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1,8-Naphthalenediylbis(dichloroborane) chloride: the first bis boron chloride chelate

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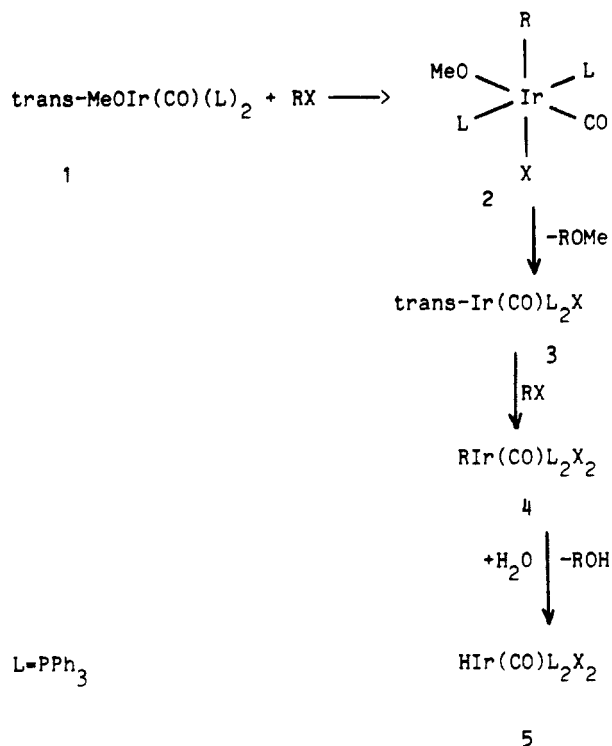## ACS Publications
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trans-MeOIr(CO)(L)$_2$ + RX ———>

R
|
MeO ∖ | ∕ L
Ir
L ∕ | ∖ CO
|
X

1

2

↓ -ROMe

trans-Ir(CO)L$_2$X

3

↓ RX

RIr(CO)L$_2$X$_2$

4

+H$_2$O ↓ -ROH

L=PPh$_3$

HIr(CO)L$_2$X$_2$

5

Figure 2. Scheme which summarizes the observed chemistry between RX and *trans*-MeOIr(CO)(PPh$_3$)$_2$. **2** has been isolated for MeI; ROMe is observed for R = CH$_3$C(O), C$_6$H$_5$C(O), and C$_6$H$_5$CH$_2$C(O); **3** is the final product for C$_6$H$_5$C(O)Cl; **4** is the product for CH$_3$C(O)Cl and C$_6$H$_5$CH$_2$C(O)Cl under anhydrous conditions; **5** is observed to form from **4** with traces of water.

Analogous products were obtained from addition of phenylacetyl chloride. In both of these cases (but especially for CH$_3$C(O)Cl) care must be taken to avoid hydrolysis of the acetyl product to the hydride HIr(CO)(PPh$_3$)$_2$Cl$_2$. The reaction of benzoyl chloride with *trans*-MeOIr(CO)(PPh$_3$)$_2$ also leads to the ester C$_6$H$_5$C(O)OMe, but a second C$_6$-H$_5$C(O)Cl does not add to *trans*-Ir(CO)(PPh$_3$)$_2$Cl, as previously reported.[17]

In contrast to the acid chlorides, methyl iodide adds to *trans*-MeOIr(CO)(PPh$_3$)$_2$ to form a stable adduct.[18] The infrared and NMR data are consistent with the geometry shown in Figure 1. Preliminary results of an X-ray structure determination support this geometry.[19] To encourage elimination of dimethyl ether, we warmed (45 °C) a solution of MeIr(OMe)(CO)(PPh$_3$)$_2$I and opened a decomposition pathway that produces CH$_4$, CH$_3$OH, and *trans*-Ir(CO)(PPh$_3$)$_2$I in variable yields depending on the solvent, but in no case was dimethyl ether observed.

The chemistry which we have observed is summarized in Figure 2. **2** has been isolated for R = Me and X = I; **3** has been isolated for R = C$_6$H$_5$C(O) and X = Cl; **4** has been isolated for R = CH$_3$C(O) and C$_6$H$_5$CH$_2$C(O) and X = Cl; and **5** has been isolated for R = CH$_3$C(O) and C$_6$H$_5$CH$_2$C(O) and X = Cl. The reactions of MeI and the acid chlorides with *trans*-MeOIr(CO)(PPh$_3$)$_2$ occur rapidly. Previous study has shown that oxidative addition of alkyl and acid halides to square-planar Ir(I) complexes occurs with a trans geometry as shown for **2**.[2,17]

Oxidative addition of acid chlorides and methyl iodide to *trans*-MeOIr(CO)(PPh$_3$)$_2$ leads to the formation of carbon–oxygen bonds giving esters but not ethers.[20] Details of these reactions, including variation of the alkoxy (R) groups, will be reported in the full paper.

(16) Purification of acid chlorides: all acid chlorides used were purchased from Aldrich. Phenylacetyl chloride and benzoyl chloride were passed down a basic alumina column and used under a nitrogen atmosphere. Acetyl chloride was predried by stirring over basic alumina (14 h), then vacuum distilled onto *N,N*-dimethylaniline, and stirred 5 min. The first one-third portion of the acid chloride was distilled and discarded, and ~90% of the remaining portion was distilled into a pressure tube fitted with a Teflon stopcock and stored until needed. Glassware was oven-dried, and the vacuum apparatus was heated prior to use.

(17) Kubota, M.; Blake, D. M. *J. Am. Chem. Soc.* **1971**, *93*, 1368.

(18) Ir(OMe)(Me)(CO)(PPh$_3$)$_2$I was prepared by addition of 0.20 mL of MeI to 0.25 g of *trans*-MeOIr(CO)(PPh$_3$)$_2$ in 40 mL of C$_6$H$_6$ under inert atmosphere. Stirring for 5 min and solvent removal led to a solid that was washed (2 × 10 mL of toluene, 2 × 20 mL of hexanes). The yield was 0.15 g (51%) of a white product with IR (1985 cm^{-1}) in KBr and ^{1}H NMR in benzene-*d$_6$* (1.13 (t, J_{P-H} = 4.8 Hz), 3.37 (s), 7.0 (m) ppm) indicating correct formulation of the product. Microanal. Calcd: C, 51.03; H, 3.93. Found: C, 49.51; H, 3.50.

(19) Bernard, K. A.; Fettinger, J. C.; Churchill, M. R.; Atwood, J. D., to be submitted for publication.

(20) As suggested by a reviewer we cannot be certain at this point that a direct interaction of the acid chlorides with the methoxy group does not occur. In the absence of evidence that a direct reaction is occurring, we prefer to consider the known oxidative addition to a square-planar Ir(I) complex.[17]

1,8-Naphthalenediylbis(dichloroborane) Chloride: The First Bis Boron Chloride Chelate

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Summary: The synthesis and chloride complexing properties of 1,8-naphthalenediylbis(dichloroborane) are reported. This compound, prepared from 1,8-bis(chloromercurio)naphthalene and BCl$_3$, forms chelate complexes with inorganic and organic chloride donors as determined by ^{11}B NMR. X-ray crystallography confirmed the presence of unprecedented B–Cl–B bridge bonds in the complexes.

We have already demonstrated[1] that 1,8-naphthalenediylbis(dimethylborane) (hydride sponge) forms stable, bridged complexes by abstracting H$^-$, F$^-$, and OH$^-$. On the other hand, it appeared from NMR data that the interaction of hydride sponge with Cl$^-$ is weak or nonexistent. Prompted by the recent interest in Cl$^-$ chelation by organotin[2] and organomercury[3] bidentate Lewis acids and the importance of chloride-abstracting Lewis

(1) Katz, H. E. *J. Org. Chem.* **1985**, *50*, 5027–5032. Katz, H. E. *J. Am. Chem. Soc.* **1985**, *107*, 1420–1421.

(2) Newcomb, M.; Madonik, A.. M.; Blanda, M. T.; Judice, J. K. *Organometallics* **1987**, *6*, 145–150.

(3) Beauchamp, A. L.; Olivier, M. J.; Wuest, J. P.; Zacharie, B. *J. Am. Chem. Soc.* **1986**, *108*, 73–77.

acids to the catalysis of Friedel–Crafts reactions[4] and the initiation of cationic polymerization,[5] we wished to prepare a bis(borane) that would form a chelated complex with Cl⁻. Since it was apparent[6] that such a compound would have to be a stronger Lewis acid than hydride sponge, we synthesized 1,8-naphthalenediylbis(dichloroborane) (1) and probed its interaction with Cl⁻.
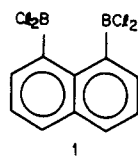
A stirred suspension of 1,8-bis(chloromercurio)napthalene[7] (640 mg, 1.07 mmol) in dry toluene (20 mL) containing excess BCl_3 (>1.3 g, 11 mmol) was heated for 6 h at reflux in an atmosphere of Ar under a dry ice cooled condenser.[8] The mixture was left to cool to ambient temperature, and the solids were allowed to settle. The supernatant solution was transferred by cannula into a Kontes fritted double tube and concentrated in vacuo. The residue was extracted with 15 mL of dry hexane, and the extract was filtered and concentrated to 270 mg of an off-white solid, representing an 86% crude yield of 1: ¹H NMR ($CDCl_3$) δ 7.6 (t, 2, J = 9 Hz, H3 and H6), 8.0 (d, 2, J = 9 Hz, H4 and H5), 8.2 (d, 2, J = 9 Hz, H2 and H7); ¹³C NMR ($CDCl_3$, tertiary carbons only) δ 125.4, 135.0, 137.0; ¹¹B NMR ($CDCl_3$ or CD_2Cl_2) δ 55. Exposure of 1 to minimal moisture gave 2,[9] while complete hydrolysis led to 3.[9]
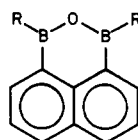
2, R = Cl
3, R = OH

Treatment of crude 1 with 0.4 mmol of PPh_4Cl or Ph_3PNPPh_3Cl in CH_2Cl_2 (vacuum transferred from P_2O_5) followed by trituration with hexane gave the respective Cl⁻ complexes: ¹¹B NMR (CD_2Cl_2) δ 13.0, consistent with fractional negative charge on B.[10] Anal. (PPh_4 derivative) Calcd for $C_{34}H_{26}B_2Cl_5P$: C, 61.46; H, 3.94; B, 3.25; Cl, 26.68; P, 4.66. Found: C, 61.29; H, 3.99; B, 3.48; Cl, 26.58; P, 4.73. The ¹¹B NMR signal was not perturbed upon the addition of 10 equiv of $PhBCl_2$; instead, a very slightly upfield shifted signal[10] for the additive was noted at 53.3 ppm, while signals for $PhBCl_3^-$ (9.7 ppm[10]) or partially complexed 1 (extremely broad between 13 and 55 ppm) were
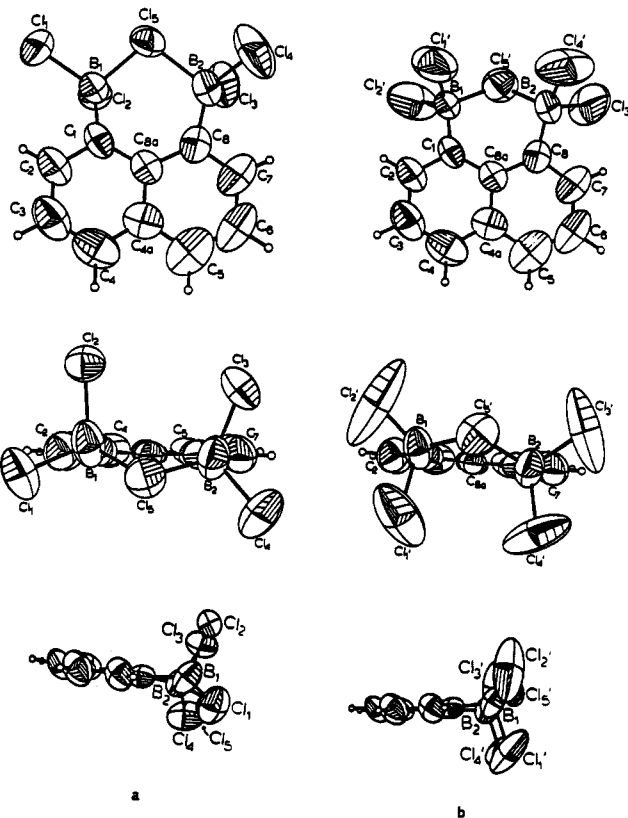

Figure 1. Perspective drawings of the anion in crystalline $(C_6H_5)_6P_2N \cdot C_{10}H_6B_2Cl_5$: (a) major orientation; (b) minor orientation.

Table I. Bond Lengths (Å) Involving B and Cl Atoms in Crystalline $\{(C_6H_5)_6P_2N\}\{Cl_5B_2C_{10}H_6\}^{a,b}$

Cl_1–B_1	1.85 (1)	Cl_1'–B_1	1.91 (1)
Cl_2–B_1	1.94 (1)	Cl_2'–B_1	1.66 (1)
Cl_3–B_2	1.86 (1)	Cl_3'–B_2	1.83 (1)
Cl_4–B_2	1.77 (1)	Cl_4–B_2	1.83 (1)
Cl_5–B_1	1.92 (1)	Cl_5'–B_1	1.88 (1)
Cl_5–B_2	2.01 (1)	Cl_5'–B_2	1.86 (1)
B_1–C_1	1.56 (1)	B_2–B_8	1.58 (1)

a The numbers in parentheses are the estimated standard deviations in the last significant digit. *b* Atoms are labeled in agreement with Figure 1a,b.

Table II. Bond Angles (deg) Involving B and Cl Atoms in Crystalline $\{(C_6H_5)_6P_2N\}\{Cl_5B_2C_{10}H_6\}^a$

$Cl_1B_1C_1$	119.6 (6)	$Cl_1'B_1C_1$	100.6 (6)
$Cl_2B_1C_1$	111.5 (6)	$Cl_2'B_1C_1$	117.1 (6)
$Cl_5B_1C_1$	113.7 (6)	$Cl_5'B_1C_1$	112.2 (6)
$Cl_1B_1Cl_2$	103.7 (5)	$Cl_1'B_1Cl_2'$	115.2 (7)
$Cl_1B_1Cl_5$	101.9 (5)	$Cl_1'B_1Cl_5'$	103.2 (5)
$Cl_2B_1Cl_5$	104.9 (4)	$Cl_2'B_1Cl_5'$	107.7 (6)
$B_1Cl_5B_2$	102.0 (4)	$B_1Cl_5'B_2$	109.7 (5)
$B_1C_1C_2$	115.1 (6)	$B_2C_8C_7$	115.3 (7)
$B_1C_1C_{8a}$	126.9 (6)	$B_2C_8C_{8a}$	128.4 (7)
$Cl_3B_2C_8$	113.4 (6)	$Cl_3'B_2C_8$	114.0 (6)
$Cl_4B_2C_8$	116.3 (66)	$Cl_4'B_2C_8$	111.9 (6)
$Cl_5B_2C_8$	112.9 (5)	$Cl_5'B_2C_8$	108.4 (6)
$Cl_3B_2Cl_4$	108.9 (5)	$Cl_3'B_2Cl_4'$	109.8 (6)
$Cl_3B_2Cl_5$	103.5 (5)	$Cl_3'B_2Cl_5'$	101.9 (5)
$Cl_4B_2Cl_5$	100.5 (5)	$Cl_4'B_2Cl_5'$	110.4 (6)

a See footnotes *a* and *b* in Figure 1.

(4) DeHaan, F. P.; Chan, W. H.; Chang, J.; Ferrara, D. M.; Wainschel, L. A. *J. Org. Chem.* **1986**, *51*, 1591–1593. Rolando, T. E.; Jones, M. B. *J. Polym. Sci. Part C: Polym. Lett.* **1986**, *24*, 233–239.

(5) Györ, M.; Kennedy, J. P.; Kelen, T.; Tüdös, F. *J. Macromol. Sci., Chem.* **1984**, *A21*, 1295–1309. Sennett, M. S.; Hagnauer, G. L.; Singler, R. E.; Davies, G. *Macromolecules* **1986**, *19*, 959–964. Nuyken, O.; Pask, S. D.; Vischer, A.; Walter, M. *Makromol. Chem.* **1985**, *186*, 1973–190.

(6) Beside the anticipated weakness in the donor–acceptor interaction between Cl⁻ and a triorganoborane, CPK models indicate that Cl⁻ is marginally small enought to fit between peri-naphthyl B atoms, whereas H⁻ and F⁻ fit much more comfortably.

(7) Letsinger, R. L.; Smith, J. M.; Gilpin, J.; MacLean, D. B. *J. Org. Chem.* **1965**, *30*, 807–812.

(8) Electrophilic substitution of HgCl by BCl_2 has been reported, but the BCl_2 derivative was not isolated: Clément, R. *C. R. Seances Acad. Sci., Sér. C.* **1966**, *263*, 1398–1400.

(9) Katz, H. E. *J. Org. Chem.* **1985**, *50*, 2575–2576.

(10) Nöth, H.; Wrackmeyer, B. *Nuclear Magnetic Resonance Spectroscopy of Boron Compounds*; Springer-Verlag: New York, 1978.

not observed. This shows that Cl⁻ is strongly chelated by 1, forming a thermodynamically more stable complex than $PhBCl_3^-$. Furthermore, the fact that δ(¹¹B) of 1·Cl⁻ is almost as far upfield as that of $PhBCl_3^-$ indicates that both

borons in 1·Cl⁻ are tetrahedral in solution, simultaneously coordinated to the bridging Cl, rather than equilibrating between trigonal and tetrahedral states. Both 1 and PhBCl₂ abstract chloride from triphenylmethyl chloride and p,p′-dimethoxybenzhydryl chloride.[11]

Crystals of 1·Ph₃PNPPh₃Cl suitable for X-ray diffraction were grown from CH₂Cl₂–hexane by vapor diffusion, and the structure was determined.[12] The B₂Cl₅ grouping appears to adopt two similar but distinguishable conformations in the lattice (Figure 1). A common occupancy factor was refined in least-squares cycles for the chlorines in both of these conformations. The major conformer, represented by nonprimed atoms Cl₁–Cl₅, was refined to a value of 0.60 (1); the minor conformer represented by primed atoms Cl₁′–Cl₅′ was refined to a value of 0.40 (1). Pertinent bond lengths and angles are listed in Tables I and II. In both conformations, the geometries at boron are mildly distorted tetrahedral, with C–B bonds <10° out of the naphthalene plane and nonbridging Cl–B bond lengths deviating by <0.2 Å from the 1.75-Å length found in BCl₃.[13] The apparently short Cl₂′–B₁ length may not be meaningful because of the large thermal disorder associated with Cl₂′. The bridging chlorides are unambiguously observed, with the major conformer featuring a bridge nearly in the plane of the naphthalene, while the minor conformer is marked by a more puckered bridge that may result from the strain involved in squeezing a relatively large anion into a restricted space. *This is the first definitive example of Cl⁻ bridging between two otherwise trigonal borons.*

It is interesting to contrast the two structures of 1·Cl⁻ with the structure of the Cl⁻ complex of o-phenylenedimercury dichloride.[3] Because secondary coordination to Hg tends to be orthogonal to the primary bonds and directionally diffuse, the latter complex features Cl⁻ "perched" over the dimercurials. The vacant orbitals on the borons in 1, however, are directional and convergent,[1] so that it is possible for bridging Cl⁻ to "nest" in the electron-deficient region between the B atoms, particularly in the major conformation.

Extensions of our work on anion complexation to rigid, tridentate Lewis acids are under active pursuit.

Mechanism of Silanone Extrusion from Alkoxyvinylsilanes

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Summary: Flash vacuum pyrolytic studies of several alkoxyvinylsilanes revealed that, if α-hydrogens were present on the alkyl group, decomposition proceeded by extrusion of Me₂Si=O. Deuterium labeling showed that the process was initiated by a novel 1,5-migration of hydrogen.

Several years ago we established[1] that the gas-phase thermolysis of α-silyl methoxysilanes (1) was a convenient route to silenes 2 and have utilized this reaction in the generation of a variety of theoretically interesting silenes.[2] Thus it was a natural extension to exploit this thermal elimination in the synthesis of 1-silaallenes 4[3] for which the only change would involve departure of the trimethylsilyl group in 3 from an sp²-hybridized carbon rather than one of sp³ hybridization.
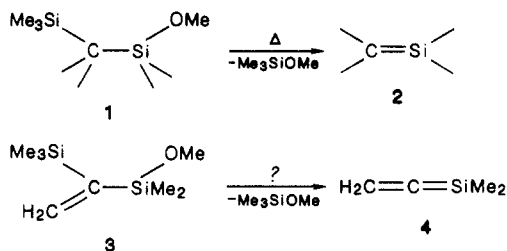
The potential silaallene precursor 3 was synthesized[4] and subjected to flash vacuum pyrolysis (FVP)[6] at temperatures of 750 and 800 °C. Two major products, isopropenylsilane 5 and disiloxane 6, were obtained in respective yields of 34–46% and 35–23% along with lesser amounts (25–12%) of cyclosiloxanes D₃ and D₄.[7] The reaction products reveal no indication of the desired silaallene 4 but strongly suggest the formation of dimethylsilanone, Me₂Si=O. Thus the cyclosiloxanes D₃ and D₄ are cyclic oligomers of dimethylsilanone,[8] 6 can be formed from the well-precedented insertion of silanone into the

(11) The ionization of benzhydryl chlorides by BCl₃ has been exploited in the study of carbocation addition to olefins: Schneider, R.; Grabis, U.; Mayr, H. *Angew. Chem., Int. Ed. Engl.* 1986, *25*, 89–90.

(12) The crystal structure analysis was performed by C. S. Day of Crystalytics Co., Lincoln, NE. A colorless, rectangular parallelepiped crystal of dimensions 0.40 × 0.55 × 0.60 mm was employed. The crystal system was monoclinic, space group P2₁/c, with lattice constants a = 9.974 (3) Å, b = 24.906 (6) Å, c = 17.504 (4) Å, β = 93.93 (2)°, V = 4338 (2) Å³, and Z = 4. The structure was refined to R = 0.055 and R_w = 0.046 by using 2539 independent reflections (≥3 σ(I)) of Mo Kα radiation, 2 θ between 3.0° and 43.0°, and T = 20 °C. The 61 non-hydrogen atoms were located using the SHELXTL Direct Methods programs. All hydrogen atoms were included in the structure factor calculations as idealized atoms (assuming sp² hybridization of the carbon atoms and a C–H bond length of 0.96 Å) "riding" on their respective carbon atoms. The isotropic thermal parameter of each hydrogen atom was fixed at 1.2 times the equivalent isotropic thermal parameter of the carbon atom to which it is covalently bonded. There were no peaks in the final difference Fourier above the background level (0.24 e/Å³).

(13) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*; Wiley: New York, 1972; p 223.

(1) Barton, T. J.; Burns, G. T.; Arnold, E. V.; Clardy, J. C. *Tetrahedron Lett.* 1981, *22*, 7.

(2) Barton, T. J.; Burns, G. T. *J. Organomet. Chem.* 1981, *216*, C5. Barton, T. J.; Vuper, M. *J. Am. Chem. Soc.* 1981, *103*, 6788. Burns, G. T.; Barton, T. J. *J. Am. Chem. Soc.* 1983, *105*, 2006.

(3) 1-Silaallenes: Ishikawa, M., et al. *J. Am. Chem. Soc.* 1982, *104*, 2872. Ishikawa, M.; Ohshita, J.; Yoshihiko, I. *Organometallics* 1986, *5*, 1518.

(4) Synthesis of 3 was accomplished in 26% yield by Grignard coupling of 1-bromo-1-(trimethylsilyl)ethene⁵ and dichlorodimethylsilane followed by reaction with LiOMe/THF. Characterization was by ¹H NMR, ¹³C NMR, and mass spectra and combustion analysis.

(5) Boeckman, R. K., Jr.; Blum, D. M.; Ganem, B.; Halvey, N. *Org. Synth.* 1978, *58*, 152.

(6) FVP was conducted by slowly distilling the neat material through a 30 cm (1.6-cm o.d.) horizontal quartz tube packed with quartz chips. Pressures typically ca. 10⁻⁴ torr are measured behind a liquid N₂ trap whereas reaction-zone pressures are typically about 10⁻³ torr.

(7) Conversion of 3 was ca. 25% at 750 °C and ca. 50% at 800 °C, and yields are based on reacted 3. At 850 °C conversion was 84% but mass recovery was only 53%. At 800 °C both D₃ and D₄ were observed, but at 750 °C only D₄ was obtained.

(8) Gusel'nikov, L. E.; Nametkin, N. S. *Chem. Rev.* 1979, *79*, 529.