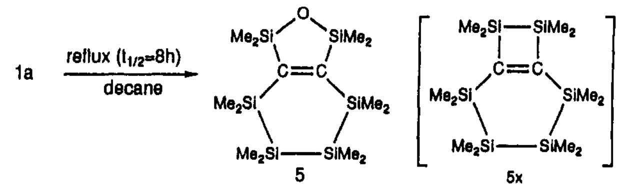

5

5x

bonyl complex **6** was formed in 21% yield.[13] Reaction of **1a** with 2,3-dimethyl-1,3-butadiene in hexane smoothly proceeded via a Diels–Alder reaction to give the cycloadduct **7**[14] and its oxidized compound **8**[15] in 29% and 19% yields, respectively. Compound **8** must have been formed by air oxidation of **7** during the purification (silica gel chromatography) of the products, since the isolated **7** was slowly converted to **8** in benzene-d_6 solution in the presence of air. However, no reaction with 1,3-diphenylisobenzofuran occurred even in refluxing hexane, probably because of steric repulsion of the phenyl groups of the isobenzofuran and the methyl substituents of **1a**. Tetrasilacyclohexyne **1a** also reacted smoothly with phenyl azide and diphenyldiazomethane at room temperature and afforded the triazole derivative **9**[16] and tetrasilacyclopentylallene derivative **11**[17] in quantitative yields, respectively. These addition reactions are uniquely characteristic of tetrasilacyclohexyne **1a**, since pentasilacycloheptyne **3** did not react with phenyl azide under the same conditions. Finally, the triazole derivative **9** was easily converted to ketenimine **10**[18] by heating and was obtained in quantitative yield.

While this work was in the process of submission, a paper on the synthesis of tetrasilacyclohexyne by the group of T. Barton was accepted for publication in *J. Am. Chem. Soc.*

Acknowledgment. This work was supported by Grants-in-Aid for Scientific Research on Priority Area of Molecular Design by Heteroatom (No. 03214101) and for General Scientific Research (No. 1430006) from the Ministry of Education, Science, and Culture of Japan. We thank Shin-Etsu Chemical Co. Ltd. for a gift of organosilicon reagents.

Registry No. **1a**, 138542-16-2; **2**, 129415-87-8; **3**, 129415-88-9; **4a**, 138542-17-3; **5**, 138542-18-4; **6**, 138542-22-0; **7**, 138542-19-5; **8**, 138542-20-8; **9**, 138542-21-9; **10**, 138570-96-4; **11**, 138570-97-5; $Cl(SiMe_2)Cl$, 754-75-6; $Cl(SiEt_2)Cl$, 87434-43-3; $BrMgC{\equiv}CMgBr$, 4301-15-9; $Co_2(CO)_8$, 10210-68-1; 2,3-dimethyl-1,3-butadiene, 513-81-5; phenyl azide, 622-37-7; diphenyldiazomethane, 883-40-9; 1,3-diphenylisobenzofuran, 5471-63-6.

Supplementary Material Available: Text giving details of the data collection and structure solution and refinement, tables of bond lengths and angles, crystallographic data, and thermal and positional parameters by X-ray analysis, and figures showing the structure of **5** (17 pages); a listing of *h*, *k*, *l*, F_o, F_c, and $d(F_o)$ (11 pages). Ordering information is given on any current masthead page.

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[13] Data are as follows for **6**: decomposition at 114–116 °C; red-black crystals; HRMS (EI, 20 eV) *m/e* calcd for $C_{16}H_{24}O_6Si_4Co_2$ 541.9314, found 541.9355; LRMS (EI, 70 eV) *m/e* 542 (M^+), 514 ($M^+ - CO$), 486 ($M^+ - 2CO$), 458 ($M^+ - 3CO$), 430 ($M^+ - 4CO$), 402 ($M^+ - 5CO$), 374 ($M^+ - 6CO$); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.20 (s, 12 H), 0.35 (s, 12 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ −6.5 (q), −0.02 (q), 94.8 (s), 200.9 (s); ^{29}Si NMR (C_6D_6, 17.6 MHz) δ −44.5, −11.3; IR (KBr) ν 2086, 2046, 2020 cm^{-1} (CO); UV (hexane) λ_{max} (ε) 260 (sh) (11 500), 359 (1750), 425 (sh) (100), 450 (sh) nm (90).

[14] Data are as follows for **7**: mp 54–56 °C; colorless crystals; HRMS (EI, 20 eV) *m/e* calcd for $C_{16}H_{34}Si_4$ 338.1738, found 338.1740; LRMS (EI, 70 eV) *m/e* 338 (M^+), 265 ($M^+ - SiMe_3$); ^{1}H NMR (C_6D_6, 90 MHz) δ 0.34 (s, 24 H), 1.70 (s, 6 H), 2.87 (s, 4 H); ^{13}C NMR (C_6D_6, 22.5 MHz) δ −6.2 (q), −1.8 (q), 18.7 (t), 39.1 (q), 123.7 (s), 147.3 (s); ^{29}Si NMR (C_6D_6, 17.6 MHz) δ −52.3, −26.2; IR (KBr) ν 2892, 1243, 806 cm^{-1}.

[15] Data are as follows for **8**: mp 94–96 °C; colorless crystals; HRMS (EI, 20 eV) *m/e* calcd for $C_{16}H_{32}Si_4$ 336.1581, found 336.1575; LRMS (EI, 70 eV) *m/e* 336 (M^+), 263 ($M^+ - SiMe_3$); ^{1}H NMR (C_6D_6, 90 MHz) δ 0.32 (s, 12 H), 0.54 (s, 12 H), 2.18 (s, 6 H), 7.59 (s, 2 H); ^{13}C NMR (C_6D_6, 22.5 MHz) δ 6.3 (q), −0.32 (q), 19.9 (q), 128.0 (s), 136.6 (s), 136.8 (d); ^{29}Si NMR (C_6D_6, 17.6 MHz) δ −53.0, −23.8; IR (KBr) ν 2950, 2892, 1243, 1131, 806 cm^{-1}.

[16] Data are as follows for **9**: mp 112–114 °C; colorless crystals; HRMS (EI, 20 eV) *m/e* calcd for $C_{16}H_{29}Si_4N_3$ 375.1439, found 375.1408; LRMS (EI, 70 eV) *m/e* 375 (M^+), 347 ($M^+ - N_2$), 332 ($M^+ - N_2 - Me$); ^{1}H NMR (C_6D_6, 500 MHz) δ 0.09 (s, 6 H), 0.22 (s, 6 H), 0.34 (s, 6 H), 0.76 (s, 6 H), 7.0–7.1 (m, 3 H), 7.18 (d, *J* = 9.5 Hz, 2 H); ^{13}C NMR (C_6D_6, 125 MHz) δ −6.7 (q), −6.6 (q), −1.6 (q), −1.3 (q), 127.6 (d), 129.3 (d), 129.7 (d), 140.4 (s), 140.7 (s), 153.2 (s); ^{29}Si NMR (C_6D_6, 17.6 MHz) δ −50.9, −48.1, −27.4, −26.8; IR (KBr) ν 2956, 2896, 1601, 1499, 1251, 816, 768 cm^{-1}.

[17] Data are as follows for **11**: mp 101–103 °C; colorless crystals; HRMS (EI, 20 eV) *m/e* calcd for $C_{23}H_{34}Si_4$ 422.1738, found 422.1774; LRMS (EI, 70 eV) *m/e* 422 (M^+), 407 ($M^+ - Me$), 349 ($M^+ - SiMe_3$); ^{1}H NMR (C_6D_6, 500 MHz) δ 0.29 (s, 12 H), 0.40 (s, 12 H), 7.1–7.3 (m, 6 H), 7.61 (d, *J* = 8.2 Hz, 4 H); ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ −7.1 (q), −2.1 (q), 92.7 (s), 96.7 (s), 125.5 (d), 127.5 (d), 128.2 (d), 138.0 (s), 206.3 (s); ^{29}Si NMR (C_6D_6, 17.6 MHz) δ −44.9, −12.2; IR (KBr) ν 1897 cm^{-1} (C=C=C); UV (hexane) λ_{max} (ε) 277 (16 480), 325 nm (sh) (400).

[18] Data are as follows for **10**: colorless oil; HRMS (EI, 20 eV) *m/e* calcd for $C_{16}H_{29}Si_4N$ 347.1377, found 347.1372; LRMS (EI, 70 eV) *m/e* 347 (M^+), 332 ($M^+ - Me$); ^{1}H NMR (C_6D_6, 500 MHz) δ 0.29 (s, 12 H), 0.42 (s, 12 H), 6.9–7.1 (m, 3 H), 7.42 (d, *J* = 7.4 Hz, 2 H); ^{13}C NMR (C_6D_6, 125 MHz) δ −6.7 (q), −0.50 (q), 95.8 (s), 123.8 (d), 126.1 (d), 130.1 (d), 143.6 (d), 171.6 (s); ^{29}Si NMR (C_6D_6, 17.6 MHz) δ −44.5, −7.4; IR (neat) ν 1997, 1968 cm^{-1} (C=C=N).

Synthesis and Structural Characterization of a Tetranuclear Organolanthanide Hydrazido Complex

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Received December 16, 1991

Summary: Reaction of Cp^*_2Sm ($Cp^* = \eta^5\text{-}C_5Me_5$) with excess hydrazine leads to the formation of a yellow crystalline material in high yield. The product was structurally characterized by a single-crystal diffraction study which shows the molecule to consist of a distorted-tetrahedron arrangement of samarium atoms with bridging hydrazido anions on each edge of the tetrahedron.

Metal complexes containing hydrazido ($NHNH_2^-$) units have been considered to play an important role in the reduction of dinitrogen to hydrazine[1] (eq 1); however, few

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Table I. Selected Bond Lengths (Å) and Angles (deg) for 2

	Bond Lengths		
Sm(1)–Sm(2)	3.552 (1)	Sm(2)–N(3)	2.433 (9)
Sm(1)–N(1)	2.564 (9)	Sm(2)–N(5)	2.489 (11)
Sm(2)–N(2)	2.626 (9)	Sm(2)–N(6)	2.510 (11)
Sm(1)–N(2)	2.437 (9)	N(1)–N(1)	1.474 (16)
Sm(2)–N(1)	2.458 (9)	N(2)–N(2)	1.518 (16)
Sm(1)–N(3)	2.451 (9)	N(3)–N(6)	1.441 (14)
Sm(2)–N(4)	2.432 (9)	N(4)–N(5)	1.451 (13)
Sm(1)–N(4)	2.458 (9)	Sm(1)–Cp*	2.502 (7)
Sm(1)–N(7)	2.664 (13)	Sm(2)–Cp*	2.619 (7)
	Bond Angles		
Sm(1)–Sm(1)–Sm(2)	50.89 (1)	N(2)–Sm(1)–N(3)	113.0 (3)
Sm(2)–Sm(1)–Sm(2)	79.91 (1)	N(2)–Sm(1)–N(3)	78.5 (4)
Sm(1)–Sm(2)–Sm(1)	78.44 (2)	N(2)–Sm(1)–N(4)	112.9 (3)
Sm(1)–Sm(2)–Sm(2)	50.15 (1)	N(3)–Sm(1)–N(4)	143.9 (3)
N(1)–Sm(1)–N(2)	69.9 (3)	N(1)–Sm(2)–Cp*	110.1 (3)
N(1)–Sm(1)–N(3)	75.9 (3)	N(1)–Sm(2)–Cp*	111.0 (3)
N(1)–Sm(1)–N(4)	76.7 (3)	N(2)–Sm(2)–Cp*	178.2 (3)
N(1)–Sm(1)–N(7)	72.1 (4)	N(3)–Sm(2)–Cp*	106.0 (3)
N(2)–Sm(1)–N(2)	36.1 (4)	N(4)–Sm(2)–Cp*	103.4 (3)

of these unsubstituted hydrazido species have been structurally characterized.[2] This is presumably due to the

$$\mathrm{M{-}N_2 + {}^3\!/_2H_2 \rightarrow M{-}N(H)NH_2} \qquad (1)$$

instability of the highly reducing $N_2H_3^-$ ion.[3] On the other hand, a number of substituted hydrazido species ($NHNR_2^-$) have been synthesized, characterized, and used to model the unsubstituted parent complexes.[4-6] Most of these studies involve metal centers having a high oxidation state and high Lewis acidity. We became interested in the potential reactivity of hydrazine with Lewis acidic centers, especially organosamarium(II) complexes, in view of the reducing ability of this metal center.[7] We report, in the present contribution, the synthesis and X-ray crystallographic characterization of a tetranuclear organolanthanide hydrazido complex.

At room temperature and under an inert atmosphere of argon, excess hydrazine was syringed into a stirred benzene solution of $Cp^*{}_2Sm$[8] (1; Cp* = η^5-C_5Me_5). Upon addition of hydrazine, the forest green solution of 1 rapidly adopts a canary yellow color. Workup of this reaction mixture leads to the isolation in high yield[9,10] of a crystalline material, 2. The ^{1}H NMR spectroscopy performed, in toluene-d_8, at room temperature was not structurally specific but showed two inequivalent resonances for C_5Me_5 at 1.79 and 1.72 ppm, respectively. In order to determine the structure of the isolated lanthanide product, a low-temperature single-crystal X-ray diffraction study was performed.[11]

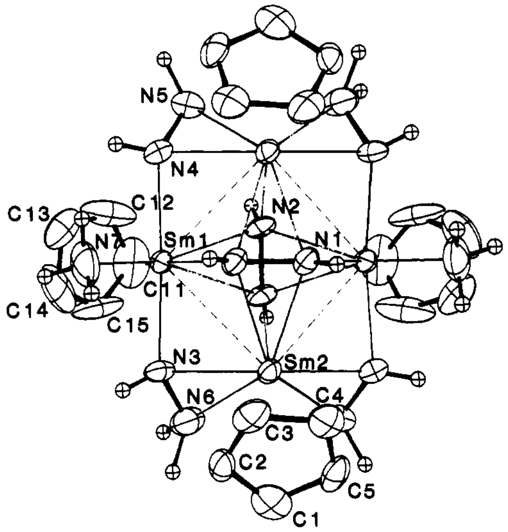

Figure 1. Molecular structure of $[Cp^*Sm]_4(NHNH)_2(NHNH_2)_4(NH_3)_2$ (2) viewed parallel to the 2-fold axis, with probability ellipsoids drawn at the 50% level. Cp* methyl groups have been omitted for clarity.

The diffraction study clearly shows complex 2 to be a tetranuclear molecule, consisting of a distorted tetrahedron of Sm atoms, and reveals the presence of two hydrazido(2–), $(NHNH)^{2-}$, anions located on the crystallographic 2-fold axis on opposite edges of the tetrahedron. Each nitrogen of the anion is within reasonable bonding distance

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(9) In a glovebox, under an inert atmosphere, 300 mg (0.71 mmol) of $Cp^*{}_2Sm$ (1) was loaded into a 25-mL flask fitted with a Teflon side valve, part of a frit assembly, which was then removed from the glovebox and hooked up to a vacuum line, whereupon 15 mL of dry benzene was vacuum-transferred into the reaction vessel at –78 °C. At room temperature and under an argon purge, 0.1 mL (3.2 mmol) of hydrazine was syringed into the stirred solution. The now yellow solution was stirred for 30 min; it was then filtered and left standing at room temperature for 4 h. After this time, the yellow crystalline material had formed. The solid was cold-filtered and washed with cold pentane to produce 212 mg (0.14 mmol) of **2** in 78.8% isolated yield.

(10) (a) Complex **2** was subjected to vacuum (10^{-6} Torr) overnight to remove the solvent of crystallization prior to characterization and elemental analysis. Characterization of **2**: IR (Nujol, NaCl, cm^{-1}) 3360 (s), 3334 (w), 3260 (s), 3189 (m), 3090 (s), 1562 (w), 1461 (s), 1376 (w), 1142 (w), 1099 (w), 1028 (m), 872 (w), 673 (s), 627 (w); ^{1}H NMR (300 MHz, C_7D_8): δ 1.72 (s, $\nu_{1/2}$ = 3.5 Hz, 30 H, C_5Me_5), 1.79 (s, $\nu_{1/2}$ = 3.5 Hz, 30 H, C_5Me_5), 2.11 (s, $\nu_{1/2}$ = 2.7 Hz, NH), 24.35 (br, s, $\nu_{1/2}$ = 140 Hz, NH). Anal. Calcd for $C_{40}H_{76}N_{12}Sm_4$: C, 36.22; H, 5.77; N, 12.67; Sm, 45.3. Found: C, 36.36; H, 5.72; N, 12.35; Sm, 45.1. (b) The magnetic susceptibility of **2**, using the Gouy method, is $\chi_M{}^{295K} = 4731.5 \times 10^{-6}$, which translates into $\chi_{Sm}{}^{295K} = 1182.9 \times 10^{-6}$ ($\mu_{eff} = 1.67\ \mu_B$) per samarium atom. This compares to $\mu = 3.4$–$3.6\ \mu_B$ for pure Sm(II) complexes and $\mu = 1.74\ \mu_B$ for Sm(III) complexes.[7c] These results show **2** to be composed of four Sm(III) centers. (c) Evans, W. J.; Bloom, I.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 6507–6508.

(11) **2** crystallizes from benzene in space group $C2/c$ with a = 21.744 (5) Å, b = 11.964 (2) Å, c = 26.100 (5) Å, $\alpha = \gamma = 90°$, β = 119.07 (2)°, V = 5935 (5) Å^3, and D_{calcd} = 1.489 g/cm^3 at T = 98 (2) K for Z = 4 including one solvent molecule in the asymmetric unit. The structure was solved by direct methods. Hydrogen atom positions for the Cp* ligands were calculated and included as a fixed contribution. All other hydrogens were located in difference Fourier maps and included in the refinement with fixed temperature factors. Least-squares refinement of the model based on 3086 observed reflections converged to a final R_F = 4.9%.

to three samarium atoms resulting in a $\mu,\ \eta^3{:}\eta^3$ designation for the anion. Four hydrazido(1–), $(NHNH_2)^-$, anions are located in bridging positions on the remaining four edges of the tetrahedron. Two ammonia molecules coordinated to samarium centers are also present in the molecule.

The distances from Sm(1) to Sm(2) (3.563 (1) Å) and Sm(1) to Sm(2′) (3.552 (1) Å) are slightly shorter than the distances between samarium atoms in the metal (3.588 and 3.620 Å).[12] The average metal–C(ring) distances in **2** are observed to be 2.80 (2) and 2.77 (3) Å for the Sm(2)–C(ring) and Sm(1)–C(ring) distances, respectively, and are in a range similar to those of other organosamarium complexes.[8,13] The average distance between the samarium and nitrogen atoms of the hydrazido anions is 2.48 (3) Å, with a range from 2.43 (2) to 2.63 (1) Å. The average N–N distance is 1.50 (1) Å in the hydrazido(2–) anions and 1.45 (1) Å in the hydrazido(1–) anions, compared to 1.46 (2) Å in the uncoordinated hydrazine molecule.[14] The Sm(1)–N(7) distance to the coordinated neutral NH_3 ligand is 2.664 (13) Å. The metal–hydrazide bonding presumably involves interaction of the nitrogen lone-pair electrons with the electron-deficient samarium atoms. The two hydrazido(2–) anions located on the crystallographic 2-fold axis are oriented with N–N bond vectors perpendicular to the long Sm–Sm bond vectors.

A tungsten(VI) complex containing a $\mu,\ \eta^2{:}\eta^2\text{-HNNH}^{2-}$ ligand has been reported by Schrock and co-workers.[3d] A $\mu,\eta^1{:}\eta^1\text{-}NH_2NH_2$ ligand is also present in this complex. In the samarium tetramer, the N–N distances in the $\mu,\eta^3{:}\eta^3$-HNNH ligands are considerably longer (1.50 (1) Å) than those reported in the tungsten complex (1.39 (2) Å for the hydrazido(2–) anion and 1.43 (1) Å for the hydrazine ligand). It is known that the presence of several metal atoms in a molecule raises the possibility of multisite substrate activation[15] as well as the potential to carry out reactions requiring a specific number of metal centers.[16] In the present case, the specific geometry of the samarium complex is apparently responsible for the longer N–N bond length, then favoring electronic interactions between the nitrogens and the next-nearest metal atom.

Examination of the volatiles generated in the course of the reaction (^{1}H NMR) allowed the identification of pentamethylcyclopentadiene (C_5Me_5H),[17] indicating that protiolytic cleavage of Cp*H had occurred,[18] and suggested that the organosamarium product was a mono-Cp* species (vide supra). Reaction of the volatiles generated in the course of the reaction between **1** and excess hydrazine with the organoyttrium alkyl complex $Cp^*_2YCH(TMS)_2$ ($Cp^* = \eta^5\text{-}C_5Me_5$; TMS = Me_3Si) confirmed the presence of dihydrogen (eq 2).[19]

$$(C_5Me_5)_2YCH(TMS)_2 + H_2 \rightarrow \tfrac{1}{2}[(C_5Me_5)_2YH]_2 + CH_2(TMS)_2 \quad (2)$$

The generation of hydrogen has also recently been observed in the stoichiometric reaction between **1** and hydrazine investigated by Evans and co-workers.[20]

$$2(C_5Me_5)_2Sm + N_2H_4 \rightarrow [(C_5Me_5)_2Sm]_2(NHNH) + H_2 \quad (3)$$

From the crystal structure, elemental analysis, and characterization of the volatiles produced in the course of the formation of **2**, the stoichiometry of the overall reaction is proposed to be as shown in eq 4.

$$4\underset{\mathbf{1}}{(C_5Me_5)_2Sm} + 6N_2H_4 \rightarrow \underset{\mathbf{2}}{[(C_5Me_5)Sm]_4(NHNH_2)_4(NHNH)_2} + 4C_5Me_5H + 2H_2 \quad (4)$$

The presence of $NHNH^{2-}$ and $NHNH_2^-$ fragments in the coordination sphere of the metals makes this molecule unique. Found in very close proximity are fragments postulated as intermediates in the reduction of hydrazine. The recently reported characterization of a molecular dinitrogen complex of samarium(II)[21] combined with the chemistry contained in the present contribution raises quite interesting possibilities regarding the conversion of nitrogen to ammonia using a reducing organosamarium system. Efforts aimed at studying this samarium- and other lanthanide-based transformations related to nitrogen fixation are presently underway.

Acknowledgment. We are grateful to Professor W. J. Evans for helpful comments and communication of his results prior to publication. S.P.N. thanks the University of New Orleans Research Council for a summer research grant and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support.

Supplementary Material Available: Tables of crystal and intensity data, atomic coordinates, selected distances and angles, anisotropic thermal displacement parameters, and hydrogen bond distances for **2** (9 pages); a table of observed and calculated structure factors (63 pages). Ordering information is given on any current masthead page.

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(18) Such protiolytic cleavages have been observed for a Sc system: Shapiro, P. J.; Henling, L. M.; Marsh, R. E.; Bercaw, J. E. *Inorg. Chem.* **1990**, *29*, 4560–4565.

(19) (a) den Haan, K. H.; de Boer, J. L.; Teuben, J. H.; Spek, A. L.; Kojic-Prodic, B. *Organometallics* **1986**, *5*, 1726–1733. (b) den Haan, K. H.; Wielstra, Y.; Teuben, J. H. *Organometallics* **1987**, *6*, 2053–2060. (c) Subsequent analysis by NMR spectroscopy of this solution showed that free alkane ($CH_2(TMS)_2$) had been produced. In order to verify that the hydrogenolysis of the metal alkyl did not occur due to some other proton source, the same experiment was repeated, but this time a solution of the organoyttrium alkyl and 1-octene was exposed to the volatiles. After deuterolysis of the organoyttrium solution, the precipitate was removed by filtration and the filtrate subjected to GC–MS analysis, which indicated that 1-octene had been hydrogenated to octane, thereby confirming that hydrogen must be produced concomitant with the formation of **2**.

(20) (a) Communicated in part: Evans, W. J. Program of the 27th Western Regional Meeting of the American Chemical Society, Anaheim, CA; Oct 7, 1991, Paper 933. (b) Evans, W. J. Private communication.

(21) Evans, W. J.; Ulibarri, T. A.; Ziller, J. W. *J. Am. Chem. Soc.* **1988**, *110*, 6877–6879.