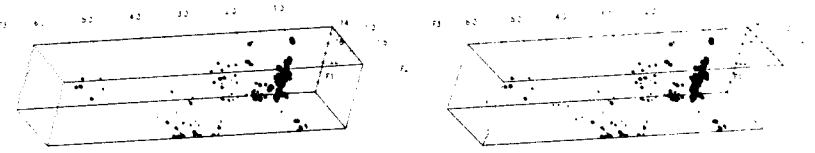

Figure 2. Stereoscopic picture of the 3D-HQQC-TOCSY spectrum of thio-(1)-cyclosporin A, processed on a Convex instrument with own software[14] and displayed on an Evans and Sutherland PS330 graphic station. The spectrum was recorded with a sample of 14 mmol/L. The crowded region on the right shows the resonances of the methyl groups, the region in the middle shows the relay peaks to the H^{β} and H^{γ} peaks, and the region on the left shows the relay peaks to the H^{α} peaks. The spectrum was recorded with 48 scans for each fid (spectral width 6250 Hz in F_3), 96 increments in t_1 (spectral width 1710 Hz), and 78 increments in t_2 (spectral width 1250 Hz), leading to high resolution and a relatively long total measuring time of 44 h. The mixing time of the MLEV-17 mixing was 75 ms. The spectrum was recorded as F_1/F_3 slices on a Bruker AMX 500 instrument. No dummy scans had to be applied; the sample was not spun.

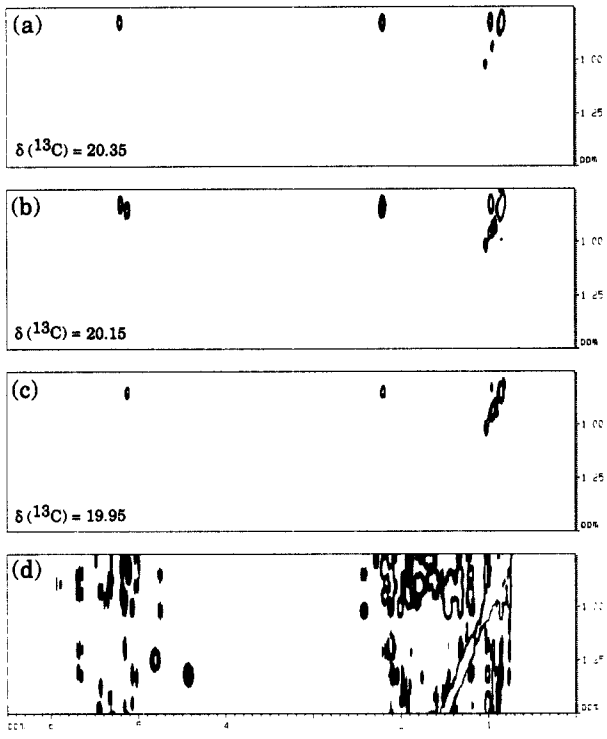

Figure 3. Parts a-c show three adjacent F_2/F_3 slices through the 3D-HQQC-TOCSY spectrum at the carbon resonances shown in the picture. The peaks result from the spin systems of MeVal-11 in both conformers of thio-(1)-cyclosporin A. Part d shows the same region of a 2D-TOCSY spectrum. The increased resolution in the 3D spectrum is clearly visible, and an assignment is straightforward, although the carbon shift of both methyl groups present in these three slices differs only by 0.14 ppm (20 Hz). The slices have been processed on a Bruker X32 data station with standard software and some additional sorting programs written in C.

multiplicities can be differentiated: Heteronuclear quadruple quantum coherence (HQQC) selects CH_3 (a), and triple quantum coherence (HTQC), CH_2 (b). A second evolution period and another transfer step lead to a 3D sequence.

We show here the application of 3D-HQQC-TOCSY (case a, selection of CH_3) to thio-(1)-cyclosporin A.[11] This molecule exists in two conformations (58:42) in $CDCl_3$ and thus exhibits resonances from 48 CH_3 groups, 14 of which are NCH_3 and show no relevant homonuclear couplings. A 2D HMQC-TOCSY was not sufficient to remove all ambiguities in the assignment of these resonances. A stereoscopic picture of the 3D-HQQC-TOCSY spectrum is shown in Figure 2. Three 2D slices from this spectrum are shown in Figure 3 and compared to their 2D analogue to demonstrate the increased resolution. It is obvious from Figure 3 that resonances with carbon chemical shift differences of only 0.14 ppm can be resolved and the proton spectrum elucidated. This would be extremely difficult by conventional methods, especially as the H^{β} resonances at 2.15 ppm are overlapped. Almost all other resonances are better separated in CH correlation (equivalent to the F_1/F_2 projection of the 3D spectrum), hence allowing a total assignment of even such a crowded spectrum. A similar result has been obtained for CH_2 groups (case b, spectrum presented elsewhere[10e]).

In conclusion, we have presented techniques that can be routinely applied to elucidate homo- and heteronuclear spin systems. The potential of these techniques lies in the simultaneous assignment of proton and carbon resonances in crowded spectra by exploiting the high resolution of carbon resonances for the identification of the total proton spin system. It should also be noted that the exclusive excitation of methyl groups works as a filter for a restricted number of amino acids. A special advantage of the proposed technique is that it can be applied to carbon in natural abundance. It is often not possible or extremely cumbersome to label a natural product whose structure elucidation is of interest. In such cases these techniques will find application.

Acknowledgment. Financial support of the Deutsche Foschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged. H.O. thanks the Bundesministerium für Forschung und Technologie (Grant 321/4003/0318909A).

(11) The sulfur analogue of cyclosporin A was obtained from Prof. D. Seebach (ETH Zürich) and is currently being investigated in our laboratory. It has been shown by NMR that the sulfur is on the amino acid in position 1 (Mebmt), thus we like to call it thio-(1)-cyclosporin A.

(12) Garbow, J. R.; Weitekamp, D. P.; Pines, A. *Chem. Phys. Lett.* **1982**, *93*, 504-509.
(13) Bax, A.; Subramanian, S. *J. Magn. Reson.* **1986**, *67*, 565-569.
(14) Oschkinat, H.; Cieslar, C.; Holak, T. A.; Clore, G. M.; Gronenborn, A. M. *J. Magn. Reson.* **1989**, *83*, 450-472.

Synthesis and Reactions of a New Rhenium(V) Oxo Hydrido Complex. Transfer of Both Oxygen and Hydrogen to Carbon Monoxide

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In recent years there has been a remarkable surge of research activity concerned with transition-metal oxo complexes.[1] These complexes find important applications in organic synthesis and in heterogeneous and biochemical catalysis. The introduction of hydride ligands into metal oxo complexes is further expected to provide model systems for investigations of metal-catalyzed reactions of such species as H_2O, O_2, peroxides, and superoxides with various organic and inorganic substrates. In view of the potential applications of metal oxo hydrido complexes, it is surprising that only three examples, viz., $(\eta^5\text{-}C_5Me_5)_2Ta(O)H$[2] and

(1) Books and reviews: (a) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; Wiley: New York, 1988. (b) Kochi, J. K.; Sheldon, R. A. *Metal-Catalyzed Oxidations of Organic Compounds*; Academic Press: New York, 1981. (c) Holm, R. H. *Chem. Rev.* **1987**, *87*, 1401. (d) Schröder, M. *Chem. Rev.* **1980**, *80*, 187. (e) Bottomley, F.; Sutin, L. *Adv. Organomet. Chem.* **1988**, *28*, 339. (f) Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1297.
(2) van Asselt, A.; Burger, B. J.; Gibson, V. C.; Bercaw, J. E. *J. Am. Chem. Soc.* **1986**, *108*, 5347.

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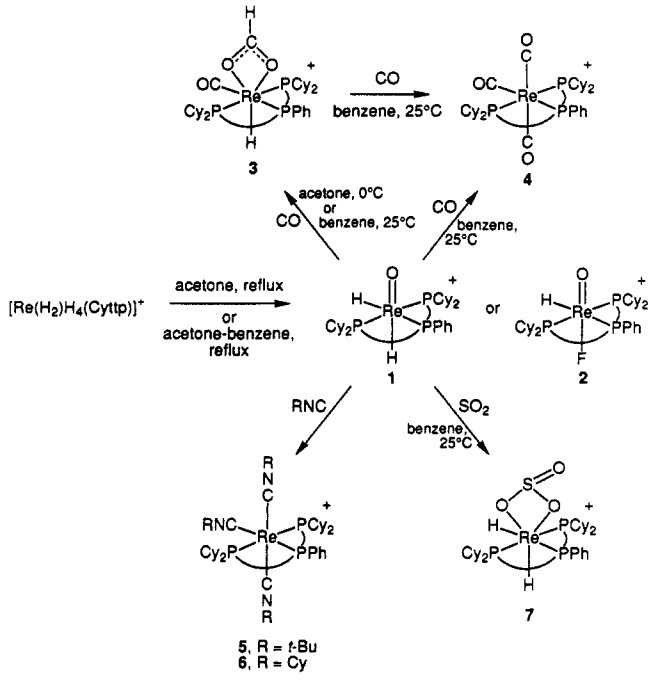
Scheme I[a]



[a] $Cy_2PP(Ph)PCy_2$ ≡ Cyttp; only the cations are shown.

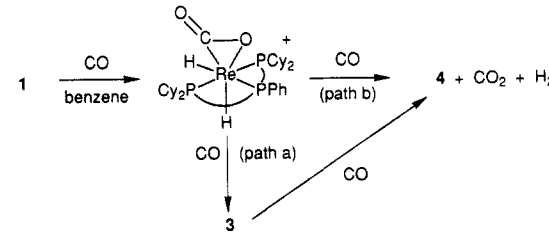
$Re(RC{\equiv}CR)_2(O)H$[3] (R = Me or Et), have been reported. No chemistry of the tantalum complex has been communicated, and the rhenium complexes were found to be rather unreactive. We now report new oxo hydrido complexes of rhenium(V), [Re(O)(H)(X)(Cyttp)]SbF_6 (X = H (**1**), F (**2**); Cyttp = PhP[$CH_2CH_2CH_2PCy_2]_2$), and show for the first time that both of the named ligands can be reactive in such compounds.

Refluxing a solution of $[Re(H_2)H_4(Cyttp)]SbF_6$[4] in dry acetone[5] under argon for 17–20 h, followed by cooling, concentration, and addition of diethyl ether, affords a light tan solid, **1** (see Scheme I), in 90% yield. Longer reaction times lead to the formation of mixtures of **1** and **2**;[6] the latter can be obtained (63% yield) free of **1** by using 1:2 acetone–benzene at reflux. Both products are stable to air in solution at ambient temperatures for several days.

An X-ray diffraction analysis of **1**·$^3/_4$MeOH[7] reveals the coordination environment afforded the rhenium atom by the Cyttp and oxide ligands. The triphosphine adopts a distorted-meridional arrangement around the metal (P_w–Re–P_c, 92.0 (1)°; P_w–Re–P_w, 137.1 (1)°); P_w = wing P, P_c = central P), whereas the oxide (Re–O, 1.732 (7) Å) is in an idealized cis position with respect to each phosphorus donor (O–Re–P, 107.3 (2)–111.1 (3)°). The two hydrogen atoms bonded to rhenium were not located; however, their presence in the positions approximately cis and trans to the oxide ligand in a severely distorted coordination octahedron of the metal is suggested by the elucidated molecular structure. Both ^{1}H NMR and IR spectra of **1** provide strong evidence for this assignment.[8]

The chemistry of **1** furnishes an excellent model for reactivity of metal oxo hydrides, as the $Re(O)H_2$ fragment accounts for all the activity while the Cyttp ligand remains coordinated. The reactions examined are set out in Scheme I and are highlighted by the behavior of **1** toward CO. Passing CO through a solution of **1** in acetone for ca. 20 min at 0 °C, followed by concentration and addition of diethyl ether, affords (79% yield) a yellow solid, **3**. **3** is formulated as a rhenium carbonyl η^2-formato hydride complex on the basis of its IR and ^{1}H, ^{13}C, and ^{31}P NMR data—including data on the isotopomers derived from **1** and ^{13}CO (**3**-^{13}C) and from **1**-^{18}O and CO (**3**-^{18}O)—as well as from chemical analysis.[6,9]

Scheme II



When the foregoing reaction was conducted to completion in benzene solution for 45 min at 25 °C, a 1:1 mixture of **3** and $[Re(CO)_3(Cyttp)]SbF_6$[6] (**4**) was obtained. Longer reaction times increase the ratio **4**:**3** to suggest that **3** gradually decomposes to **4** under CO in solution. This was confirmed by monitoring the behavior of a benzene solution of **3** under CO at 25 °C; after 15 h, a ca. 1:1 mixture of **3** and **4** was observed. However, the rate of the conversion of **3** to **4** is slower than the formation of **4** from **1** and CO under similar conditions. Therefore we conclude that **1** reacts with CO by two pathways: (a) to give **3** (and then, depending on the conditions, **4**) and (b) to give **4** directly (Scheme II).

Although reactions of metal oxo complexes with CO to generate CO_2 (path b) have been reported,[1] participation of both oxide and hydride ligands in trapping the substrate CO (or another substrate; path a) is unprecedented. We suggest that the formation of **3** and **4** proceeds by addition of CO to Re=O and its oxidation to ligated CO_2. Dissociation of CO_2 would then lead to the formation of **4**, whereas shift of a coordinated hydride to η^2-CO_2 would generate the formate ligand in **3**. However, an alternative pathway in which the entering CO initially reacts with hydride to give the formyl, which then combines with the oxide ligand, cannot be ruled out. The decarboxylation of **3** is precedented in metal formate chemistry.[3,10]

Reactions of **1** with an excess of the isocyanides *t*-BuNC and CyNC in benzene at 25 °C are complete within a few minutes and afford the trisisocyanide complexes **5** and **6**[6] as white solids in 98 and 69% respective yields. When the reaction between **1** and *t*-BuNC in acetone-d_6 or benzene is examined by ^{1}H NMR or IR spectroscopy, **5** and *t*-BuN=C=O[11] are observed. Thus it appears that the oxidation of *t*-BuNC proceeds by a mechanism similar to that of path b for CO, although a route analogous to path a, viz., formation of an η^2-*N*-*t*-butylformamidato-*O*,*N* complex and its decomposition to **5**, *t*-BuN=C=O, and H_2, cannot be excluded.[12]

A solution of **1** in benzene turns violet when treated with dry gaseous SO_2 for 1–2 min at 25 °C. Concentration of the solution and addition of diethyl ether induces the precipitation (84% yield) of the bright violet η^2-sulfito-*O*,*O*′ complex **7**·C_6H_6.[6,13] The product is stable in the solid under vacuum at ambient temper-

(3) Spaltenstein, E.; Erikson, T. K. G.; Critchlow, S. C.; Mayer, J. M. *J. Am. Chem. Soc.* **1989**, *111*, 617.

(4) Kim, Y.; Deng, H.; Meek, D. W.; Wojcicki, A. *J. Am. Chem. Soc.* **1990**, *112*, 2798.

(5) Deliberate addition of H_2O markedly decreases the yield of **1** and causes the formation of other, uncharacterized products.

(6) Analytical and relevant spectroscopic data for all new compounds are provided in the supplementary material. This information will be published in our full paper.

(7) See the supplementary material for details.

(8) Selected spectroscopic data for **1**: IR (Nujol) ν(ReH) 2030 (w), 1716 (m), ν(ReO) 923 (m) cm^{-1}; ^{1}H NMR (CD_2Cl_2) δ −12.62 (dtd, $^2J_{HPc}$ = 57.5 Hz, $^2J_{HPw}$ = 35.0 Hz, $^2J_{HH}$ = 5.0 Hz, 1 ReH), −1.04 (tt, $^2J_{HPw}$ = 25 Hz, $^2J_{HPc}$ = $^2J_{HH}$ = 5.0 Hz, 1 ReH).

(9) Selected spectroscopic data for **3**: IR (Nujol) ν(CO) 1904 (s), ν_a(OCO) 1546 (s), ν_s(OCO) 1364 (s) (**3**-^{13}C ν_s(OCO) 1506 (m), ν_s(OCO) 1342 (m); **3**-^{18}O ν_a(OCO) 1535 (s), ν_s(OCO) 1346 (s)) cm^{-1}; ^{1}H NMR (acetone-d_6) δ −5.03 (td, $^2J_{HPw}$ = 51.6 Hz, $^2J_{HPc}$ = 12.4 Hz, 1 ReH) (**3**-^{13}C (CD_2Cl_2) δ 8.24 (d, $^1J_{CH}$ = 217.3 Hz, H^{13}COO)).

(10) Darensbourg, D. J.; Rokicki, A.; Darensbourg, M. Y. *J. Am. Chem. Soc.* **1981**, *103*, 3223.

(11) The resonance at δ 1.37 (in acetone-d_6) and the absorption at 2255 cm^{-1} (in benzene) are identical with the data for an authentic sample of *t*-BuN=C=O.

(12) We favor the former pathway, since the decomposition of the formamidato complex, by analogy with the decomposition of the formato complex, might be expected to proceed relatively slowly under these conditions.

(13) The structure of **7**·C_6H_6 was confirmed by X-ray crystallography; this analysis will be published in our full paper.

atures; however, its solutions in benzene lose SO_2 at 50 °C to regenerate **1**.[14]

The foregoing examples of the behavior of **1** toward various unsaturated compounds demonstrate that metal oxo hydride complexes may react by transfer of oxygen alone or of both oxygen and hydrogen to a substrate. The latter type of reaction appears to be less common than the former, possibly because it requires breaking of an M-H bond, which is generally quite strong.[15] This duality of action of **1** on unsaturated substrates is under further investigation.

Acknowledgment. We are grateful to the National Science Foundation and The Ohio State University for financial support and to Haibin Deng for help with calculations on the structure. Studies on metal complexes of Cyttp were initiated in these laboratories by the late Professor Devon W. Meek; the work reported here has developed from his early investigations.

Supplementary Material Available: Description of reactions, analytical and spectroscopic data for **1**-**7**, and details of structure determination of **1**·$^3/_4$MeOH, including an ORTEP plot, crystal data, data collection and refinement, positional parameters, temperature factor expressions, and selected bond distances and angles (15 pages). Ordering information is given on any current masthead page.

(14) Similar behavior toward SO_2 was recently reported for $(\eta^5$-$C_5Me_5)_2Re_2(\mu$-$O)_2(O)_2$; see: Herrmann, W. A.; Jung, K. A.; Herdtweck, E. *Chem. Ber.* **1989**, *122*, 2041.

(15) Pearson, R. G. *Chem. Rev.* **1985**, *85*, 41.

Mixed Aggregates: Crystal Structures of a Lithium Ketone Enolate/Lithium Amide and of a Sodium Ester Enolate/Sodium Amide

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Previously we reported the first structural evidence for a mixed lithium ketone enolate/lithium diisopropyl amide aggregate depicted as **1** in Scheme I.[1] It was suggested that mixed aggregates of general structure **2** are commonly formed when alkali metal amide bases react with enolizable substrates. The salient nature of **1** in enantioselective condensation reactions initiated with chiral amide bases as noncovalently bound auxiliaries was noted.[2] Further support for the existence of these complexes in solution comes from NMR studies.[3] Finally, the correspondence between solid-state and solution structures of enolates is bolstered by recent colligative property and thermochemical measurements.[4] Now we wish to strengthen and generalize our work by presenting the first structural evidence for two, nonchelated enolate/amide base aggregates. These new structures are composed of a simple lithium ketone enolate complexed with lithium hexamethyldisilazide (LHMDS) and of a sodium ester enolate complexed with sodium hexamethyldisilazide (NHMDS). It is important to elucidate the structural details of these mixed aggregates for use as models in stereo- and enantioselectively enhanced enolate and related reactions.[5]

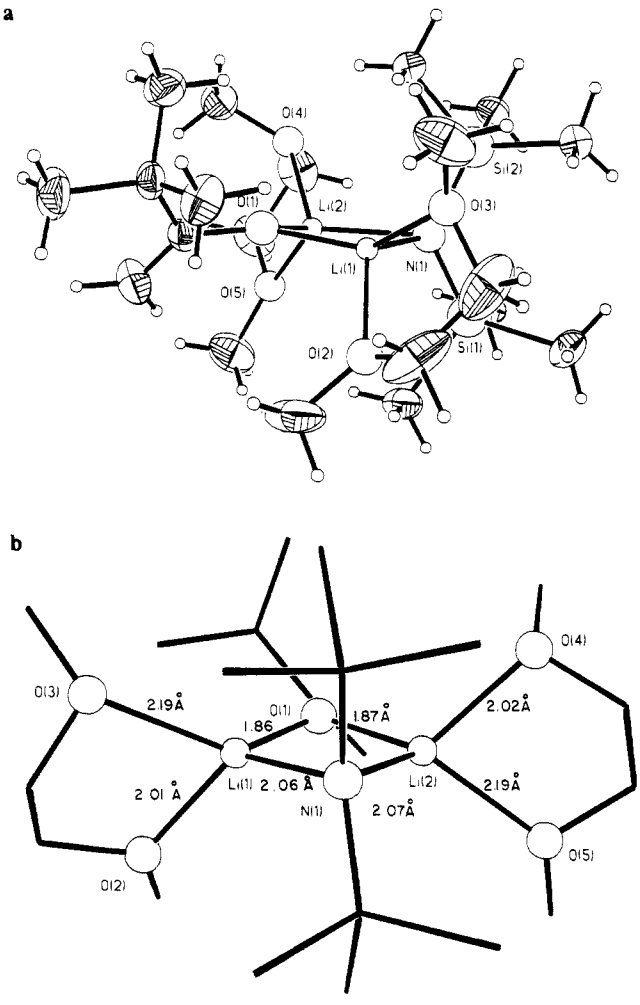

Figure 1. (a) Thermal ellipsoid plot at 50% probability of the mixed pinacolone enolate/LHMDS/DME mixed aggregate **3**. Note that the methyl groups on the DME's point toward the enolate residue. (b) Perspective view of the aggregate **3** emphasizing the main skeletal features. The Li-O-Li-N core is essentially planar; the enolate residue is twisted at an angle of approximately 35.6° around the O(1)-C(2) axis relative to this plane, and the Si-N-Si axis is tilted at an angle of 4.4° relative to the planar core. The enolate oxygen O(1) is slightly pyramidalized by ~0.16 Å out of the plane defined by Li(1), Li(2), and C(2).

Initial attempts to obtain a crystalline sample of a structure analogous to **2** were unsuccessful. When the more symmetrical amide base LHMDS and the bidentate ligand dimethoxyethane (DME) were substituted in place of lithium diisopropylamide (LDA) and THF, respectively, we succeeded in crystallizing the mixed aggregate **3**.[6] Previously, only two lithium ketone enolates with dicoordinate, planar enolate oxygens have been crystallized.[7]

The presence of a bridging enolate oxygen is reflected in the bond lengths of **3**. The Li-(enolate-O) distances are relatively short (av 1.87 Å) and the Li-N distances are slightly longer (av 2.07 Å) than in mixed ketone enolate/LHMDS aggregates with tricoordinate enolate oxygens.[8] Note in Figure 1 that the methyl

(1) Williard, P. G.; Hintze, M. J. *J. Am. Chem. Soc.* **1987**, *109*, 5539.

(2) (a) Muraoka, J.; Hisashi, K. *Tetrahedron Lett.* **1988**, *29*, 337. (b) Ando, A.; Shioiri, T. *J. Chem. Soc., Chem. Commun.* **1987**, *656*, 1620. (c) Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1624 (see Table 9). (d) Shirai, R.; Tanaka, M.; Koga, K. *J. Am. Chem. Soc.* **1986**, *108*, 543. (e) See also: Denmark, S. E.; Ares, S. J. *J. Am. Chem. Soc.* **1988**, *110*, 4432.

(3) (a) Heinzer, J.; Oth, J. F. M.; Seebach, D. *Helv. Chim. Acta* **1985**, *68*, 1848. (b) See footnote 141 and p 1632 in ref 2c. (c) Professor D. Collum, Cornell University, private communication.

(4) Arnett, E. M.; Fischer, F. J.; Nichols, M. A.; Ribeiro, A. A. *J. Am. Chem. Soc.* **1990**, *112*, 801.

(5) (a) Corey, E. J.; Kim, S. S. *J. Am. Chem. Soc.* **1990**, *112*, 4976. (b) Tomioka, K.; Shindo, M.; Koga, K. *J. Am. Chem. Soc.* **1989**, *111*, 8266.

(6) The aggregate **3** of molecular composition $[(C_6H_{11}OLi)\cdot(C_6H_{18}Si_2N$-$Li)\cdot(C_4H_{10}O_2)_2]$ crystallized in the centrosymmetric, monoclinic space group $P2_1/c$ with unit cell parameters a = 8.738 (9) Å, b = 12.645 (7) Å, c = 27.794 (8) Å, and β = 90.36 (2)° after regeneration of the amide base by addition of a second equivalent of *n*-BuLi. Data collection at low temperature, structure solution, and refinement (R = 0.042 and R_w = 0.056) proceeded normally. Specific details of the diffraction analysis along with tables of atomic coordinates and structural parameters have been submitted as supplementary material and to the Cambridge Crystallographic Database.

(7) (a) Laube, T.; Dunitz, J. D.; Seebach, D. *Helv. Chim. Acta* **1985**, *68*, 1373. (b) Amstutz, R.; Dunitz, J. D.; Laube, T.; Schweizer, W. B.; Seebach, D. *Chem. Ber.* **1986**, *119*, 434.

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