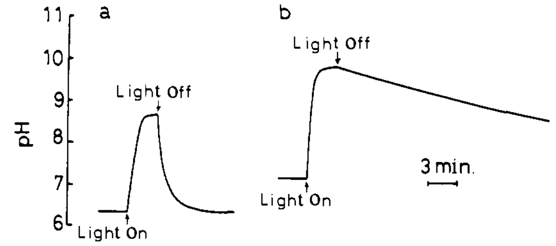


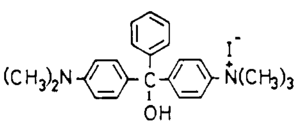
Figure 2. Light-induced pH increase of aqueous solutions containing (a) compound **2** (5×10^{-3} mol/L) and (b) compound **3** (1×10^{-3} mol/L) at 30 °C.

green oxalate did not induce any detectable increase of pH. These results present unambiguous evidence that the large pH increase is ascribable to photodissociation of the leucohydroxide.

Ultraviolet light pumps the leucohydroxide, surrounded by surfactants, to the excited state. The excited leucohydroxide dissociates into ion pairs, triphenylmethyl cation and hydroxide anion, and the hydroxide ion is released from the surfactants to the aqueous phase, causing the increase in pH.

The amount of the ejected hydroxide ion is a function of the quantum yield of the dissociation, the concentration of the emitter, and the light intensity. The rapid increase of pH to the photostationary pH of 10.0 under present experimental conditions (the emitter concentration is 4.8×10^{-4} mol/L) suggests that the quantum yield is fairly large. By changing the light intensity with use of neutral density filters, the photostationary pH could be controlled. The pH with full light intensity, 9.9, decreased to 6.3 when the intensity was reduced to 0.008. Titration of this solution with sodium hydroxide demonstrated that the pH change corresponds to 90% reduction of the photoejected hydroxide ions. The light-intensity dependence suggests second-order recombination decay of the hydroxide ions.

Two simple methods for preparing water-soluble compounds are to introduce a quaternary amine or a sulfonate into the structure. Compounds **2** and **3** were synthesized.[10] Both compounds were quite soluble in water and showed reversible photochromic behavior. Figure 2 shows the photoresponse of the pH of aqueous solutions containing **2** (a) and **3** (b). The relatively low photostationary pH value of aqueous solution containing **2** is attributable to the fast recombination rate of the ion pairs. The positive charge on the quaternary amine in addition to that of the photogenerated triphenylmethyl cation may accelerate the recombination rate due to the increase in Coulombic force. Sulfonated triphenylmethane leucohydroxide (**3**) showed a similar photoresponse of pH on irradiation, although return of the pH in the dark was very slow. The slow recovery of pH may be explained by the absence of a strong Coulombic force between sulfonated triphenylmethyl cation and hydroxide ion.


(2)


(3)

The hydroxide emitters described here, triphenylmethane leucohydroxide derivatives, may be useful for controlling many aspects of chemical reactions in aqueous solutions as well as in vesicles.

Registry No. 1 (X = OH; Y = H), 76-84-6; **1** (X = OH; Y = N(CH_3)$_2$), 510-13-4; **2**, 84961-00-2; **3**, 6362-29-4.

---

(10) Compound **2** was prepared by treating 4,4′-bis(dimethylamino)triphenylmethane leucohydroxide with methyl iodide in toluene in sealed glass at 90 °C in the dark for 20 h. Anal. Calcd for $C_{24}H_{29}N_2OI$ (**2**): C, 59.02; H, 5.98; N, 5.73. Found: C, 59.02; H, 5.92; N, 5.65. Compound **3** was prepared by directly sulfonating compound **1** by chlorosulfonic acid. Anal. Calcd for $C_{23}H_{26}N_2O_4S$ (**3**): C, 61.59; H, 5.62; N, 6.25. Found: C, 61.60; H, 5.95; N, 6.22.

η^8 Coordination of Planar $C_8H_8^{2-}$ to Vanadium. Structural Characterization of (η^8-C_8H_8)V[$(C_2H_5)_2C_2B_4H_4$](1)

Robert G. Swisher, Ekk Sinn, Greg A. Brewer, and
Russell N. Grimes*

Department of Chemistry, University of Virginia
Charlottesville, Virginia 22901

Received November 22, 1982

Cyclooctatetraenide dianion, $C_8H_8^{2-}$, a planar 10π-electron aromatic system, forms symmetrically bonded (η^8) sandwich complexes with large metals including the actinides,[2a,b] lanthanides (in which the metal–ligand bonding is mainly ionic),[2c] and second-row transition metals (especially zirconium[2d-f]), but η^8 coordination to first-row transition metals is rare;[3] structurally established examples are limited to several titanium complexes, all oxygen-sensitive,[4] in one of which[4d] the crystallographic *R* factor is 21%.

We report here the preparation and X-ray structure determination of the vanadacarborane title complex (**1**), which represents, to our knowledge, the first example of η^8 binding of a C_8 ring to a first-row transition metal other than titanium. The metal in **1** is the smallest atom yet shown to coordinate symmetrically to a ring as large as planar $C_8H_8^{2-}$ (estimated[5] covalent radii of V and Ti are respectively 1.22 and 1.32 Å). At this writing, **1** is the only structurally characterized vanadium–cyclooctatetraene complex of any geometry, although mass spectrometric evidence for ions such as $(C_5H_5)V(C_8H_8)^+$ has been observed in ion–molecule reactions.[6]

Compound **1** was obtained in the in vacuo reaction of $K_2C_8H_8$ with the nido-carborane anion $[2,3\text{-}(C_2H_5)_2C_2B_4H_5]^-$ and VCl_3 (~equimolar ratio) in tetrahydrofuran (THF) for 2 h at 0 °C followed by warming to room temperature. Workup in air and chromatography in 25% CH_2Cl_2 in *n*-hexane on a silica gel plate gave **1** as a dark green air-stable solid, mp 240 °C dec, R_f 0.47, yield 41 mg (0.14 mmol, 3.2% of theory). The EI mass spectrum exhibits a strong parent group with a high-mass cutoff at *m/e* 286, corresponding to the $^{51}V^{13}C^{12}C_{13}{}^{11}B_4{}^{1}H_{22}{}^+$ ion, and a base peak at *m/e* 155, which is assigned to $V(C_8H_8)^+$. The parent envelope is closely consistent with the pattern calculated from natural isotope distributions except that slight loss of hydrogen is indicated. The IR spectrum (KBr pellet) contains an intense B–H doublet at 2530 and 2500 cm^{-1}, a strong C_2H_5 multiplet between 2880 and 2980 cm^{-1}, and weak C–H stretching bands at 3025 and 3075 cm^{-1} attributed to the C_8H_8 ligand. The paramagnetism of **1** precluded obtaining useful NMR data.

X-ray diffraction data were collected on a crystal of **1** grown from benzene solution, and the structure (Figure 1) was solved by standard Patterson and Fourier procedures.[7] The complex

---

(1) Organotransition Metal Metallacarboranes. 3. Part 2: Swisher, R. G.; Sinn, E.; Grimes, R. N. *Organometallics*, in press.

(2) (a) Streitweiser, A., Jr.; Muller-Westerhoff, U.; Sonnichsen, G.; Mares, F.; Morrell, D. G.; Hodgson, K. O.; Harmon, C. A. *J. Am. Chem. Soc.* **1973**, *95*, 8644 and references therein. (b) Avdeef, A.; Raymond, K. N.; Hodgson, K. O.; Zalkin, A. *Inorg. Chem.* **1972**, *11*, 1083. (c) Hodgson, K. O.; Mares, F.; Starks, D. F.; Streitweiser, A., Jr. *J. Am. Chem. Soc.* **1973**, *95*, 8650 and references therein. (d) Brauer, D. J.; Krüger, C. *J. Organomet. Chem.* **1972**, *42*, 129; **1975**, *14*, 3053. (e) Brauer, D. J.; Krüger, C. *Inorg. Chem.* **1975**, *14*, 3053. (f) Brauer, D. J.; Krüger, C. *Organometallics* **1982**, *1*, 204; 208 and references therein.

(3) Fray, G. I.; Saxton, R. G. "The Chemistry of Cyclo-octatetraene and Its Derivatives"; Cambridge University Press: London, 1978.

(4) (a) (η^8-C_8H_8)Ti(η^4-C_8H_8): Dietrich, H.; Soltwisch, M. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 765. (b) [(η^8-C_8H_8)Ti]$_2$(η^4, η^4-C_8H_8): Dietrich, H.; Dierks, H. *Ibid.* **1966**, *5*, 898. (c) (η^8-C_8H_8)Ti(η^5-C_5H_5): Kroon, P. A.; Helmholdt, R. B. *J. Organomet. Chem.* **1970**, *25*, 451. (d) [(η^8-C_8H_8)-$TiC_2(C_6H_5)(CH_3)$]$_2$: Veldman, M. E. E.; van der Waal, H. R.; Veenstra, S. J.; de Liefde, H. J. *Ibid.* **1980**, *197*, 59.

(5) Pauling, L. "The Nature of the Chemical Bond", 3rd ed.; Cornell University Press: Ithaca, NY, 1960; p 256.

(6) Müller, J.; Goll, W. *Chem. Ber.* **1974**, *107*, 2084.

0002-7863/83/1505-2079$01.50/0

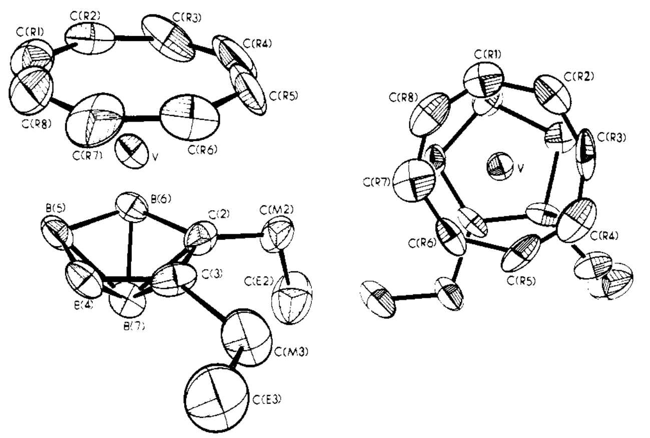


Figure 1. Molecular structure of **1** viewed obliquely (left) and along the V–B(7) axis (right). In the right view the C_8 and C_2B_3 rings are projected onto the same plane so that the ring sizes are directly comparable. Hydrogen atoms are omitted for clarity. Bond lengths (Å) involving the $C_8H_8^{2-}$ ligand are as follows: C(R1)–C(R2), 1.460 (17); C(R2)–C(R3), 1.405 (16); C(R3)–C(R4), 1.360 (17); C(R4)–C(R5), 1.336 (15); C(R5)–C(R6), 1.497 (13); C(R6)–C(R7), 1.389 (15); C(R7)–C(R8), 1.377 (17); C(R8)–C(R1), 1.327 (19); V–C(R1), 2.264 (4); V–C(R2), 2.295 (11); V–C(R3), 2.288 (8); V–C(R4), 2.365 (10); V–C(R5), 2.286 (4); V–C(R6), 2.230 (9); V–C(R7), 2.254 (9); V–C(R8), 2.276 (11). Bond distances in the $(C_2H_5)_2C_2B_4H_4^{2-}$ carborane ligand are normal.

contains formal V^{4+} sandwiched between $(C_2H_5)_2C_2B_4H_4^{2-}$ and $C_8H_8^{2-}$ ligands with vanadium completing a seven-vertex VC_2B_4 pentagonal-bipyramidal (closo) cage that is isostructural with other MC_2B_4 systems;[8] however, the metal is electron deficient with only 17 electrons in its valence shell.[9] The C_8 ring is planar within normal limits of experimental error (largest deviation from the calculated least-squares plane is 0,02 Å, comparable to that observed in uranocene, $U(C_8H_8)_2$[2b]). The mean ring C–C bond length is 1.394 Å, with variations in the eight values (Figure 1) that may reflect, to a degree, large thermal motions of the ring carbons. The V–C_{ring} distances are nearly equal (mean value 2.282 Å), the longest and shortest differing by only 6%.

The vanadium atom is located 1.375 Å from the C_8 plane and 1.830 Å from the C_2B_3 ring of the carborane ligand; the latter value is unexpectedly high and may reflect weaker metal–carborane bonding than has been observed previously in complexes of first-row transition-metal ions with $R_2C_2B_4H_4^{2-}$ ligands.[8] The C_8 and C_2B_3 ring planes are nearly parallel, with a dihedral angle of 3.3°.

The paramagnetism of **1** was investigated via ESR and magnetic susceptibility measurements. The magnetic moment exhibits a slight temperature dependence with a maximum near 6 K, which indicates a much smaller orbital effect than would be expected for pure octahedral ($^2T_2$) symmetry with a d^1 configuration and is consistent with the observed molecular structure. The room-temperature ESR spectrum of a solid sample gives g = 1.94, which compares with the value of 1.91 estimated by extrapolation of the higher temperature magnetic moment data. The room-temperature spectrum of **1** in toluene/CH_2Cl_2 solution exhibits vanadium hyperfine coupling ($\langle A \rangle = 155$ G), but no clear evidence of ligand hyperfine arising from interaction with boron can be seen. At low temperatures, extreme broadening of the signal indicates formation of a rigid glass at about −80 °C; at −160 °C, the appearance of a sharp eight-line spectrum confirms $A_{vanadium}$, but no boron hyperfine is observed.

The stable existence of **1**, which has exhibited no signs of decomposition on standing in air for months or on repeated chromatography in organic solvents, seems to reflect the ability of $R_2C_2B_4H_4^{2-}$ carborane ligands to stabilize unusual organometallic structures and metal–hydrocarbon bonding modes.[1,10] Investigations in this area are continuing.

Acknowledgment. This work was supported by the National Science Foundation, Grant CHE 81-19936.

Supplementary Material Available: Tables of positional and thermal parameters (2 pages). Ordering information is given on any current masthead page.

---

[7] Crystal data: space group $Pna2_1$, $a = 14.264$ (5) Å, $b = 12.595$ (4) Å, $c = 8.449$ (2) Å, $V = 1518$ Å^3; $Z = 4$; $2\theta_{max} = 52°$ (Mo Kα radiation); 1506 reflections were collected, of which 1271 had $F_0^2 > 3\sigma(F_0^2)$ and were used in refinement, which gave final R and R_w values of 0.047 and 0.053. An absorption correction was applied (absorption coefficient = 6.7; maximum and minimum transmission coefficients = 0.90 and 0.88). Full details on this structure determination will be reported later.

[8] (a) Grimes, R. N. In "Comprehensive Organometallic Chemistry"; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 1. (b) Grimes, R. N. *Acc. Chem. Res.* **1983**, *16*, 22 and references therein.

[9] Based on formal assignments of six- and ten-electron bonding interactions between V^{4+} (one electron) and the $(C_2H_5)_2C_2B_4H_4^{2-}$ and $C_8H_8^{2-}$ ligands, respectively. Our assumption that the electron deficiency resides on the metal, rather than in the metallacarborane framework bonding MOs, is consistent with the observation of regular closo geometry in **1** and in several earlier examples; see: Maynard, R. B.; Wang, Z.-T.; Sinn, E. *Inorg. Chem.*, in press, and papers cited therein.

[10] Abstracts of Papers, 182nd National Meeting of the American Chemical Society, New York, Aug 1981; INOR-10, INOR-11.

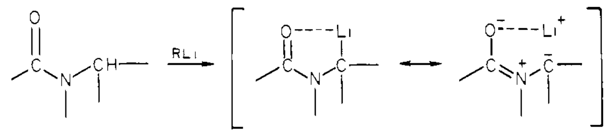
Dipole-Stabilized Carbanions: Evidence for a Complex in the α′-Lithiation of *N*,*N*-Dimethyl-2,4,6-triisopropylbenzamide

Munther Al-Aseer, Peter Beak,* David Hay, Dale J. Kempf, Sander Mills, and Stanley G. Smith*

Roger Adams Laboratory, Department of Chemistry
University of Illinois, Urbana, Illinois 61801

Received November 5, 1982

Although interaction of the metal of an organolithium base with a directing group in a complex formed prior to metalation often is postulated to be an important factor in determining the regiochemistry of the reaction, direct experimental evidence that relates the complex to the lithiation has been lacking.[1] For example, in the formation of dipole-stabilized carbanions from amides, the difference between the experimental observation of syn α′ lithiation, shown for the conversion of **1** to **2**, and ab initio SCF calculations, which predict the anti isomer should be favored as the free carbanion, is attributed to association of the lithium with the carbonyl oxygen, a postulate consistent with strong lithium ion–amide binding.[2-5]



1 2

---

[1] Suggestions of lithium complexes in metalations generally are reasonable interpretations based on established donor–acceptor interactions. (a) For cases involving ortho lithiations see: Jastrzebski, J. T. B. H.; van Koten, G.; Konijn, M.; Stam, C. H. *J. Am. Chem. Soc.* **1982**, *104*, 5490. Ellison, R. A.; Kotsonis, F. N. *Tetrahedron* **1973**, *29*, 805. Finnegan, R. A.; Altschemd, J. W. *J. Organomet. Chem.* **1967**, *9*, 193. For an excellent review see: Gschwend, H. W.; Rodriguez, H. R. *Org. React.* **1979**, *26*, 1. (b) For cases involving formally dipole-stabilized carbanions see: Beak, P.; Reitz, D. B. *Chem. Rev.* **1978**, *78*, 275.

[2] Rondan, N. G.; Houk, K. N.; Beak, P.; Zajdel, W. J.; Chandrasekhar, J.; Schleyer, P. V. R. *J. Org. Chem.* **1981**, *46*, 4316.

[3] Lithiation of primarily the syn-methyl group has been established for **3** under similar reaction conditions: Schlecker, R.; Seebach, D.; Lubosh, W. *Helv. Chim. Acta* **1978**, *61*, 3100.

[4] The syn- and anti-methyl groups of **3** are nonequivalent on the laboratory time scale. For a related case see: Staab, H. A.; Lauer, D. *Chem. Ber.* **1968**, *101*, 864.

0002-7863/83/1505-2080$01.50/0 © 1983 American Chemical Society