Synthesis and crystal structure of the first yttracarborane sandwich complex: an analog of a yttrocene derivative

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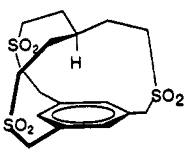
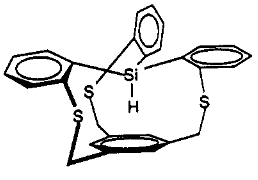
Si–O–C bond angles are all between 130 and 137°, (3) there is a jawlike opening in the cage because of the 1,2,4-substitution pattern, and (4) the silicon atom is 3.50 Å from the mean plane of the benzene ring. Compound **2** has (1) its benzene ring essentially planar, (2) Si–O–C bond angles between 138 and 140°, and (3) a 3.58-Å silicon-to-benzene ring distance.

Pascal and co-workers have studied several related macrocyclics.[1,9–11] Two of these, **3** and **4**, also have three four-atom arms making them analogous to **2**.[1,9] The X-ray structures of **3**, **4**, and related molecules show that their methine hydrogens are directed inside the macrocycle. Molecular mechanics calculations indicate that the "in" hydrogen isomer is the more stable one.[10,11]



3



4

In compounds **1** and **2**, the bulky *tert*-butyl group precludes formation of the "in" isomer. Ours are the first X-ray structures of such small *out*-cyclophanes. Pascal and co-workers have reported evidence of strain in **4** in that the benzylic carbon atoms are 0.39 Å above the nearly planar basal benzene ring. Pascal's compound **3** has its benzylic carbons averaging 0.16 Å above the nearly planar basal benzene ring. Analysis of **2** reveals distortions that are essentially the same as **3** with the benzylic carbons averaging 0.16 Å above the mean plane of the benzene ring. In **1** we find that the para-situated benzylic carbons average 0.32 Å above the mean plane of the slightly distorted benzene ring, indicating, as can be readily seen in Figure 1, a boatlike benzene ring.

Other cyclotrimerization reactions in this and related systems have also been studied. While the $i\text{-}Bu_3Al/TiCl_4$ catalyst system gives high yields for cyclotrimerizations of 1-hexyne, 3-hexyne, 5-chloro-1-pentyne, and $t\text{-}Bu(CH_3)_2SiOCH_2CH_2CH_2C{\equiv}CH$, it does not work for $CH_3Si(OCH_2CH_2CH_2C{\equiv}CH)_3$ or $HOCH_2CH_2CH_2C{\equiv}CH$. Somewhat surprisingly, $(CH_3)_3SiOCH_2CH_2CH_2C{\equiv}CH$ is cyclotrimerized to a ~4/1 ratio of 1,2,4/1,3,5 in only about 10% yield. Thus, it appears that the effectiveness of this catalyst system is quite sensitive to the presence of oxygen in the alkyne. The $i\text{-}Bu_3Al/TiCl_4$ catalyst also fails to cyclotrimerize $ClCH_2CH_2CH_2C{\equiv}CSi(CH_3)_3$ and $(CH_3)_3SiOCH_2CH_2CH_2C{\equiv}CSi(CH_3)_3$.

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Supplementary Material Available: Single-crystal structure reports for compounds 1 and 2, including tables of crystal data, atomic coordinates and isotropic thermal parameters, bond lengths and angles, and anisotropic thermal parameters (17 pages); tables of structure factors (11 pages). Ordering information is given on any current masthead page.

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[8] Crystal data for **2**, the 1,3,5-isomer of $C_{19}H_{30}O_3Si$: formula weight 334.5, monoclinic, $P2_1/m$, a = 8.533 (2) Å, b = 11.232 (2) Å, c = 10.028 (2) Å, β = 95.15 (1)°, V = 957.2 (3) Å^3, Z = 2, D_{calc} = 1.161 g/cm^3. Intensity data: Nicolet P3F autodiffractometer, data collected at room temperature, Mo Kα (λ = 0.71073 Å), θ–2θ scan mode, $3.0 < \theta < 45.0$, 4116 reflections measured, of which 1338 were unique (R_{int} = 0.021) and 1027 were observed [$F > 4\sigma(F)$]. The structure was solved by direct methods and refined using full-matrix least-squares techniques. Final residues R = 0.066 and R_w = 0.088. The model was originally solved and refined in the space group $P2_1$. There was significant disorder present in the acentric space group, and many of the anisotropic displacement parameters and bond lengths were unreasonable. This model converged with R = 0.044 and R_w = 0.053 for 1554 observed data and 246 variables. Examination of the ordered and disordered positions suggested the presence of a mirror plane. Although the final residues are higher in the centrosymmetric space group, the resulting displacement parameters, bond distances, and bond angles are more reasonable. All results presented are for the solution in $P2_1/m$.

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[10] Pascal, R. A., Jr.; Grossman, R. B. *J. Org. Chem.* 1987, *52*, 4616–17.

[11] Pascal, R. A., Jr.; Winans, C. G.; Van Engen, D. *J. Am. Chem. Soc.* 1989, *111*, 3007–10.

Synthesis and Crystal Structure of the First Yttracarborane Sandwich Complex: Analogue of an Yttrocene Derivative

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Summary: The first carborane analogue of an yttrocene derivative, **1**, was synthesized from $Li^+{}_2[2,3\text{-}(SiMe_3)_2\text{-}2,3\text{-}C_2B_4H_4]^{2-}$ and YCl_3 in a molar ratio of 2:1 in dry benzene (C_6H_6) in 83% yield. Compound **1** consists of a dianionic $\{Y(Cl)(THF)[\eta^5\text{-}(SiMe_3)_2C_2B_4H_4]_2\}^{2-}$ sandwich complexed with an exo-polyhedral $Li(THF)^+$ cation, and the net negative charge is balanced by a discrete cationic $Li^+(THF)_4$ unit outside the coordination sphere as shown by X-ray structure analysis. The (C_2B_3 centroid 1)–Y–(C_2B_3 centroid 2) angle of 129.7°, Y–centroid distance of 2.38 Å, Y–Cl distance of 2.582 (4) Å, Cl–Y–O(THF) angle of 89.5 (3)°, and the bent geometry of **1** all resemble those of an yttrocene analogue. As in the Cp systems, the average (ring centroid)–Y–O(THF) (103°) and (ring centroid)–Y–Cl (111°) angles constitute a distorted-tetrahedral geometry for **1**.

The cyclopentadienide anion and a number of its C-substituted derivatives have been the ligands of choice in the production of sandwiched and/or half-sandwiched π-complexes of both metals and nonmetals. Thus, a wide variety of Cp (Cp = $\eta^5\text{-}C_5R_5$, R = organic or organometallic group) complexes involving the majority of the s-, p-, d-, and f-block elements have been reported.[1] The dianions of the carboranes, including the C_2B_9 and C_2B_4 systems, are isoelectronic with the Cp ligands, and while fewer in

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[1] (a) *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, U.K., 1982. (b) *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon: New York, 1987. (c) *Dictionary of Organometallic Compounds*; Macintyre, J. E., Ed.; Chapman and Hall: New York, 1984. *Ibid.*, Suppl. Vol. 1-5, 1985–1989. (d) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Wiley: New York, 1988; and references therein.

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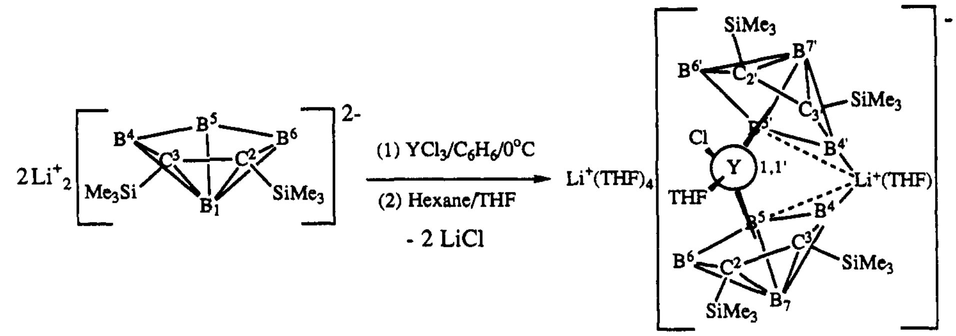
Scheme I



B = BH

1

number than the Cp systems, a variety of commo (sandwiched) and closo (half-sandwiched) metallacarboranes of both the main-group and transition metals are known.[2] Synthetic and structural studies of the corresponding lanthanide and actinide series have also recently begun.[3] The carborane ligands possess significant advantages over the cyclopentadienides. The inwardly tilted frontier carborane orbitals, the lower electronegativity and greater polarizability of boron, and the dinegative charge on the ligand all promote strong covalent binding of the carborane faces to the metal center.[2] In order to exploit further the similarities and the differences between the two ligands, we have extended our studies on metallacarboranes of early transition elements to yttrium metal, a lanthanide congener, whose carborane derivatives have not been synthesized. We report herein the synthesis, characterization, and crystal structure of the first bent yttrium sandwich complex of a C_2B_4 carborane system along with the comparison of its structure with that of a Cp derivative.

Treatment of the dilithium salt of the $[2,3\text{-}(SiMe_3)_2\text{-}2,3\text{-}C_2B_4H_4]^{2-}$ dianion[4] with anhydrous YCl_3 in a molar ratio of 2:1 in dry benzene (C_6H_6), followed by extraction and crystallization of the product from anhydrous *n*-hexane (90%) and THF (10%) solution resulted in the isolation of colorless, air-sensitive crystals of the previously unknown yttracarborane complex 1 in 83% yield as shown in Scheme I.[5]

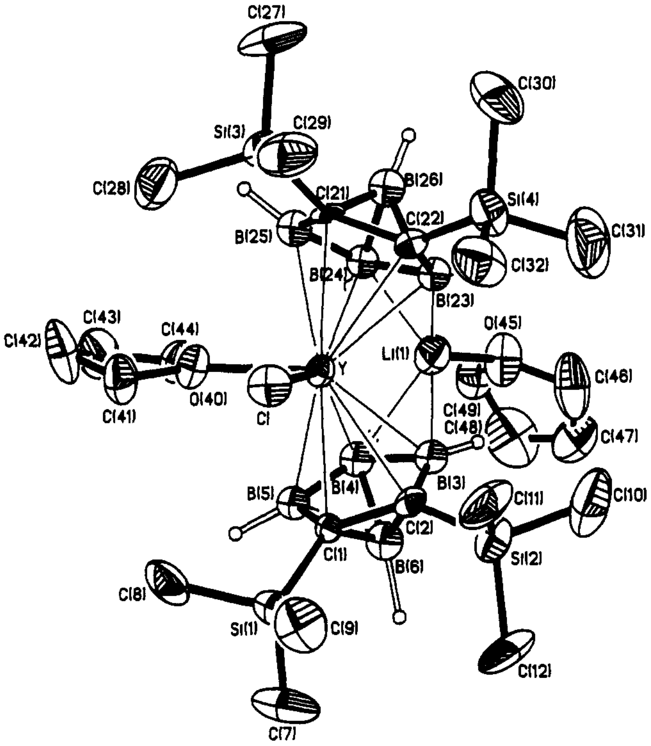


Figure 1. Perspective view of 1 (with thermal ellipsoids drawn at the 40% probability level) showing the atom-numbering scheme. The cationic $Li^+(THF)_4$ unit and the hydrogen atoms of $SiMe_3$ groups and THF molecules are omitted for clarity. Pertinent parameters include the following: Y–C(1) = 2.70 (2), Y–C(2) = 2.73 (2), Y–B(3) = 2.71 (2), Y–B(4) = 2.72 (2), Y–B(5) = 2.71 (2), Y–C(21) = 2.74 (2), Y–C(22) = 2.74 (2), Y–B(23) = 2.75 (2), Y–B(24) = 2.78 (2), Y–B(25) = 2.70 (2), Y–O(40) = 2.35 (1), Y–Cl = 2.582 (4), Y–(C_2B_3 centroid 1) = 2.36, Y–(C_2B_3 centroid 2) = 2.39, Li(1)–B(3) = 2.38 (4), Li(1)–B(4) = 2.41 (4), Li(1)–B(23) = 2.31 (4), Li(1)–B(24) = 2.27 (4), Li(1)–O(45) = 1.90 (4), Li(1)–Y = 3.34 (4) Å; (centroid 1)–Y–O(40) = 103.4, (centroid 2)–Y–O(40) = 103.2, (centroid 1)–Y–Cl = 110.5, (centroid 2)–Y–Cl = 111.6, (centroid 1)–Y–(centroid 2) = 129.7 Cl–Y–O(40) = 89.5°.

The ^1H, ^{11}B, and ^{13}C NMR and IR solution spectra and the microanalytical data of 1 all indicate the presence of

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(3) Fronczek, F. R.; Halstead, G. W.; Raymond, K. N. *J. Am. Chem. Soc.* **1977**, *99*, 1769. Manning, M. J.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1988**, *110*, 4458. Khattar, R.; Knobler, C. B.; Johnson, S. E.; Hawthorne, M. F. *Inorg. Chem.* **1991**, *30*, 1970. Manning, M. J.; Knobler, C. B.; Khattar, R.; Hawthorne, M. F. *Inorg. Chem.* **1991**, *30*, 2009.

(4) A 3.64-mmol (0.81-g) sample of *nido*-$2,3\text{-}(SiMe_3)_2\text{-}2,3\text{-}C_2B_4H_6$ (Hosmane, N. S.; Sirmokadam, N. N.; Mollenhauer, M. N. *J. Organomet. Chem.* **1985**, *279*, 359) in 25 mL of THF was slowly added under high vacuum to 7.27 mmol of *tert*-butyllithium, *t*-BuLi (12.36 mL of 1.7 M solution in pentane), at −196 °C. The mixture was slowly warmed to −78 °C, stirred constantly for 2 h, and then warmed to room temperature gradually over a period of 6 h, during which time the solution turned to golden yellow. At this point, the solvents (pentane and THF) and the volatile *t*-BuH were removed to collect a fluffy white solid that was identified by spectroscopy and microanalysis as the THF-solvated $Li^+_2\text{-}[2,3\text{-}(SiMe_3)_2\text{-}2,3\text{-}C_2B_4H_4]^{2-}$ (for the preparation and characterization of the unsolvated dilithium salt of the $[2,3\text{-}(SiMe_3)_2\text{-}2,3\text{-}C_2B_4H_4]^{2-}$ dianion, see: Barreto, R. D.; Hosmane, N. S. *Inorg. Synth.*, in press). All of this solid was immediately used as described in ref 5.

(5) A 3.60-mmol sample of the $Li^+_2[2,3\text{-}(SiMe_3)_2\text{-}2,3\text{-}C_2B_4H_4]^{2-}$ salt[4] was allowed to react with 1.79 mmol of anhydrous YCl_3 (0.35 g) in dry benzene (25 mL) at 0 °C for 24 h, during which time the solution turned yellow. At this point, the heterogeneous product mixture was filtered through a frit *in vacuo* and the residue was washed repeatedly with a solvent mixture of hexane (90%) and THF (10%) to collect a clear pale yellow filtrate. After slow removal of the solvents from the filtrate *in vacuo*, a colorless, air-sensitive crystalline solid, identified as $[Li^+(THF)_4]\{1\text{-}Cl\text{-}1\text{-}(C_4H_8O)\text{-}2,2',3,3'\text{-}(SiMe_3)_4\text{-}4,4',5,5'\text{-}Li(C_4H_8O)\text{-}[1,1'\text{-}$*commo*$\text{-}Y(C_2B_4H_4)_2]\}^-$ (1), was obtained in 83% yield (1.45 g, 1.513 mmol; reasonably soluble in polar and slightly soluble in nonpolar organic solvents; mp 110 °C dec).

a heterocarborane complex.[6] The X-ray crystal structure reveals that compound 1 is the novel yttracarborane sandwich complex [Li$^+$(THF)$_4$]{1-Cl-1-(C$_4$H$_8$O)-2,2′,3,3′-(SiMe$_3$)$_4$-4,4′,5,5′-Li(C$_4$H$_8$O)-[1,1′-*commo*-Y(C$_2$B$_4$H$_4$)$_2$]}$^-$ (1; Figure 1),[7] in which the yttrium metal adopts an essentially η^5-bonding posture with respect to each of the C$_2$B$_3$ faces with Y–cage atom distances of 2.70–2.78 Å.[8] However, these distances are slightly longer than the Y–η^5-carbon distances of 2.60–2.67 Å in the dimer (η^5-C$_5$Me$_5$)$_2$Y(μ-Cl)YCl(η^5-C$_5$Me$_5$)$_2$[9] and 2.66 Å in the monomer (η^5-C$_5$Me$_5$)$_2$YCl(THF).[10] Comparable Y–C distances could be found in the structure of [(η^5-C$_5$H$_4$Me)$_2$YH(THF)]$_2$.[11] The (C$_2$B$_3$ centroid 1)–Y–(C$_2$B$_3$ centroid 2) angle in 1 is somewhat contracted at 129.7° when compared to 136.4° found in the structure of (η^5-C$_5$Me$_5$)$_2$YCl(THF).[10] Nonetheless, the Y–centroid distance of 2.38 Å, the Y–Cl distance of 2.582 (4) Å, the Cl–Y–O(THF) angle of 89.5 (3)°, and the bent geometry of 1 all resemble those of an yttrocene analogue. As in the Cp systems, the average (ring centroid)–Y–O(THF) (103°) and (ring centroid)–Y–Cl (111°) angles constitute a distorted-tetrahedral geometry for 1 (see Figure 1). Since the yttrium in the anionic unit is bonded to a chlorine atom as well as to the carborane cages, for charge compensation an additional Li$^+$(THF) moiety is bound to two adjacent borons in each cage with distances ranging from 2.27 to 2.40 Å. In a formal sense compound 1 is a "salt" consisting of a dianionic {Y(Cl)(THF)[η^5-(SiMe$_3$)$_2$C$_2$B$_4$H$_4$]$_2$}$^{2-}$ sandwiched species that is complexed with an exo-polyhedral Li$^+$(THF) cation, and the net negative charge is balanced by a discrete cationic Li$^+$(THF)$_4$ unit outside the coordination sphere. Thus, compound 1 differs from the structurally characterized Cp analogues[1,9–11] and metallacarboranes that exhibit bent-sandwich geometries.[3,12,13] The Li–Y distance of 3.34 (4) Å indicates that no interaction exists between these metals. The eclipsed conformation of the C$_{\text{cage}}$–SiMe$_3$ groups of the opposing ligands in 1 is similar to those found in the structures of zirconium and hafnium sandwich complexes which have also incorporated a Li metal for charge balance.[12,13] Therefore, it is possible that the presence of a Li$^+$(THF) moiety could be responsible for the eclipsed conformation of the carborane ligands observed in the structures of these sandwiched compounds. To the best of our knowledge, compound 1 represents the first yttrium sandwich carborane complex ever to be reported.

The present work, together with the studies on zwitterionic *commo*-zircona- and *commo*-hafnacarborane complexes,[12,13] demonstrates that, by using a small carborane ligand, a second metal atom such as lithium can be incorporated into the structure of sandwich complexes as a counterion. One of the limitations of carborane ligands in f-element chemistry is that, with two dianionic ligands and a 3+ charge on the metal, there is little possibility of adding reactive anionic ligands such as alkyls without forming a highly charged species. The title complex offers a convenient solution to that problem. Studies on the reactivities of 1 and other related compounds are currently underway in our laboratories.

Acknowledgment. This work was supported by grants from the National Science Foundation (Grant No. CHE-9100048), the Robert A. Welch Foundation (Grant No. N-1016), and the donors of the Petroleum Research Fund, administered by the American Chemical Society. We also thank the reviewers of this paper for their valuable comments and suggestions.

Supplementary Material Available: Tables of crystal data and data collection and refinement parameters, positional and thermal parameters, and selected bond distances, bond angles, and torsion angles (11 pages); a listing of observed and calculated structure factors (10 pages). Ordering information is given on any current masthead page.

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[6] Spectroscopic and microanalytical data: ^{1}H NMR (C$_6$D$_6$, 200 MHz) δ 3.62 [s, 4 H, THF], 1.63 [s, 4 H, THF], 0.58 [s, 3 H, SiMe$_3$], 0.48 [s, 3 H, SiMe$_3$]; ^{11}B NMR (C$_4$D$_8$O, 64.2 MHz, external BF$_3$·OEt$_2$) δ 26.23 [br, ill-defined peak, 1 B, basal BH, ^1J(^{11}B–^{1}H) unresolved], 18.79 [br, ill-defined peak, 1 B, basal BH, ^1J(^{11}B–^{1}H) unresolved], 1.47 [br, ill-defined peak, 1 B, basal BH, ^1J(^{11}B–^{1}H) unresolved], –29.09 [br, ill-defined peak, 1 B, apical BH, ^1J(^{11}B–^{1}H) unresolved]; ^{13}C NMR (C$_6$D$_6$, 50.3 MHz) δ 110.63 [s (v br), cage carbons (SiCB)], 68.63 [t, THF, ^1J(^{13}C–^{1}H) = 147.0 Hz], 25.66 [t, THF, ^1J(^{13}C–^{1}H) = 133.1 Hz], 3.82 [q, SiMe$_3$, ^1J(^{13}C–^{1}H) = 118.3 Hz]; IR (cm^{-1}; C$_6$D$_6$ vs C$_6$D$_6$): 2980 (vs), 2960 (vs) [ν(CH)], 2530 (s), 2480 (s, sh), 2449 (m, sh) [ν(BH)], 1460 (w), 1410 (w) [δ(CH)$_{\text{asym}}$], 1370 (w, br), 1350 (w), 1250 (vs) [δ(CH)$_{\text{sym}}$], 1180 (s), 1130 (w, br), 1070 (vs), 1050 (vs), 900 (s, br), 840 (vvs, br) [ρ(CH)], 760 (s), 680 (s), 630 (s) [ν(YCl)], 430 (s), 400 (s). Anal. Calcd for C$_{40}$H$_{92}$O$_6$B$_8$Si$_4$ClLi$_2$Y: C, 47.69; H, 9.21; Si, 11.15; Cl, 3.52. Found: C, 47.43; H, 9.08; Si, 11.54; Cl, 4.45. Since complex 1 is extremely sensitive to air and/or moisture, attempts to obtain reproducible analyses (obtained from Oneida Research Services, Inc., Whitesboro, NY) for Y and Li were unsuccessful.

[7] In the name of 1, the IUPAC numbering system (see Scheme I) is used.

[8] Crystal data for 1: C$_{40}$H$_{92}$O$_6$B$_8$Si$_4$ClLi$_2$Y, fw = 1006.2, monoclinic, $P2_1/c$, a = 12.123 (5) Å, b = 26.480 (9) Å, c = 18.795 (6) Å, β = 95.00 (3)°, V = 6011 (4) Å^3, Z = 4, D_{calcd} = 1.112 g/cm^3, μ = 1.148 mm^{-1}. Of 5874 data collected on a Nicolet R3m/V diffractometer (Mo Kα, 2θ = 3.5–40°, at –43 °C) 5385 reflections were unique and 2675 were observed [$I > 2.0\sigma(I)$]. Data were corrected for Lorentz, polarization, and absorption effects. The structure was solved by direct methods and refined by block-diagonal least-squares techniques using SHELXTL-PLUS (Sheldrick, G. M. Structure Determination Software Program Package; Siemens Analytical X-ray Instruments, Inc., 1990). Two of the four Li$^+$-bound THF's [O(60), C(61)–C(64) and O(65), C(66)–C(69)] were disordered, and their bonds were constrained. Cage B and the disordered THF C atoms were refined isotropically. All other non-H atoms were refined anisotropically. Cage H atoms were located on difference Fourier maps, and other H atoms, except for the disordered THF's, were calculated. The final refinement of 1 converged at R = 0.088, R_{w} = 0.091, and GOF = 1.65 for observed reflections. The maximum and minimum residual electron densities are +0.66 and –0.60 e/Å^3, respectively.

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