. M.; Frigo, D. M.; White, E. A. D. *Semicond. Sci. Technol.* **1988**, *3*, 1053. See, also: Bradley, D. C.; Faktor, M. M.; Frigo, D. M.; Young, K. V. *Chemtronics* **1988**, *3*, 50. Andrews, D. A.; Davies, G. J.; Bradley, D. C.; Faktor, M. M.; Frigo, D. M.; White E. A. D. *Semicond. Sci. Technol.* **1988**, *3*, 1053.

0002-7863/89/1511-4986$01.50/0

compound semiconductors such as GaAs and InP. Our approach for III/V semiconductors has been to combine both elements into the same molecule via a strong two-center, two-electron bond and to employ ligands which undergo facile decomposition processes such as β-hydrogen elimination. Examples of such molecules are $[Me_2Ga(\mu\text{-}t\text{-}Bu_2As)]_2$ and $[Me_2In(\mu\text{-}t\text{-}Bu_2P)]_2$.[2,3] We have also sought routes to II/V semiconductors such as Zn_3P_2, Cd_3P_2, and CdP_2 which are used for doping photoelectrics.[4] Current methods for growing Zn_3P_2 involve either vapor diffusion of the elements or the use of Me_2Zn and PH_3.[4] Although a few diorganophosphide derivatives of zinc[5] and mercury[6] are known, to our knowledge no phosphido complexes of cadmium have been reported. We have recently discovered that the reactive, mononuclear binary phosphido compound $Ga(t\text{-}Bu_2P)_3$[7] acts as a smooth phosphido transfer reagent both for main group and transition-metal species.

Reaction of the group 12 dimethyl compounds Me_2M (M = Zn, Cd, Hg) with $Ga(t\text{-}Bu_2P)_3$ at room temperature affords phosphido derivatives of these metals in high yields. For Zn and Cd one methyl group is replaced to give the new trimeric derivatives $[MeM(\mu\text{-}t\text{-}Bu_2P)]_3$ (M = Zn, (**1**); Cd, (**2**)). For Hg both methyl groups are exchanged to give $Hg(t\text{-}Bu_2P)_2$ (**3**) which has been described previously[8] although no structural details have been reported. To our knowledge **2** is the first diorganophosphido complex of cadmium, and an X-ray diffraction study was undertaken in order to provide structural information. Interestingly the structure of **2** contains planar three-coordinate Cd, which to our knowledge is the first such geometry to be reported for an organometallic derivative of Cd. We describe here the syntheses of **1**–**3** and X-ray structures of **2** and **3**.

Reaction of excess Me_2Zn or Me_2Cd with a frozen orange matrix of $Ga(t\text{-}Bu_2P)_3$ in toluene at 77 K and slow warming to room temperature affords a very pale yellow solution. Removal of volatile materials under vacuum and recrystallization of the residue from hexane at −30 °C give the colorless, trimeric phosphido derivatives **1** and **2** in 85–95% yield based on $Ga(t\text{-}Bu_2P)_3$ (eq 1). The other product from these reactions is

$$12Me_2M \xrightarrow[\text{toluene, 77 K}]{6Ga(t\text{-}Bu_2P)_3} 4[MeM(t\text{-}Bu_2P)]_3 + 3[Me_2Ga(t\text{-}Bu_2P)]_2 \qquad M = Zn, Cd \quad (1)$$

$[Me_2Ga(\mu\text{-}t\text{-}Bu_2P)]_2$[7] which is relatively insoluble in hexane, and so the products may be purified by fractional crystallization.[9] The analogous reaction with Me_2Hg gave yellow crystals of $Hg(t\text{-}Bu_2P)_2$ (**3**) in 76% yield (eq 2). Here the slightly reduced yield

$$2Me_2Hg \xrightarrow[\text{toluene, 77 K}]{2Ga(t\text{-}Bu_2P)_3} 2Hg(t\text{-}Bu_2P)_2 + 1[Me_2Ga(t\text{-}Bu_2P)]_2 \quad (2)$$

may be due to the fact that **3** is photolytically unstable, and reductive elimination of the diphosphine $t\text{-}Bu_4P_2$ and the formation of elemental mercury occur.[8]

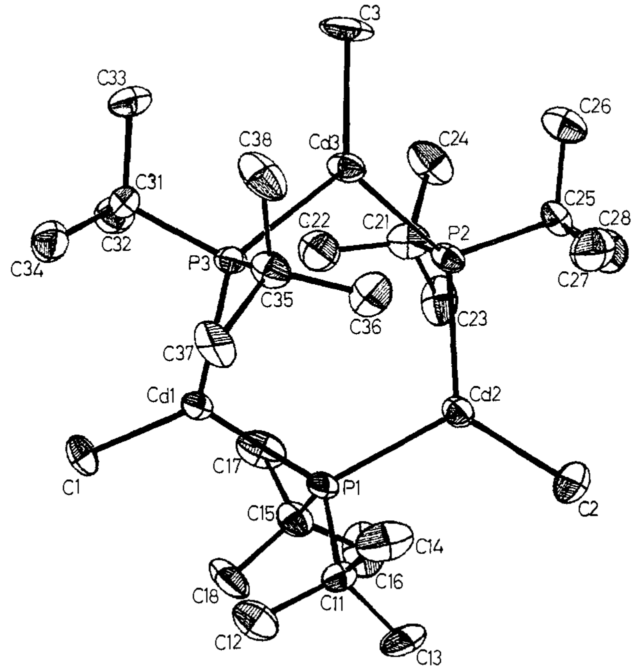

Figure 1. ORTEP view of **2**, showing the atom numbering scheme, typical bond lengths (Å), and angles (deg): Cd(1)–P(1) 2.568 (4), Cd(1)–P(3) 2.586 (3), Cd(2)–P(1) 2.586 (4), Cd(1)–C(1) 2.13 (2), Cd(2)–C(2) 2.18 (2), Cd(3)–C(3) 2.18 (2), Cd(1)–P(1)–Cd(2) 118.6 (1), P(1)–Cd(2)–P(2) 115.3 (1).

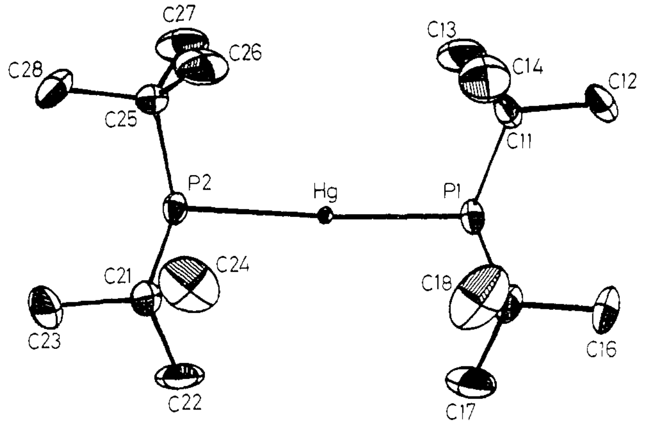

Figure 2. ORTEP view of **3**, showing the atom numbering scheme, typical bond lengths (Å), and angles (deg): P(1)–C(11) 1.89 (2), P(1)–C(15) 1.88 (2), Hg–P(1)–C(11) 102.3 (5), Hg–P(1)–C(15) 101.2 (5).

The $^{31}P\{^1H\}$ NMR spectrum of **2** at room temperature shows a sharp single line at δ 21.81 with ^{113}Cd and ^{111}Cd satellites indicative of a second-order spin system. The ^1H NMR contains peaks for $Cd\text{–}CH_3$ protons at δ 0.27 with accompanying ^{113}Cd and ^{111}Cd satellites and $t\text{-}Bu_2P$ protons at δ 1.32. The spectroscopic data for **1** is similar to that of **2**, and so we propose that it has a similar structure in solution.

An ORTEP view of **2** is shown in Figure 1.[10] The central Cd_3P_3 core adopts a twist-boat conformation in which one phosphido group (P(1)) lies in the Cd_3 plane, while the other two (P(2),P(3)) are above and below it. This core geometry is similar to that found in some trinuclear transition-metal phosphido complexes such as $Co_3(\mu\text{-}Cy_2P)_3(CO)_6$[11] and main-group derivatives such as $(Me_2InAsMe_2)_3$.[12] The pairs of *tert*-butyl groups attached to each phosphorus are located so as to minimize their steric interactions.

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(4) See, for example: Smith, S. A.; Watts, R. *Sol. Cells* **1984**, *11*, 41. Kuroda, T.; Sawada, Y.; Yasuhiro, S.; Usagawa, T. *Jpn. Kokai Tokkyo Koho* JP 61 51,822 [86 51,822] Mar 14, 1986, Appl 84/173,254, Aug 22, 1984. Solar Energy Research Institute (Golden, CO USA) Report **1982**, SERI/TR-8062-1-T16 (*Energy Res. Abst.* **1982**, *7*, Abstr. No. 49632.) Radautsan, S. I.; Morozova, V. I.; Knyazev, A. F.; Koval, L. S.; Arushanov, E. K.; Nateprov, A. N. *Fiz. Tekh. Poluprovodn.* **1985**, *19*, 1127.

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(8) Baudler, M.; Zarkadas, A. *Chem. Ber.* **1972**, *105*, 3844.

(9) Full spectroscopic details for **1** and **2** are provided in the Supplementary Material. The spectroscopic data for **3** corresponded to that previously reported (ref 8).

(10) Details of the X-ray structures of **2** and **3** are given in the Supplementary Material.

(11) Albright, T. A.; Kang, S.-K.; Arif, A. M.; Bard, A. J.; Jones, R. A.; Leland, J. K.; Schwab, S. T. *Inorg. Chem.* **1988**, *27*, 1246.

(12) Cowley, A. H.; Jones, R. A.; Kidd, K. B.; Nunn, C. M.; Westmoreland, D. L. *J. Organomet. Chem.* **1988**, *341*, C1.

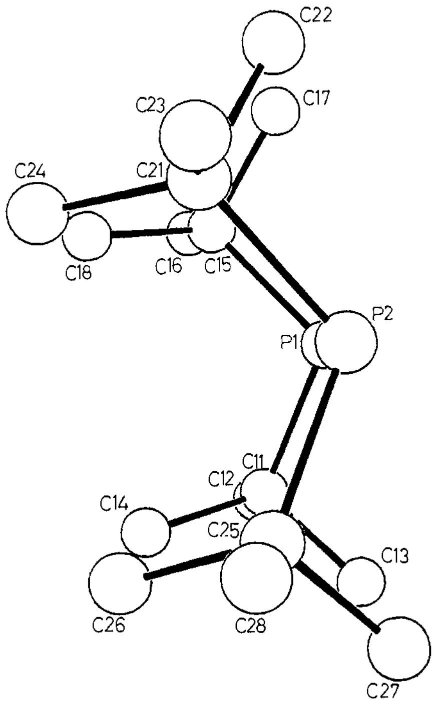

Figure 3. View down the P(2)-Hg-P(1) axis of **3**. The Hg atom is obscured by P(2).

Thus, those on P(2) point down, away from the Cd_3 plane, those on P(3) are above it, and those on P(1) lie both above and below the plane. The Cd-methyl groups all lie essentially in the Cd_3 plane giving each Cd atom a novel planar three-coordinate geometry.[13] The Cd-P bond distances are all similar and range from 2.568 (4) to 2.598 (3) Å (2.585 (4) Å av) and compare well with the sum of the Bragg-Slater radii[14] for Cd(II) (1.55 Å) and P(1.00 Å). The Cd-C(methyl) distances range from 2.13 (2) to 2.18 (2) Å (2.16 (2) Å av). They may be compared to the Cd-C distance of 2.14 Å (av) in $[(Me_3SiCH_2)_2Cd](bipy)$.[15]

An ORTEP view of $Hg(t\text{-}Bu_2P)_2$ (**3**) is shown in Figure 2. As expected the central Hg atom has a two-coordinate linear geometry (P(1)-Hg-P(2) = 177.5 (1)°). The Hg-P bond lengths are similar at 2.442 (3) (Hg-P(1)) and 2.451 (3) (Hg-P(2)). The structure of **3** contains an interesting feature which concerns the orientation of the P-*t*-Bu groups and phosphorus lone pairs. Each phosphorus has a pyramidal geometry, however, the P-*t*-Bu groups on the two phosphides are eclipsed with respect to each other. A view along the P(1)-Hg-P(1) direction, which illustrates this feature is shown in Figure 3. Thus both phosphorus lone pairs occupy the same side of the molecule. This suggests that steric factors do not play an important role in determining the molecular geometry of **3** in the solid state. This may be due to the large size of the Hg atom.

Although the apparent M:P stoichiometries of **1** and **2** do not correspond to those of the binary compounds such as Zn_3P_2 and Cd_3P_2, we are currently exploring the use of these and related complexes as potential precursors to solid-state materials.

Acknowledgment. We thank the Robert A. Welch Foundation and the National Science Foundation for support. R.A.J. also thanks the Alfred P. Sloan Foundation for a fellowship (1985-1989).

Supplementary Material Available: Details of the synthesis and spectroscopic characterization of **1**, **2**, and **3**, the X-ray crystallography of **2** and **3**, the $^{31}P\{^1H\}$ NMR spectrum of **2**, table of least-squares planes for **2**, and tables of bond lengths, angles, positional parameters, and thermal parameters (17 pages); tables of observed and calculated structure factors (38 pages). Ordering information is given on any current masthead page.

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[13] Sum of angles around Cd = 359.8 (4)° (av). For a rare example of three coordinate Zn, see: Al-Juaid, S. S.; Buttrus, N. H.; Eaborn, C.; Hitchcock, P. B.; Roberts, A. T. L.; Smith, J. D.; Sullivan, A. C. *J. Chem. Soc., Chem. Commun.* **1986**, 908. Deviations (Å) from the least-squares plane through Cd(1)-Cd(2)-Cd(3) and P(1) are as follows: P(1) 0.056 (4), Cd(1) -0.037 (1), Cd(2) -0.037 (1), Cd(3) 0.018 (1), P(2) 0.618 (4), P(3) -0.731 (4).

[14] Slater, J. C. *J. Chem. Phys.* **1964**, *41*, 3199.

[15] Bushnell, G. W.; Stobart, S. R. *Can. J. Chem.* **1980**, *58*, 574. See also Khan et al. (Khan, O. F. Z.; Frigo, D. M.; O'Brien, P.; Hower, A.; Hursthome, M. B. *J. Organomet. Chem.* **1987**, *334*, C27) for the X-ray structure of bis[2-((dimethylamino)methyl)phenyl]cadmium(II) where Cd-C = 2.154 (8) Å.

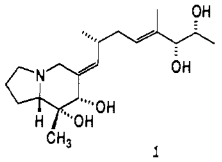
Stereoelectronic Requirements of a Pd(0)-Catalyzed Cyclization. A Synthesis of *allo*-Pumiliotoxin 339B

Barry M. Trost* and Thomas S. Scanlan

Department of Chemistry, Stanford University
Stanford, California 94305

Received February 9, 1989

The widespread occurrence and diverse biological activity of indolizidine[1] and pyrrolizidine[2] alkaloids and the presence of many in only minute quantities from the natural sources have made them attractive research objectives. In asking how transition-metal-catalyzed allylic alkylations might solve the structural problems presented by these alkaloids, we targetted *allo*-pumiliotoxin 339B (**1**),[3] one of the most complex indolizidines, and supinidine (**2**),[4]



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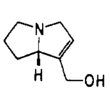

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since both would derive from common chemistry in terms of construction of the basic nucleus. While many syntheses of supinidine exist,[5] the architecturally challenging pumiliotoxins—a diverse class of amphibian toxins[1,6]—have been successfully tackled synthetically only through the excellent efforts of the Overman group.[7]

These targets also provide an ideal format to probe the more general question regarding geometrical requirements of palladium-catalyzed cyclizations involving allylic alkylations. Examination of eq 1 reveals that cyclization mode "a" invokes an exocyclic transition state in terms of the orientation of the palladium complex with respect to the forming ring, whereas mode "b" invokes an endocyclic cyclization, a process that should become disfavored as the tether is shortened.[8,9] The facility of the en-

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[3] Tokuyama, T.; Daly, J. W.; Highet, R. J. *Tetrahedron* **1984**, *40*, 1183.

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