

**Figure 2.** An ORTEP drawing of the  $W_2(2\text{-Me-allyl})_2(NMe_2)_4$  molecule showing the gauche ethane-like central  $CN_2W=WN_2C$  core. Thermal ellipsoids are drawn at a 50% probability limit. H atoms, which were refined anisotropically, have been given an artificially small thermal parameter and are shown as open circles. Pertinent bond distances (Å) and angles (deg) (averaged where appropriate) are as follows:  $W-W = 2.286$  (1),  $W-N = 1.96$  (1),  $W-C = 2.18$  (1),  $C-C = 1.50$  (2) and  $C=C = 1.34$  (2),  $W-W-N = 104$  (1),  $W-W-C = 100$  (1).

the correct symmetry to interact with the  $M-M$   $\pi$ -bonding orbitals which are filled in unbridged  $(M\equiv M)^{6+}$  containing compounds. The symmetry match is shown schematically by IV. Fenske-Hall calculations on the model compound  $W_2(NH_2)_4(\mu-C_3H_5)_2$  using the atomic coordinates found for  $W_2(\mu-C_3H_5)_2(NMe_2)_4$  indicate<sup>9</sup> that there is indeed a mixing of  $M-M$   $\pi$ , allyl,  $\pi^*$ , and filled N p orbitals such that back-bonding from the  $d^3-d^3$  center is understandable in causing a lengthening of the  $W-W$  distance and the  $C-C$  distances in the  $\mu$ -allyl ligand. Note the  $C-C$  bond distances 1.47 Å (av) are as expected for  $C_{sp^2}-C_{sp^2}$  single bonds<sup>10</sup> and the  $W-W$  distance of 2.48 Å is typical of a  $(W=W)^{8+}$  distance.<sup>11</sup>

Because of the presence of two isomers in solution, for the  $W_2(\mu-\eta^3-C_3H_5)_2(NMe_2)_4$  compound, we sought to prepare the 2-methylallyl analogue and indeed reactions employing  $C_4H_7MgCl$  (2 equiv) and  $W_2Cl_2(NMe_2)_4$  yield  $W_2(C_4H_7)_2(NMe_2)_4$ , as a hydrocarbon-soluble crystalline product. The  $^1H$  and  $^{13}C$  NMR spectra of this compound in toluene- $d_8$  over the temperature range +80 to -100 °C were indicative of a mixture of anti and gauche ( $\sim 1:5$ )  $W_2R_2(NMe_2)_4$  ( $M\equiv M$ ) compounds.<sup>12</sup> Most notable was the large diamagnetic anisotropy exerted by the  $M\equiv M$  bond and the typical barriers to rotation about  $M-N$  bonds. It was also evident that the bonding of the 2-methylallyl ligand was undergoing a  $\sigma \rightleftharpoons \pi$  interconversion such that the methylene protons were not frozen-out even at -100 °C, though at this temperature exchange was sufficiently slow that they were broadened into the base line. The molecular structure found in the solid state is shown in Figure 2.

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(12)  $^1H$  NMR (toluene- $d_8$ , 300 MHz), -80 °C: gauche rotamer,  $NMe$  4.11 ppm, s, 1 H, 4.10 ppm, s, 1 H, 2.44 ppm, s, 1 H, 2.41 ppm, s, 1 H;  $(CH_2)_2CMe$ , 1.87 ppm, s, 1 H,  $(CH_2)_2CMe$ , 4.00 ppm, v br; anti rotamer,  $NMe$ , 4.07 ppm, s, other resonances obscured. +24 °C: gauche rotamer,  $NMe$  4.10 ppm, s, br, 6 H, 3.95 ppm, v br, 2.56 ppm, v br, 2.47 ppm, s, br, 6 H,  $(CH_2)_2CMe$ , 1.73 ppm, s, 6 H,  $(CH_2)_2CMe$ , 3.78 ppm, s, 8 H; anti rotamer,  $(CH_2)_2CMe$ , 1.74 ppm, s,  $\sim 1$  H,  $(CH_2)_2CMe$ , s,  $\sim 1.4$  H,  $NMe$  in base line at this temperature.  $^{13}C$  NMR (benzene- $d_6$ , 125.8 MHz) 23 °C: gauche isomer (multiplicity  $^1H$  coupled in parentheses)  $NMe$ , 59.7 ppm (q), br, 57.0 ppm, v br; 42.0 ppm, br, 40.7 ppm (q), br,  $(CH_2)_2CMe$ , 25.5 ppm (q),  $(CH_2)_2CMe$ , 82.8 ppm (t),  $(CH_2)_2CMe$ , 150.7 ppm (s); anti rotamer  $(CH_2)_2CMe$ , 25.6 ppm (t),  $(CH_2)_2CMe$ , 82.0 ppm (t),  $(CH_2)_2CMe$ , 151.2 ppm (s);  $NMe$  carbons are in base line at this temperature.

While we are not able to unequivocally assign the NMR spectra for the  $W_2(C_3H_5)_2(NMe_2)_4$  compound, it is not unreasonable to suppose that there exists a slow (NMR time scale) equilibrium between the isomers  $W_2(\mu-\eta^3-C_3H_5)_2(NMe_2)_4$  and the  $\sigma$ -allyl isomer  $W_2(\eta^1-C_3H_5)_2(NMe_2)_4$ . Substitution of allyl by 2-Me-allyl causes sufficient steric crowding at the dinuclear center such that the  $\mu-\eta^3-C_4H_7$  ligand is not observed. Although some questions remain, it is important to recognize what the present findings demonstrate. (1) That as  $\sigma^2 + \pi^2$  donors  $NMe_2^- > allyl^-$ , hence the ethane-like central  $(C)N_2W=WN_2(C)$  moiety in  $W_2(\eta^1-C_4H_7)_2(NMe_2)_4$ . (2) The ability of the allyl ligand to accept electron density from the dinuclear center is maximized when it spans the  $d^3-d^3$  center. The importance of the interactions between III and IV are (a) manifest in the long  $W-W$  and  $C-C$  distances in the  $W_2(\mu-\eta^3-C_3H_5)_2(NMe_2)_4$  and (b) require that the  $\mu-\eta^3-C_3H_5$  ligands be mutually cis. The importance of this type of  $\mu-\eta^3-C_3$  type of interaction has not been recognized heretofore—although a pair of cis bridging ligands have been seen in the solid-state structures of  $Cr_2(allyl)_4$ <sup>14</sup> and  $Mo_2(allyl)_4$ .<sup>15</sup>

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**Supplementary Material Available:** Tables of atomic positional parameters and complete listings of bond angles and bond distances and stereoviews (11 pages). Ordering information is given on any current masthead page.

(13) Crystal data for  $W_2(C_4H_7)_2(NMe_2)_4$  at -155 °C:  $a = 18.283$  (2) Å,  $b = 10.584$  (2) Å,  $c = 13.285$  (2) Å,  $\beta = 118.35$  (1)°,  $Z = 4$ ,  $d_{\text{calc}} = 1.92$  g  $cm^{-3}$  and space group  $P2_1/a$ . Of 3585 reflections collected (Mo  $K\alpha$ , 6° <  $2\theta$  < 45°), 2952 were unique, and the 2715 having  $F > 2.33\sigma(F)$  were used in the full-matrix least-squares refinement. Final residuals are  $R(F) = 0.0407$  and  $R_w(F) = 0.0418$ .

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## Concave Functionality: Some Exceptionally Large Binding Constants of Phenol Sticky Hosts

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There is a considerable current interest in the design of host molecules possessing rigidly defined cavities capable of avidly binding guests with a high degree of specificity.<sup>1-4</sup>

We have previously reported the synthesis of cyclophane **1** (the major isomer of the indicated cyclization) (see Scheme 1). By virtue of its concave-oriented pyridine it binds phenols in nonaqueous media with high specificity<sup>5</sup> and binding constants ( $K_{\text{assoc}} \sim 3000 M^{-1}$  for *p*-nitrophenol).

Contrary to our expectations<sup>6</sup> the minor meso isomer **2** is far and above the better phenol binder of the two hosts. The following observations are salient.

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(5) Acid para substituted phenols only. Ortho and meta substituents do not fit into the cavity.

(6) Based on comparable cavity size and the greater rigidity of **1**.

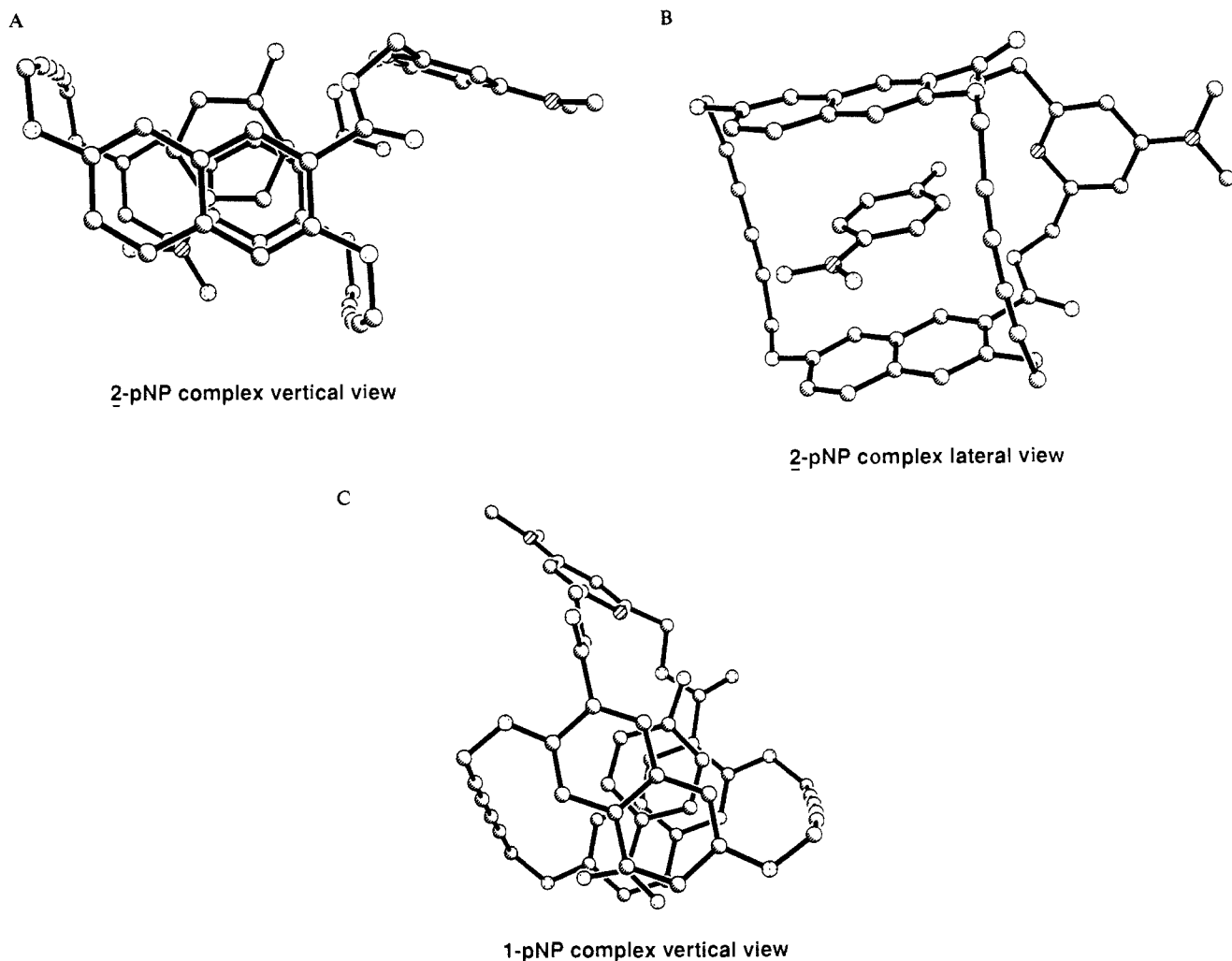
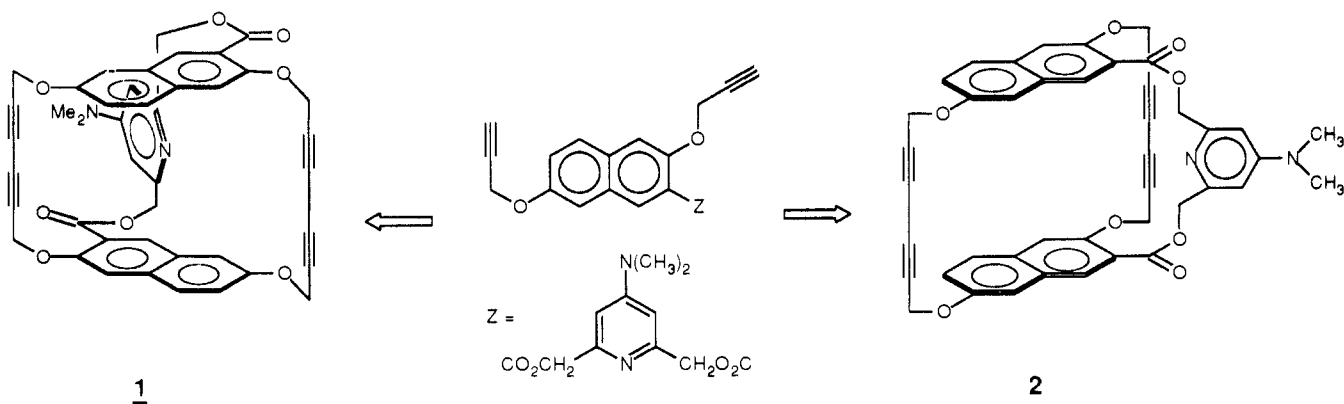


Figure 1. (A) 2-pNP complex vertical view, (B) 2-pNP complex lateral view, and (C) 1-pNP complex vertical view.

Scheme I



(1) In  $\text{CDCl}_3$ ,  $K_{\text{assoc}}^7$  for phenols and **2** are 4–8 times larger than for **1**. For *p*-nitrophenol and **2**  $K_{\text{assoc}} = 13\,700\ \text{M}^{-1}$  ( $3000\ \text{M}^{-1}$  for **1**); for 4-(2',4'-dinitrophenylazo)phenol,  $12\,600\ \text{M}^{-1}$  ( $2200\ \text{M}^{-1}$  for **1**); for *p*-cyanophenol,  $9800\ \text{M}^{-1}$  ( $1150\ \text{M}^{-1}$  for **1**); for 4-(4'-nitrophenylazo)phenol,  $3420\ \text{M}^{-1}$  ( $525\ \text{M}^{-1}$  for **1**).

(2) The binding magnification associated with **2** is such that even benzoic acids bind,  $K_{\text{assoc}} = 5700\ \text{M}^{-1}$  for **2** and *p*-propoxybenzoic acid (versus  $<100\ \text{M}^{-1}$  for **1**). This is the first indication that these concave functionalized hosts may show anything other than phenol stickiness.

(3) There is good agreement between the chemical shifts of protons in the 1:1 host–guest complex as determined by the regression analysis and by direct observation of complex at low temperature. The NMR of a **2**-pNP solution ( $\text{CDCl}_3$ ) broke into two separate spectra at  $-40\ ^\circ\text{C}$ .<sup>8</sup> The  $\delta$  (host H1) of 7.59 may be compared with  $\delta$  7.41 calculated ( $23^\circ$ ) from the titration. Similar results were observed for a number of host–phenol interconversions.

(4) Titration of **2** (and **1**) with phenols over a temperature range permits calculation of  $\Delta H^\circ$  and  $\Delta S^\circ$  for complex formation.  $\Delta S^\circ$  values are negative, ranging from  $-2\ \text{eu}$  (**1** and 4-(4'-nitro-

(7) Determined by NMR titrations and nonlinear regression as in ref 1. Because of convergence problems of the regression technique employed those  $K_{\text{assoc}} > 10^4\ \text{M}^{-1}$  are inexact: they are lower limits.

(8) This corresponds to  $\Delta G^\ddagger \cong 11\ \text{kcal/mol}$  for the host–complex interconversion at  $-40\ ^\circ\text{C}$ .

phenylazo)phenol) to  $-22$  eu (**2** and 4-hydroxy-4'-nitrostilbene). This has a dramatic effect on the temperature dependence of  $K_{\text{assoc}}$ : at  $-17$  °C **2** and the nitrostilbene have  $K_{\text{assoc}}$  of  $25\,900\text{ M}^{-1}$ ; at  $-22$  °C **2** and the nitrophenylazophenol have  $K_{\text{assoc}}$  in excess of  $44\,000$ .

(5) As was the case with **1** the **2**-pNP complex could be isolated. Its single-crystal X-ray (two views) is shown below together with a vertical view of **1**-pNP. The complexes are qualitatively the same; the guest pNP is docked within the cavity and tied down by a single hydrogen bond to the pyridine. There is however one striking difference between the complexes. In **1**-pNP the pyridine is held rigidly pointing into the cavity, while in **2**-pNP the pyridine parallels the cavity walls, forming a near ideal hydrogen bond with the projecting phenolic hydroxyl. We suggest that it is the flexibility of **2**, its ability to undergo minor conformational changes to accommodate the guest, that inter alia accounts for the remarkably stable nature of **2**-phenol complexes.<sup>9</sup> An excess of rigidity is perhaps not for the best.

(9) Partial support by the National Science Foundation.

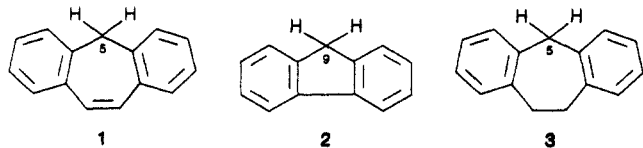
### Enhanced Formation of $8\pi(4n)$ Conjugated Cyclic Carbanions in the Excited State: First Example of Photochemical C-H Bond Heterolysis in Photoexcited Suberene

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The formation of carbanions via ionization of carbon acids is well-known in the ground state.<sup>1</sup> Förster cycle<sup>2</sup> calculations of a number of hydrocarbons and their conjugate bases show that the benzylic protons of these compounds become vastly more acidic in the excited singlet state, by as many as 30 orders of magnitude. However, to our knowledge, there are no known examples of C-H bond heterolysis in the excited state, although Förster cycle calculations indicate that hydrocarbons such as fluorene ( $\text{p}K_{\text{a}}(\text{S}_1) \approx -9$ )<sup>2</sup> should ionize readily in the singlet excited state, in neutral or even acidic medium, and therefore should be expected to undergo rapid exchange of the acidic proton with solvent protons (or deuterons). Tolbert<sup>2a</sup> noted that experimental verification of the increased thermodynamic acidity of these hydrocarbons in the excited state has not been available because of the inherent slow rate of proton transfer from carbon, which does not compete favorably with other deactivational processes available for excited states. We report here the first example of photochemical C-H bond ionization, in which 5H-dibenzo[*a,d*]cycloheptene (**1**) (su-



berene) on photolysis in  $\text{D}_2\text{O}/\text{CH}_3\text{CN}$  undergoes rapid proton exchange at the benzylic 5-position (for deuterium). Additionally, the proposed carbanion intermediate is an  $8\pi(4n)$  system (in the

\*NSERC Canada University Research Fellow, 1984-1989.

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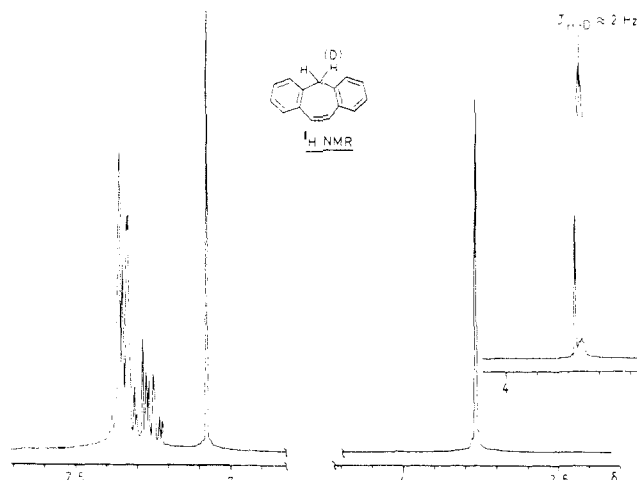
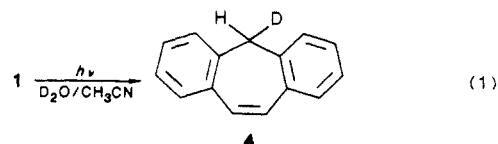


Figure 1. Proton (250 MHz) NMR of suberene (**1**) before and after photolysis. The upper insert is the spectrum of the photolyzed sample showing decrease in intensity of the methylene singlet of **1** at  $\delta$  3.78 and formation of the methylene proton of **4** at  $\delta$  3.76 as a 1:1:1 triplet ( $J_{\text{H-D}} \approx 2$  Hz). The region  $\delta$  7-7.4 remains unchanged in the photolyzed sample.

internal cyclic array), which has antiaromatic character in the ground state, but its formation is greatly enhanced in the excited state, compared to the corresponding carbanions derived from fluorene (**2**,  $6\pi$  internal cyclic array) and 10,11-dihydro-5H-dibenzo[*a,d*]cycloheptene (suberane) (**3**, nonconjugated internal array) systems, which do not undergo observable benzylic proton exchange on excitation.

We recently reported<sup>3</sup> that the suberenyl carbanion<sup>4</sup> is formed much more efficiently than similar dibenzannulated carbanions, including the fluorenyl anion, via photodecarboxylation of the corresponding carboxylic acids. Cycloheptatrienyl anions in the ground state have been shown to be antiaromatic or at least greatly destabilized compared to similar systems lacking the  $8\pi$  conjugated cyclic array.<sup>5</sup> We made the hypothesis<sup>3</sup> that in the excited singlet state, ground-state antiaromatic carbanions are stabilized compared to ground-state aromatic carbanions or related nonconjugated cyclic systems. As an additional test of this hypothesis, suberene (**1**) should have a much greater propensity to undergo benzylic C-H bond heterolysis than fluorene (**2**) or suberane (**3**). Photolysis of  $10^{-3}$  M solution of **1** in 50%  $\text{D}_2\text{O}/\text{CH}_3\text{CN}$  (v/v) at 254 nm in a Rayonet reactor for 30-60 min resulted in  $\approx 40\%$  conversion to  $\alpha$ -deuteriosuberene (**4**) (eq 1). Photodecomposition



of **1** was insignificant. No deuterium incorporation was observed when an identical solution was kept in the dark. The quantum yield for formation of **4** is ca. 0.03, which is low but substantial for such a process. The structure of **4** was confirmed by its mass spectrum and more definitively by both  $^1\text{H}$  (250 MHz) and  $^{13}\text{C}$  NMR. As shown in Figure 1, the product mixture after photolysis in  $\text{D}_2\text{O}/\text{CH}_3\text{CN}$  of a sample of pure **1** consists of two methylene signals: a sharp singlet at  $\delta$  3.78 due to **1** and a 1:1:1 triplet ( $J_{\text{H-D}} \approx 2$  Hz) at  $\delta$  3.75 due to **4**. Integration of these two methylene signals gave a yield of 40-50% of **4**, after taking into account that **4** has only one observable proton per molecule. The aromatic and

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