from the reaction of **5a** with methylenetriphenylphosphorane (Scheme II).[12]

Our findings indicate that this new reaction type leading to **1c** is fundamentally different from the previously reported base-induced formation of **1a**.[4] The intramolecular H transfer in the postulated (η^2-aryne)($CH_2{=}PPh_3$)$ZrCp_2$ intermediate can formally be described as a homo-1,3-hydrogen migration: an organometallic analogue of a thermally induced methylcyclopropane to 1-butene rearrangement. The question whether the organometallic hydrogen shift proceeds by a similar stepwise mechanism[13] is the subject of further studies.

Acknowledgment. Financial aid from the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie (grants to G.E.) is gratefully acknowledged.

Registry No. **1c**, 96482-76-7; **2d**, 96482-77-8; **1e**, 96482-78-9; **2**, 3487-44-3; **3**, 37342-97-5; **4**, 12636-72-5; **5**, 51177-89-0; **5a**, 63672-39-9; **7**, 1291-45-8.

Supplementary Material Available: Listings of observed and calculated structure factors, anisotropic thermal parameters, atomic coordinates, interatomic distances, and bond angles (48 pages). Ordering information is given on any current masthead page.

---

[12] A mixture of **1d** and **1e** was obtained analogously to **1c** (71.2% isolated yield). Anal. Calcd for $C_{36}H_{33}PZr$ (587.85): C, 73.56; H, 5.66. Found: C, 73.04; H, 5.94. **1e** (para isomer): ^1H NMR (CD_2Cl_2) δ 5.85 (s, 10 H, Cp), 5.55 (d, $^2J_{HP}$ = 13.6 Hz, 1 H, C*H*=P), 1.24 (s, 3 H, CH_3), 6.67–8.09 (m, 19 H, Tol, PPh_3); $^{31}P\{^1H\}$ NMR (C_6D_6) δ 15.9; ^{13}C NMR (CD_2Cl_2) δ 108.3 (d, $^1J_{CH}$ = 172 Hz, Cp); 105.4 (dd, $^1J_{CH}$ = 116 Hz, $^1J_{CP}$ = 28 Hz, ylide-C), 176.9 (s, C1), 142.8 (d, $^1J_{CH}$ = 154 Hz, C2), 126.6 (d, $^1J_{CH}$ = 152 Hz, C3), 132.1 (s, C4), 21.2 (q, $^1J_{CH}$ = 126 Hz, CH_3), 128–135 (-PPh_3). **1d** (meta isomer): ^1H NMR (CD_2Cl_2) δ 5.85 (s, 10 H, Cp), 5.57 (d, $^2J_{HP}$ = 13.6 Hz, 1 H, C*H*=P), 1.17 (s, 3 H, CH_3), 6.67–8.09 (m, 19 H, Tol, PPh_3) $^{31}P\{^1H\}$ NMR (C_6D_6) δ 15.8; ^{13}C NMR (CD_2Cl_2) (atom numbering according to Figure 1) δ 108.2 (d, $^1J_{CH}$ = 172 Hz, Cp), 105.7 (dd, $^1J_{CH}$ = 116 Hz, $^1J_{CP}$ = 28 Hz, ylide-C), 181.5 (s, C1), 143.8 (d, $^1J_{CH}$ = 152 Hz, C2), 134.2 (s, C3), 123.9 (d, $^1J_{CH}$ = 154 Hz,C4), 125.3 (d, $^1J_{CH}$ = 154 Hz, C5), 139.7 (d, $^1J_{CH}$ = 154 Hz, C6), 21.8 (q, $^1J_{CH}$ = 125 Hz, CH_3), PPh_3: 134.7 (d, $^1J_{CP}$ = 80 Hz), 133.4 (dd, $^1J_{CH}$ = 162 Hz, $^1J_{CP}$ = 9 Hz, ortho-C), 128.7 (dd, $^1J_{CH}$ = 163 Hz, $^3J_{CP}$ = 11 Hz, meta-C), 131.2 (dd, $^1J_{CH}$ = 162 Hz, $^4J_{CP}$ = 2.5 Hz, para-C).

[13] Gajewski, J. J. "Hydrocarbon Thermal Isomerizations"; Academic Press: New York, 1981: pp 35–39.

A Skewed Bridging Alkyne Adduct of a d^3–d^3 Tungsten Dimer: $W_2(\mu\text{-}NMe_2)_2(\mu\text{-}C_2Me_2)Cl_4(py)_2$

Kazi J. Ahmed, Malcolm H. Chisholm,* and John C. Huffman

Department of Chemistry and Molecular Structure Center
Indiana University, Bloomington, Indiana 47405

Received March 13, 1985

Summary: Addition of MeC≡CMe (1 equiv) to a hydrocarbon solution of $W_2Cl_2(NMe_2)_4$ gives, in the presence of pyridine, $W_2Cl_2(NMe_2)_4(py)_2(\mu\text{-}C_2Me_2)\cdot py$, I, which is unstable with respect to ligand redistribution yielding $W_2Cl_4(NMe_2)_2(py)_2(\mu\text{-}C_2Me_2)$, II, and $W_2(NMe_2)_6$. Molecules of II have a virtual C_2 axis of symmetry and a W_2C_2 unit which appears intermediate between a dimetallatetrahedrane (a perpendicular alkyne adduct) and a 1,2-dimetallacyclobutadiene (a parallel alkyne adduct).

Bridging alkyne adducts of dinuclear transition-metal complexes fall into two general types, namely, those containing perpendicular (θ = 90°) or parallel (θ = 0°) bonded alkynes where the nomenclature is derived from the angle, θ, between the μ-C–C and M–M bond vectors.[1] Hoffman, Hoffmann, and Fisel[1] have elaborated upon the reasons for this general occurrence and noted that the preference for one structure over the other has in most instances an understandable electronic origin. Though deviations from the idealized perpendicular and parallel modes of bonding have been observed, the twisting has always been relatively small. Only in dinuclear compounds containing *two* bridging alkynes have the μ-C–C bond vectors been notably twisted, e.g., twisted from the idealized perpendicular geometry by an average of 11° in $Cp_2Nb_2(CO)_2(C_2Ph_2)_2$[2] and 20° in $(t\text{-}BuO)_4W_2(\mu\text{-}C_2Ph_2)_2$.[3] However, these compounds are not in the same class as 1:1 alkyne adducts and their limiting structures cannot conform to either dimetallatetrahedranes or 1,2-dimetallacyclobutadienes. We describe here our discovery of a compound where θ = 55° which is approaching the idealized intermediate geometry for the interconversion of a perpendicular acetylene (a dimetallatetrahedrane) with a parallel acetylene complex (a 1,2-dimetallacyclobutadiene). This finding contrasts with over a dozen structurally characterized alkyne adducts of d^3–d^3 tungsten dimers: $W_2(OR)_6(py)_n(\mu\text{-}C_2R_2')$[4-6] (R = *t*-Bu, *n* = 1, R′ = H; R = *i*-Pr, *n* = 2, R′ = H; R = CH_2-*t*-Bu, *n* = 2, R′ = H; R = CH_2-*t*-Bu, *n* = 1, R′ = Me, Et and Ph) and $W_2Cl_n(NMe_2)_{6-n}L_2(\mu\text{-}RCCR')$[7,8] (L = PMe_3, PMe_2Ph, or py; R = R′ = H, Me; R = H, R′ = Ph), all of which adopt the perpendicular bonding mode.

Addition of MeC≡CMe (1 equiv) to a toluene solution of $W_2Cl_2(NMe_2)_4$ in the presence of pyridine (>3 equiv) at room temperature produces a blue-green microcrystalline precipitate within 1.5 h. This solid is formulated as $W_2(\mu\text{-}NMe_2)_2(NMe_2)_2Cl_2(py)_2(\mu\text{-}C_2Me_2)\cdot(py)$, I, on the basis of elemental analyses and low-temperature ^1H NMR spectroscopy.[9] Compound I is not stable in aromatic hydrocarbon solvents at room temperature and is labile to ligand redistribution reactions. Compound II is isolated as an orange cyrstalline solid in ca. 70% yield based on the ligand redistribution reaction shown in eq 1.[9]

$$2W_2Cl_2(NMe_2)_4(py)_2(C_2M_2)\cdot(py) \xrightarrow[\text{toluene}]{25\ °C} \underset{\text{II}}{W_2Cl_4(NMe_2)_2(C_2Me_2)(py)_2} + W_2(NMe_2)_6 + MeCCMe + 4py \quad (1)$$

---

[1] Hoffman, D. M.; Hoffmann, R.; Fisel, C. R. *J. Am. Chem. Soc.* **1982**, *104*, 3858.

[2] Nesmayanov, A. N.; Gusev, A. I.; Pasynskii, A. A.; Asisimov, K. N.; Kolobova, N. E.; Struchkov, Yu. T. *J. Chem. Soc., Chem. Commun.* **1968**, 1365.

[3] Cotton, F. A.; Schwotzer, W.; Shamshoum, E. S. *Organometallics* **1983**, *2*, 1167.

[4] Chisholm, M. H.; Folting, K.; Hoffman, D. M.; Huffman, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 6794.

[5] Chisholm, M. H.; Hoffman, D. M.; Huffman, J. C. *Chem. Soc. Rev.* **1985**, *14*, 69.

[6] Chisholm, M. H.; Conroy, B. K.; Hoffman, D. M.; Huffman, J. C., results to be published.

[7] Ahmed, K. J.; Chisholm, M. H.; Folting, K.; Huffman, J. C. *J. Chem. Soc., Chem. Commun.* **1985**, 152.

[8] Ahmed, K. J.; Chisholm, M. H.; Huffman, J. C., results to be published.

[9] Dry and oxygen-free solvents and atmospheres were used throughout. Anal. Found (Calcd) for $W_2Cl_2(NMe_2)_4(py)_2(C_2Me_2)\cdot(py)$, I: C, 31.8 (32.3); H, 4.4 (4.5); N, 8.9 (9.8); Cl, 8.1 (7.1). For $W_2Cl_4(NMe_2)_2(py)_2(C_2Me_2)$, II: C, 26.5 (26.7); H, 3.4 (3.5); N, 6.8 (6.9); Cl, 17.3 (17.5). ^1H NMR data for $W_2Cl_2(NMe_2)_4(py)_2(C_2Me_2)\cdot py$ (−45 °C, 360 MHz, CD_2Cl_2, δ in ppm relative to Me_4Si): δ 7.10–9.25 (m, 15 H, py), 3.10 (s, 6 H, NMe), 2.96 (s, 6 H, NMe), 2.84 (s, 6 H, NMe), 2.80 (s, 6 H, NMe), 2.38 (s, 6 H, C_2Me_2). ^1H NMR data for II (+22 °C, 360 MHz, CD_2Cl_2): δ 9.23 (d, *J* = 7.5 Hz, 4 H, py), 8.03 (t, *J* = 7.04 Hz, 2 H, py), 7.62 (t, *J* = 7.3 Hz, 4 H, py), 4.23 (s, 6 H, NMe), 3.68 (s, 6 H, NMe), 2.45 (s, 6 H, C_2Me_2). $^{13}C\{^1H\}$ NMR spectral data for II (+22 °C, 75.4 MHz, CD_2Cl_2, δ in ppm relative to Me_4Si) δ 213.5 (C_2Me_2), 154.9, 140.2, 124.7 ($N\mathit{C}_5H_5$), 64.1, 57.0 ($N(\mathit{C}H_3)_2$), 22.2 ($C_2\mathit{Me}_2$).

0276-7333/85/2304-1312$01.50/0

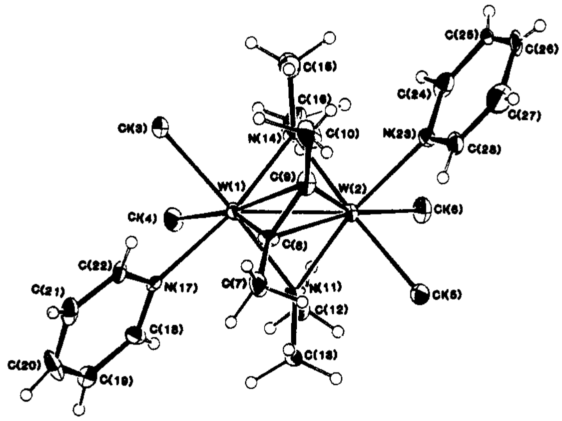


Figure 1. A view of the $W_2Cl_4(NMe_2)_2(py)_2(\mu\text{-}C_2Me_2)$ molecule looking down the virtual C_2 axis of symmetry, giving the number scheme for the non-hydrogen atoms. Selected bond distances (Å) and bond angles (deg) are W(1)–W(2) = 2.436 (1); W(1)–Cl(3) = 2.395 (3); W(1)–Cl(4) = 2.411 (3); W(1)–N(11) = 2.186 (9); W(1)–N(14) = 2.142 (9); W(1)–N(17) = 2.281 (9); W(1)–C(8) = 2.020 (11); W(1)–C(9) = 2.447 (11); W(2)–Cl(5) = 2.398 (3); W(2)–Cl(6) = 2.416 (3); W(2)–N(11) = 2.163 (9); W(2)–N(14) = 2.182 (9); W(2)–N(23) = 2.281 (10); W(2)–C(8) = 2.438 (11); W(2)–C(9) = 2.024 (11); C(8)–C(9) = 1.372 (17); W(1)–C(8)–C(7) = 144.2 (10); W(1)–C(8)–C(9) = 90.3 (8); W(2)–C(8)–C(7) = 138.1 (9); C(7)–C(8)–C(9) = 124.7 (12); W(1)–C(9)–C(8) = 55.6 (6); W(1)–C(9)–C(10) = 139.3 (9); W(2)–C(9)–C(8) = 89.7 (7); C(8)–C(9)–C(10) = 125.6 (11).

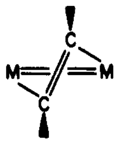
Compound II is very sparingly soluble in toluene and benzene but is appreciably soluble in methylene chloride and pyridine. The ^1H NMR data[9] for II in CD_2Cl_2 are consistent with expectations based on the molecular structure found in the solid state[10] which has a virtual C_2 axis of symmetry. See Figure 1.

As in a number of other alkyne adducts of d^3–d^3 Mo or W compounds, the geometry may superficially be viewed as derived from a confacial bioctahedron with two bridging NMe_2 ligands and one $\mu\text{-}C_2Me_2$ moiety forming the common face. However, the $\mu\text{-}C_2Me_2$ ligand in II is severely distorted from the perpendicular alkyne bonding mode previously seen.[4-8] The angle $\theta = 55°$ reveals a twist of 35° from the perpendicular orientation. The torsion angle C–C–C–C of the $\mu\text{-}C_2Me_2$ ligand is 42°. The C–C–C angle is 125° (averaged) close to those normally seen in parallel alkyne adducts and smaller than those typically seen for perpendicular alkyne adducts which span a range 135–150°.[1]

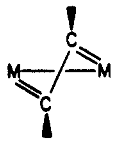
Initially one might wish to attribute the twisting of the μ-C–C bond vector relative to the W–W axis to steric pressure imposed by the $\mu\text{-}NMe_2$ ligands which have proximal and distal methyl groups with respect to the $\mu\text{-}C_2Me_2$ functionality. However, there is no apparent distortion of the $\mu\text{-}NMe_2$ ligands and space-filling diagrams do not support the notion that twisting occurs to relieve steric repulsive interactions. Thus we believe that an electronic reason must be sought. There are two features in II which have not been encountered previously. (1) The presence of four terminal Cl ligands and the absence of any strong π-donor ligand, such as NMe_2 or OR, in terminal positions. (2) The presence of a molecular C_2 axis of symmetry rather than a molecular plane of symmetry. Either or both of these factors could be responsible for favoring the twisted structure.

Without further speculation about the origin of the twist, the salient feature of note in the molecular structure of II is that we can see incipient 1,2-dimetallacyclobutadiene characteristics. (1) The W–W distance 2.44 Å is typical of a $(W{=}W)^{8+}$ bonding distance[11] and is notably shorter than those in perpendicular alkyne adducts of the $(W{\equiv}W)^{6+}$ center, which fall in the range 2.55–2.67 Å, more consistent with W–W single bonds and the description of the $W_2(C_2R_2)$ center as a dimetallatetrahedrane.[4-6] (2) The two very different W–C distances, 2.02 and 2.44 Å, are approaching M–C double[12] and nonbonding distances. Note the W–C distance of 2.02 Å is shorter than those seen in the ditungstatetrahedranes which were ca. 2.10 Å. Also the chemical shift for the $\mu\text{-}C_2$ carbon atoms is at 213.5 ppm relative to Me_4Si, suggestive of alkylidene character[12] and notably downfield from the range of carbon chemical shifts (120–160 ppm) in other $W_2(\mu\text{-}C_2R_2)$-containing compounds.

This leads us to suggest that the $W_2(\mu\text{-}C_2Me_2)$ moiety has bonding contributions that may be depicted by the valence bond descriptions shown in III and IV. These are intermediates between the limiting dimetallatetrahedrane and planar 1,2-dimetallacyclobutadiene descriptions that may be formed by the coupling of M≡M and C≡C bonds in the perpendicular and parallel modes, respectively.



III



IV

In view of the present finding it is interesting to speculate that the conversion of a perpendicular to parallel bonding mode for the alkyne may be involved in the reaction pathway leading to metathesis of W≡W and C≡C bonds (eq 2) which has been noted for a variety of acetylenes in their reactions with $W_2(OR)_6$ compounds.[4,13,14]

$$W{\equiv}W + RC{\equiv}CR \rightarrow W_2(\mu\text{-}C_2R_2) \rightarrow 2W({\equiv}CR) \quad (2)$$

Further studies are in progress.[15]

Registry No. I, 96503-06-9; II, 96503-07-0; $W_2(NMe_2)_6$, 54935-70-5; $W_2Cl_2(NMe_2)_4$, 63301-81-5; MeC≡CMe, 503-17-3.

Supplementary Material Available: Tables of fractional coordinates and isotropic thermal parameters, anisotropic thermal parameters, crystal data, bond distances, bond angles, and structure factor amplitudes, VERSORT drawings, ORTEP drawings, and space-filling-model drawings (39 pages). Ordering information is given on any current masthead page.

---

(10) Crystal data for II at −160 °C: $a = 10.918\ (4)$ Å, $b = 13.440\ (5)$ Å, $c = 16.558\ (7)$ Å, $\beta = 104.45\ (2)°$, $Z = 4$, $d_{calcd} = 2.29$ g cm^{-3}, and space group $P2_1/n$. Of the 4173 reflections collected (Mo Kα, $6° < 2\theta < 45$) 3093 were unique and the 2671 having $F > 3.00\sigma(F)$ were used in the full least-squares refinement (isotropic for H atoms and anisotropic for W, N, C, and Cl atoms). Final residuals are $R(F) = 0.039$ and $R_w(F) = 0.040$. The thermal elipsoids for C7–C10 are somewhat "misshaped". A difference Fourier phased on all atoms, excluding C7–C10, failed to indicate any disorder. We assume the large anisotropic shape is an artifact of the absorption correction as opposed to a thermal and/or disorder problem.

(11) For listings of W–W bond distances and W–W bond order assignments see: Chisholm, M. H. *Polyhedron* **1983**, *2*, 681.

(12) For a listing of W—C, W=C, and W≡C bond distances and correlations of ^{13}C carbon chemical shifts see ref 4 and Chisholm, M. H.; Hoffman, D. M.; Huffman, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 6815.

(13) Listemann, M. L.; Schrock, R. R. *Organometallics* **1985**, *4*, 74.

(14) Schrock, R. R.; Listemann, M. L.; Sturgeoff, L. G. *J. Am. Chem. Soc.* **1982**, *104*, 4291.

(15) We thank the National Science Foundation and the Wrubel Computing Center for support.