(2)–P(2) = 2.478 (1), and Ru(3)–P(2) = 2.316 (1) Å] and the overall five-coordinate stereochemistry at phosphorus. Apart from the three metal atoms, the two remaining coordination sites at P(2) are occupied by two phenyl rings, one of which has undergone metalation [Ru(4)–C(30) = 2.151 (3) Å] and formation of an η^2-arene interaction to Ru(1) [Ru(1)–C(30) = 2.327 (3) and Ru(1)–C(29) = 2.335 (3) Å]. The stereochemical change at P(2) is best described as a transformation from tetrahedral to square-pyramidal geometry. The Ru–P bond lengths associated with this novel coordination mode are slightly longer than those found for normal μ_2-phosphido-bridged clusters.[3,10]

While the μ_3-phosphido metal bonding in **2** is unprecedented for a bis(aryl)phosphido group, there are a few examples of compounds in the literature where *weaker* secondary interactions to μ_2-PR_2 ligands have been demonstrated. Two clusters, (H)$Ru_3(CO)_9(\mu\text{-}PPh_2)$[11] and an iron analogue $HFe_3(CO)_9[\mu\text{-}P(C_6H_4OMe)(CH_2C_6H_5)]$,[12] may have weak M···P contacts with a third metal site; $HRu_3Rh(\mu\text{-}CO)(CO)_6(PPh_3)_2[\mu\text{-}P(C_6H_4)Ph]$[13] has a long Rh···P (phosphido) contact, and $Fe_3(CO)_{10}(\mu\text{-}RP{=}CH_2)$[14] contains a coordinatively stabilized phosphaalkene. Finally, insertion of alkynes into metal–phosphinidene (μ_3- or μ_4-RP) bonds affords μ-RP{C(R)C(R′)} ligands related to that in **2**.[15]

The ^{13}C NMR shifts of the η^1,η^2-bound phenyl ring [δ = 98.52 d ($^2J_{PC}$ = 36.8 Hz) C(29), δ = 143.7 dd ($^2J_{PC}$ = 40.0, 4.9 Hz) C(30)][16] are typical of C_β and C_α shifts for σ–π-bound alkenyl ligands. In solution, **2** undergoes a dynamic exchange process which can be frozen out at 193 K. The two isomers (ratio 45:55)[6] differ in the location of the hydride along the Ru(2)–Ru(3) or Ru(3)–Ru(4) edges.[5]

Heating a C_6H_{14} solution of **2** at 60 °C under a CO purge reforms **1** in high yield (Scheme I). Although the involvement of bridging ligands via C–H or C–P activation during reactions performed under forcing conditions is well documented,[17] very few examples of facile reversibility of these reaction types are known.[18] The reversibility of the present ortho-metalation and η^2-arene transformation, under mild conditions, is notable. The demonstration of a triply bridging mode for a phosphido group in **2** provides additional evidence to support the involvement of five-coordinate μ-PR_2 ligands in ligand-exchange processes and skeletal rearrangements in phosphido bridge containing clusters.

Acknowledgment. We are grateful to the Natural Sciences and Engineering Council of Canada for financial support of this work and to the Government of Ontario for a scholarship (to J.F.C.).

Registry No. 1, 120806-43-1; **2** (isomer I), 142780-92-5; **2** (isomer II), 142780-93-6.

Supplementary Material Available: Details of the structure determination of complex **2** (Table S1) and tables of atomic positional parameters (Table S2), bond distances (Table S3), bond angles (Table S4), anisotropic thermal parameters (Table S5), and hydrogen atom positions (Table S6) (9 pages); table of observed and calculated structure factors (Table S7) (30 pages). Ordering information is given on any current masthead page.

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(16) $^{13}C\{^1H\}$ NMR ($CDCl_3$, 298 K, δ): 202.5 (d, CO, $^2J_{PC}$ = 8.32 Hz), 202.2 (d, CO, $^2J_{PC}$ = 10.4 Hz), 199.8 (d, CO, $^2J_{PC}$ = 17.6 Hz), 197.9 (d, CO, $^2J_{PC}$ = 33.2 Hz), 195.2 (s, CO), 192.2 (s, CO), 191.8 (d, CO, $^2J_{PC}$ = 13.5 Hz), 188.5 (d, CO, $^2J_{PC}$ = 12.4 Hz), 188.2 (t, CO, $^2J_{PC}$ = 10.1 Hz), 153.3 (d, C ipso, $^1J_{PC}$ = 27.1 Hz), 149.58 (d, C ortho, $^2J_{PC}$ = 16.6 Hz), 145.1 (d, C ipso, $^1J_{PC}$ = 33.4 Hz), 143.7 (dd, C ortho, $^2J_{PC}$ = 40.0 Hz, $^2J_{PC}$ = 4.4 Hz), 142.42 (d, C meta, $^3J_{PC}$ = 8.8 Hz), 138.8 (d, C ipso, $^2J_{PC}$ = 27.1 Hz), 133.6 (d, C ortho, $^2J_{PC}$ = 11.4 Hz), 132.80 (d, C ortho, $^2J_{PC}$ = 11.4 Hz), 132.04 (d, C ortho, $^2J_{PC}$ = 11.43 Hz), 130.78 (s, C para), 129.8 (d, C meta, $^2J_{PC}$ = 11.4 Hz), 128.3–128.9 (phenyl region), 124.3 (s, C para), 98.52 (d, C ipso, $^1J_{PC}$ = 36.8 Hz).

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Double Partial Cone Conformation for $Na_8\{calix[6]arene\ sulfonate\}\cdot 20.5H_2O$ and Its Parent Acid

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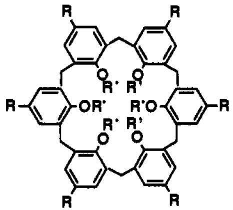
Received March 25, 1992

The chemistry of calixarenes has recently become a very active area of endeavor.[2-5] Of the numerous stimulating findings to appear thus far in the literature, one of the most intriguing concerns the discovery of certain uranophiles by Shinkai.[6,7] It was reported that calix[5]arene sulfonate, calix[6]arene sulfonate, and the two corresponding derivatives substituted at the base by carboxymethoxy groups, **1** with R′ = CH_2COOH, exhibited stability constants for the uranyl ion of $K = 10^{18.4-19.2}$. Indeed, in competition experiments these calixarenes showed selectivity factors of 10^{12-17} for uranyl over the Ni^{2+}, Zn^{2+}, and Cu^{2+} ions. This selectivity was attributed to a moderately rigid calix[6]arene structure which was preorganized to match the rather unusual pseudoplanar hexacoordination needs of the UO_2^{2+} ion[6,7] as shown in **2**. However, on the basis of this study this premise appears untenable.



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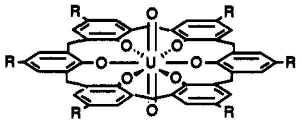

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Considering the importance of the abovementioned findings, the structural chemistry of derivatives of calix[6]arene has been slow to develop. In the available selection[8-14] it is difficult to find

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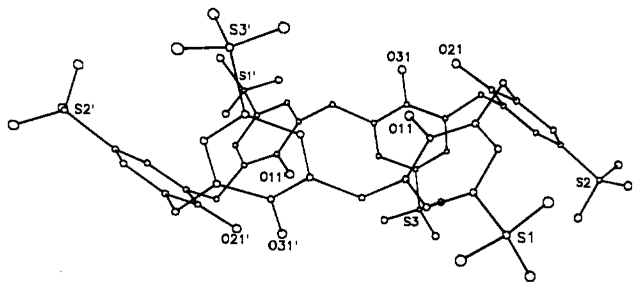
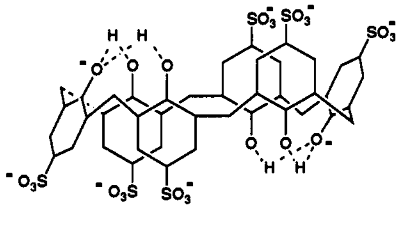


Figure 1. View of the Na_8\{calix[6]arene sulfonate\} structure illustrating the three "up", three "down" sulfonate arrangement of the double partial cone conformation.

general conformational features, apart from the elliptical cone conformation exhibited by the parent *p-tert*-butylcalix[6]arene.[8] Since our group has found a rich and often surprising inclusion chemistry for calix[4]arene sulfonates,[15-18] we decided to investigate the structure of calix[6]arene sulfonate and its alkali metal salts.

In the stability constant studies by Shinkai on calix[6]arene sulfonate, **1** with R = SO_3H and R′ = H, the pH was set at 9.5 with an ammonium buffer.[6,7] There are contradictory reports in the literature concerning the value of the pK_a's of the sulfonic acid and phenolic protons, making it unclear whether an 8–, 9–, or 10– anion would be expected at basic pH.[19] However, the compound which crystallizes at this pH[20] is the \{calix[6]arene sulfonate\}$^{8-}$. In view of this confusion surrounding the pK_a values for calix[6]arene sulfonate,[19] we redetermined the protonation constants via a potentiometric titration.[21] Iterative computer refinement[21] revealed that only two phenolic groups have ionizable protons with pK_a values of 4.76 (3) [β_{11} = 4.76 (3)] and 3.44 (4) [β_{12} = 8.02 (4)]. These values compare favorably to those reported by Scharff, Mahjoubi, and Perrin, who determined pK_a values of 5.02 and 3.45,[19] and are comparable to the second two values of 3 and 4 reported by Shinkai.[19] Shinkai's first pK_a value of 1 is reasonably assigned by us to removal of a sulfonate-bound proton. Arenesulfonic acids are highly acidic and typically show pK_a values near 1.0 (pK_a of benzenesulfonic acid = 0.7); therefore they are completely dissociated in the pH range examined here.[22] From our experimental pK_a values, one can easily rationalize the formation of the \{calix[6]arene sulfonate\}$^{8-}$ ion under our experimental conditions.

In the solid state[23] (Figure 1), \{calix[6]arene sulfonate\}$^{8-}$ adopts a structure that may be described as a double partial cone;[2,24] that is to say, the anion resides on a crystallographic center of inversion and presents three adjacent SO_3 groups "up" and three "down", as shown schematically in **3**.[25] This conformation appears to be



3

stabilized by intramolecular hydrogen bonding between the three phenolic oxygen atoms and the two remaining hydrogen atoms on each half of the molecule, as shown in **3**. The corresponding O···O separations are O11···O21 (2.64 (1) Å) and O21···O31 (2.50 (1) Å).[26] The strong hydrogen bonding noted here may account for the relative nonacidity of the last four phenolic protons as evidenced by our pK_a studies. While the complex in which two phenolic oxygen atoms are deprotonated is the species present at basic pH, it is interesting to note that the parent acid exhibits essentially the same double partial cone conformation.[27]

From scrutiny of Figure 1 it is clear that calix[6]arene sulfonate, in either the acidic or basic form, is not preorganized into a pseudoplanar hexacoordination geometry appropriate for the uranyl ion.[28] The ellipsoidal cone conformation found for *p-tert*-butylcalix[6]arene has been replaced by the new double partial cone geometry shown in **3**. Strong uranyl ion coordination can only be realized by a metal ion-induced calixarene reorganization. We have prepared a uranylcalix[6]arene sulfonate complex and find that binding constant studies are complicated by competitive uranyl hydrolysis. Future studies on this system are in progress.

Acknowledgment. We are grateful to Dr. P. H. Smith for helpful discussions and experimental assistance. This work was supported by the National Science Foundation and (in part) by a grant for International Joint Research Project from the NEDO, Japan. Work at Los Alamos was sponsored by the Office of Health and Environmental Research, U.S. Department of Energy, under contract W-7405-eng-36 with the University of California.

Registry No. 1, 142801-39-6; **3**, 142801-40-9.

Supplementary Material Available: Tables of crystallographic data, hydrogen atom coordinates, and anisotropic thermal parameters for **1** and final fractional coordinates and bond distances and angles for **1** and **2** (14 pages); tables of observed and calculated structure factors for **1** and **2** (26 pages). Ordering information is given on any current masthead page.

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(23) Na_8\{calix[6]arene sulfonate\}·20.5H_2O belongs to the monoclinic space group $P2_1/c$ with a = 13.741 (2), b = 12.356 (3), c = 20.729 (2) Å, β = 101.45 (1)°, and D_{calcd} = 1.61 g cm^{-3} for Z = 2. Refinement based on 3091 observed reflections led to R = 0.091.

(24) The conformation found in the title compounds has some structural features similar to those found for the metal-coordinated calix[6]arenes in refs 11 and 12. The conformation was described as a "hinged-3-up-3-down" conformation in ref 3, p 218. However, in view of the existing partial cone nomenclature in calix[4]arene chemistry and in view of the close structural similarity between the partial cone conformation and that of the title compounds (Rizzoli, C.; Andreetti, G. D.; Ungaro, R.; Pochini, A. *J. Mol. Struct.* **1982**, *82*, 133; Hamada, F.; Bott, S. G.; Orr, G. W.; Coleman, A. W.; Zhang, H.; Atwood, J. L. *J. Incl. Phenom.* **1990**, *9*, 195), the term double partial cone is applied in this contribution.

(25) Gutshe and Bauer have referred to essentially this conformation as "hinged": Gutsche, C. D.; Bauer, L. J. *J. Am. Chem. Soc.* **1985**, *107*, 6052.

(26) These distances are not significantly outside the range found for *p-tert*-butylcalix[6]arene in ref 8.

(27) \{Calix[6]arene sulfonic acid\}·23H_2O is isostructural with the sodium salt of its 8– anion: a = 13.442 (7), b = 12.107 (7), c = 20.954 (9) Å, β = 100.37 (4)°, and D_{calcd} = 1.52 g cm^{-3} for Z = 2. Refinement based on 1187 observed reflections led to an R value of 0.129. The rather high R value in for this structure and for the one of the sodium salt may be attributed in part to a large number of disordered water molecules in the crystal lattice.

(28) The solid-state conformation is assumed to reflect that of the solution state. This premise is especially reasonable in view of the large number of water molecules which surround the calix[6]arene in the solid-state structure.