equatorial sites.[32] The inclusion of the Si–Si bond in two fused three-membered rings can help explain its length.[33]

Acknowledgment. We thank Dr. William Kroenke of BFGoodrich Co. for mass spectra, Professor Robert West for providing information prior to publication, and the Office of Naval Research for support.

Registry No. 1a, 113999-66-9; **1b**, 113999-67-0; **1c**, 113999-68-1; $PtCl_2(PEt_3)_2$, 15390-95-1; $LiSiHPh_2$, 17950-77-5; $PhSiH_3$, 694-53-1.

Supplementary Material Available: Tables of data collection and refinement details, atomic positional parameters, thermal parameters, and bond lengths and angles for the cocrystallized dimers **1a–c** and dichloride dimer **1b** (10 pages); observed and calculated structure factors for **1a–c** and **1b** (27 pages). Ordering information is given on any current masthead page.

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Diallyl- and Bis(2-methylallyl)tetrakis(dimethylamido)ditungsten: $W_2(\mu\text{-}\eta^3\text{-}C_3H_5)_2(NMe_2)_4$ and $W_2(\eta^1\text{-}C_4H_7)_2(NMe_2)_4$ (M≡M). Comments on Ligand–Metal π-Interactions at $(W{\equiv}W)^{6+}$ Centers

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Received February 8, 1988

We have now established a fairly extensive chemistry surrounding d^3–d^3 dinuclear compounds of molybdenum and tungsten.[1] We are currently examining the relative π-donating abilities of ligands in unbridged ethane-like dimers and recently reported[2] the preparation and characterization of $1,2\text{-}M_2(P(t\text{-}Bu)_2)_2(NMe_2)_4$ compounds. The relative π-donating abilities of the ligands were in the order $NMe_2^- > P(t\text{-}Bu)_2^-$. We were curious to examine how allyl ligands might compete with NMe_2^- ligands in compounds of formula $1,2\text{-}M_2X_2(NMe_2)_4$ (X = allyl). The compounds could be analogues to the alkyl, aryl, and benzyl complexes (X = R, Ar, or Bz) previously reported having M–C σ-bonds,[3,4] or alternatively the π-donating properties of the hydrocarbyl ligands could compete with the NMe_2 ligands causing quite different structures. We report here our initial findings.

The reaction between allylmagnesium bromide (2 equiv) and $1,2\text{-}W_2Cl_2(NMe_2)_4$ in ether leads to a brown, hexane-soluble crystalline product. The variable temperature ^1H and ^{13}C NMR spectra are complex and indicate the presence of two isomers in solution.[5] Exchange between these isomers is not rapid on the NMR time-scale. Crystals suitable for an X-ray study[6] were obtained, and the molecular structure in the solid state is shown in Figure 1.

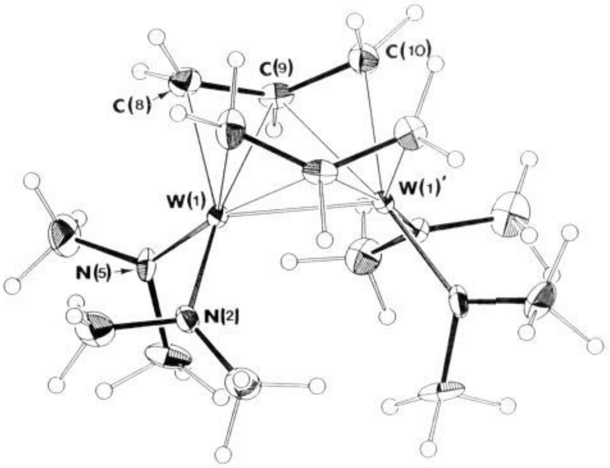
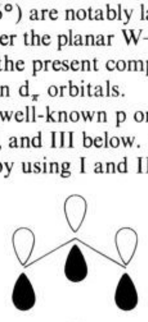


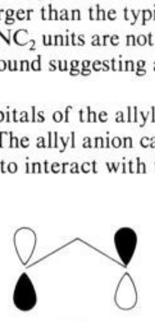
Figure 1. An ORTEP drawing of the $W_2(allyl)_2(NMe_2)_4$ molecule giving the atom number scheme for the pertinent atoms. Thermal ellipsoids are drawn at a 50% probability limit. H atoms, which were refined isotropically, have been given an artificially small thermal parameter and are shown as open circles. Pertinent bond distances (Å) and angles (deg) are as follows: W–W = 2.480 (1); W(1)–N(2) = 1.97 (1), W(1)–N(5) = 1.99 (1), W(1)–C(8) = 2.22 (1), W(1)–C(9) = 2.44 (2), W(1)–C(9)′ = 2.46 (1), W(1)′–C(10) = 2.22 (1), C(8)–C(9) = 1.474 (19), C(9)–C(10) = 1.465 (19), W(1)′–W(1)–N(2) = 112.2 (3), W(1)′–W(1)–N(5) = 115.6 (3), W(1)′–W(1)–C(8) = 94.7 (3), W(1)′–W(1)–C(9) = 60.1 (3), W(1)′–W(1)–C(10) = 89.4 (4), and C(8)–C(9)–C(10) = 129.7 (12).

The structure is quite unlike any other seen for a d^3–d^3 ditungsten compound, and it is apparent that the μ-allyl ligand has caused a significant change in the bonding of the central $(W{\equiv}W)^{6+}$ unit. For example, in contrast to ethane-like $W_2X_2(NMe_2)_4$ or bridged $W_2(L\text{-}L')_2(NMe_2)_4$ structures (L-L = triazine[7] or the anion derived from 2-hydroxypyridine[8]) the W–W–N angles (112° and 116°) are notably larger than the typical values of 103–105°. Moreover the planar $W\text{–}NC_2$ units are not aligned along the M–M axis in the present compound suggesting a rehybridization of the tungsten d_π orbitals.

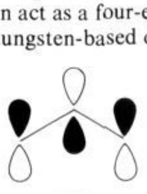
The well-known p orbitals of the allyl fragment are depicted by I, II, and III below. The allyl anion can act as a four-electron donor by using I and II to interact with tungsten-based orbitals in the *xy* plane (defining the *z* axis as the M–M axis). It then becomes apparent that the antibonding orbital of allyl, III, has



I



II



III

IV

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[5] ^{13}C NMR (–60 °C, toluene-d_8) isomer 1: 85.5 ($^1J_{C\text{-}H}$ = 174 Hz), *C*H; 56.7 ($^1J_{C\text{-}W}$ = 39 Hz, $^1J_{C\text{-}H}$ = 145 Hz), CH_2; 41.5 ($^1J_{C\text{-}H}$ = 151 Hz), CH_2; isomer 2: 76.3 ($^1J_{C\text{-}H}$ = 149 Hz), *C*H; 67.3 ($^1J_{C\text{-}W}$ = 21 Hz, $^1J_{C\text{-}H}$ = 149 Hz), CH_2; $N(CH_3)_2$, 48.8, 46.0, 45.9.

[6] Crystal data for $W_2(allyl)_2(NMe_2)_4$ at –155 °C: $a = 10.840$ (2) Å, $b = 7.886$ (1) Å, $c = 11.159$ (3) Å, $\beta = 96.24$ (2)°, $Z = 2$, $d_{calcd} = 2.193$ g cm^{-3}. Of 2017 reflections collected, $6° < 2\theta < 45°$, 1241 were unique, and the 1145 having $F > 2.33\sigma$ were used in the refinement. Final residuals are $R(F) = 0.037$ and $R_w(F) = 0.041$.

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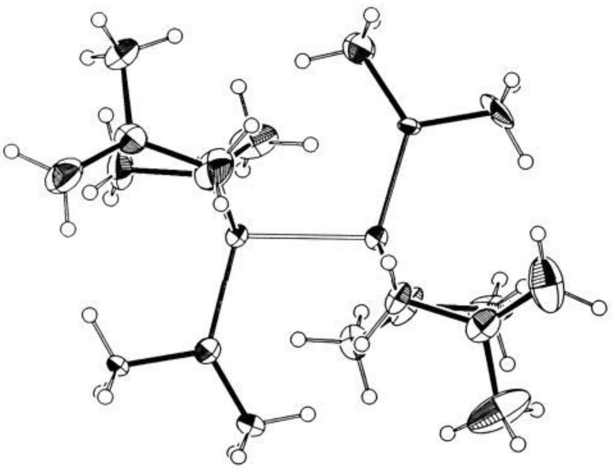

Figure 2. An ORTEP drawing of the $W_2(2\text{-Me-allyl})_2(NMe_2)_4$ molecule showing the gauche ethane-like central $CN_2W{\equiv}WN_2C$ core. Thermal ellipsoids are drawn at a 50% probability limit. H atoms, which were refined anisotropically, have been given an artificially small thermal parameter 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 π-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 $W_2(NH_2)_4(\mu\text{-}C_3H_5)_2$ using the atomic coordinates found for $W_2(\mu\text{-}C_3H_5)_2(NMe_2)_4$ indicate[9] that there is indeed a mixing of M–M π, allyl, π*, 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 μ-allyl ligand. Note the C–C bond distances 1.47 Å (av) are as expected for C_{sp^2}–C_{sp^2} single bonds[10] and the W–W distance of 2.48 Å is typical of a $(W{=}W)^{8+}$ distance.[11]

Because of the presence of two isomers in solution, for the $W_2(\mu\text{-}\eta^3\text{-}C_3H_5)_2(NMe_2)_4$ 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 (~1:5) $W_2R_2(NMe_2)_4$ (M≡M) compounds.[12] Most notable was the large diamagnetic anisotropy exerted by the M≡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 $\sigma \rightleftarrows \pi$ 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.

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 $W_2(\mu\text{-}\eta^3\text{-}C_3H_5)_2(NMe_2)_4$ and the σ-allyl isomer $W_2(\eta^1\text{-}C_3H_5)_2(NMe_2)_4$. Substitution of allyl by 2-Me-allyl causes sufficient steric crowding at the dinuclear center such that the $\mu\text{-}\eta^3\text{-}C_4H_7$ 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 $(C)N_2W{\equiv}WN_2(C)$ moiety in $W_2(\eta^1\text{-}C_4H_7)_2(NMe_2)_4$. (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 $W_2(\mu\text{-}\eta^3\text{-}C_3H_5)_2(NMe_2)_4$ and (b) require that the $\mu\text{-}\eta^3\text{-}C_3H_5$ ligands be mutually cis. The importance of this type of $\mu\text{-}\eta^3\text{-}C_3$ type of interaction has not been recognized heretofore—although a pair of cis bridging ligands have been seen in the solid-state structures of $Cr_2(\text{allyl})_4$[14] and $Mo_2(\text{allyl})_4$.[15]

Acknowledgment. We thank the National Science Foundation for support. K.G.M. acknowledges support from CSIR, South Africa and the University of Durban-Westville for study leave.

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.

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(12) ^1H NMR (toluene-d_8, 300 MHz), −80 °C: gauche rotamer, N*Me* 4.11 ppm, s, 1 H, 4.10 ppm, s, 1 H, 2.44 ppm, s, 1 H, 2.41 ppm, s, 1 H; $(CH_2)_2$C*Me*, 1.87 ppm, s, 1 H, $(\mathit{CH_2})_2$CMe, 4.00 ppm, v br; anti rotamer, N*Me*, 4.07 ppm, s, other resonances obscured. +24 °C: gauche rotamer, N*Me* 4.10 ppm, s, br, 6 H, 3.95 ppm, v br, 2.56 ppm, v br, 2.47 ppm, s, br, 6 H, $(CH_2)_2$C*Me*, 1.73 ppm, s, 6 H, $(\mathit{CH_2})_2$CMe, 3.78 ppm, s, 8 H; anti rotamer, $(CH_2)_2$C*Me*, 1.74 ppm, s, ~1 H, $(\mathit{CH_2})_2$CMe, s, ~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) N*Me*, 59.7 ppm (q), br, 57.0 ppm, v br; 42.0 ppm, v br, 40.7 ppm (q), br, $(CH_2)_2$C*Me*, 25.5 ppm (q), $(\mathit{C}H_2)_2$CMe, 82.8 ppm (t), $(CH_2)_2$*C*Me, 150.7 ppm (s); anti rotamer $(CH_2)_2$C*Me*, 25.6 ppm (t), $(\mathit{C}H_2)_2$CMe, 82.0 ppm (t), $(CH_2)_2$*C*Me, 151.2 ppm (s); NMe carbons are in base line at this temperature.

(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, β = 118.35 (1)°, Z = 4, d_{calcd} = 1.92 g cm^{-3} and space group $P2_1/a$. Of 3585 reflections collected (Mo Kα, 6° < 2θ < 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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Received January 28, 1988

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.[1–4]

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

Contrary to our expectations[6] 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**.

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