2264 *Organometallics* 1987, *6*, 2264-2265

$W_2(n\text{-Pr})_2(\eta^2\text{-}C_2Me_2)_2(O\text{-}i\text{-Pr})_4$, $W_2(\mu\text{-}C_2Me_2)_2(O\text{-}i\text{-Pr})_4$, and $W_4(\mu\text{-CEt})_2(\mu\text{-}C_2Me_2)_2(\eta^2\text{-}C_2Me_2)_2(O\text{-}i\text{-Pr})_6$. Competitive α- and β-CH Activation Pathways at a Dimetal Center

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Received May 26, 1987

Summary: 1,2-$W_2(R)_2(NMe_2)_4$ compounds (where R = *i*-Bu or *i*-Pr) react in hydrocarbon solvents with *i*-PrOH (4 equiv) and MeC≡CMe (2 equiv) to give $W_2(R)_2(\eta^2\text{-}C_2Me_2)_2(O\text{-}i\text{-Pr})_4$ (I), where R = *n*-Pr or *i*-Bu. Compound I(*n*-Pr) slowly reacts further in solution at room temperature (t_∞ = ca. 5 days) to give $W_2(\mu\text{-}C_2Me_2)_2(O\text{-}i\text{-Pr})_4$ (IIa) and $W_4(\mu\text{-CEt})_2(\mu\text{-}C_2Me_2)_2(\eta^2\text{-}C_2Me_2)_2(O\text{-}i\text{-Pr})_6$ (III) in a 1:2 ratio with elimination of propane, propene, and *i*-PrOH. Formally, the formation of IIa and III represent competing β- and α-CH activation processes, respectively. Formation of III is a rare example of a W–O bond cleavage facilitating W–C multiple-bond formation. The molecular structure of III reveals an unusual W_4 chain containing a grossly unsymmetrical crosswise $W_2(\mu\text{-}C_2)$ moiety. Thermal decomposition of I(*i*-Bu) produces IIa selectively in high yield.

Single-crystal X-ray crystallography often reveals new classes of compounds for which useful synthetic routes remain to be established. The structural characterization of $(t\text{-BuO})_2W(\mu\text{-}C_2Ph_2)_2W(O\text{-}t\text{-Bu})_2$,[1] as one component separable only by crystal selection from other products in the reaction between $W_2(O\text{-}t\text{-Bu})_6$(*M*≡*M*) and PhC≡CPh at +70 °C in toluene, suggested the possible existence of a new class of compounds of formula $(R'O)_2W(\mu\text{-}C_2R''_2)_2W(OR')_2$ (II). These species would represent isomers of $(R'O)_2W(\mu\text{-CR}'')(\mu\text{-}C_3R''_3)W(OR')_2$ compounds that we have recently prepared from C–C bond-forming reactions involving $(R'O)_2W(\mu\text{-CR}'')_2W(OR')_2$ compounds and alkynes.[2-4] We reasoned that a rational synthesis of the bis(alkyne)-bridged compounds II would involve a β-hydrogen atom initiated, alkyl group elimination (eq 1). This reaction is analogous to an established alkyl group disproportionation from a dinuclear molybdenum center.[5]

$$1,2\text{-}W_2R_2(OR')_4 + 2R''C{\equiv}CR'' \rightarrow (R'O)_2W(\mu\text{-}C_2R''_2)_2W(OR')_2 + \text{alkane} + \text{alkene} \quad (1)$$

We describe here our initial findings prompted by this line of reasoning. These studies show that α-CH activation competes effectively with β-CH activation to produce an interesting and unexpected divergence in products.

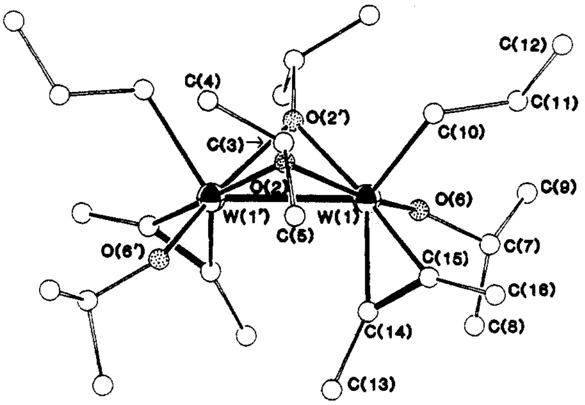

Figure 1. A ball-and-stick drawing of the $W_2(n\text{-Pr})_2(\eta^2\text{-}C_2Me_2)_2(O\text{-}i\text{-Pr})_4$ molecule. Pertinent bond distances (Å) and angles (deg) are as follows: W(1)–W(1)′ = 2.681 (1), W(1)–C(10) = 2.18 (1), W(1)–C(alkyne) = 2.05 (3) (average), W(1)–O(6) = 1.88 (1), W(1)–O(2) = 2.05 (1), W(1)′–O(2) = 2.15 (1); W(1)–O(2)–C(3) = 138.9 (6), C(13)–C(14)–C(15) = 137 (1).

Addition of *i*-PrOH (4 equiv) to 1,2-$W_2(i\text{-Pr})_2(NMe_2)_4$[6] in hexane at 0 °C followed by the addition of MeC≡CMe (2 equiv) produces 1,2-$W_2(n\text{-Pr})_2(\eta^2\text{-}C_2Me_2)_2(O\text{-}i\text{-Pr})_4$ [I(*n*-Pr)] in high yield according to eq 2.[7] Compound I(*n*-Pr)

$$1,2\text{-}W_2(i\text{-Pr})_2(NMe_2)_4 + 4i\text{-PrOH} \xrightarrow[\text{hexane}]{0\ ^\circ\text{C}} \xrightarrow{2\text{MeC}{\equiv}\text{CMe}} \underset{\text{I}(n\text{-Pr})}{1,2\text{-}W_2(n\text{-Pr})_2(\eta^2\text{-}C_2Me_2)_2(O\text{-}i\text{-Pr})_4} + 4\ \text{HNMe}_2 \quad (2)$$

can be crystallized from hexane in a 59% yield and has been characterized by ^1H and $^{13}C\{^1H\}$ NMR, IR, and electronic absorption spectroscopy, elemental analysis, and X-ray crystallography.[8] The solid-state structure of I(*n*-Pr) is shown in Figure 1. The formation of I(*n*-Pr) in reaction 2 results from an alkyl isomerization (*i*-Pr → *n*-Pr) and requires a β-hydrogen atom abstraction followed by a reinsertion of propene into the W–H bond. When reaction 2 is carried out employing 1,2-$W_2(i\text{-Bu})_2(NMe_2)_4$, 1,2-$W_2(i\text{-Bu})_2(\eta^2\text{-}C_2Me_2)_2(O\text{-}i\text{-Pr})_4$ [I(*i*-Bu)] is formed in a 44% isolated yield. Compound I(*i*-Bu) has been characterized by ^1H and $^{13}C\{^1H\}$ NMR and IR spectroscopy.

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(7) Note the use of dry and oxygen-free solvents and inert atmospheres (N_2) throughout.

(8) Crystal data for I(*n*-Pr) at −155 °C: a = 23.133 (8) Å, b = 8.543 (2) Å, c = 17.020 (5) Å, β = 112.56 (1)°, Z = 4, d_{calcd} = 1.707 g cm^{-1}, and space group C2/c. For 1816 reflections having $F > 3\sigma(F)$ (from 2277 total reflections, Mo Kα, 6° < 2θ < 45°) the final residuals are $R(F)$ = 0.034 and $R_w(F)$ = 0.036. Crystal data for III at −155 °C: a = 17.477 (7) Å, b = 10.379 (4) Å, c = 13.072 (4) Å, β = 93.65 (1)°, Z = 4, d_{calcd} = 1.948 g cm^{-3}, and space group $P2_1/a$. For the 3110 reflections having $F > 3\sigma(F)$ (from a total of 4241 reflections, Mo Kα, 6° < 2θ < 45°) the final residuals are $R(F)$ = 0.036 and $R_w(F)$ = 0.036. Anal. Calcd for $W_2O_4C_{26}H_{54}$ [I(*n*-Pr)]: C, 39.11; H, 6.82. Found: C, 38.60; H, 6.49. Anal. Calcd for $W_2O_4C_{20}H_{40}$ (IIa): C, 33.73; H, 5.62. Found: C, 33.53; H, 5.48. Anal. Calcd for $W_4C_{40}O_6H_{76}$ (III) (mol wt 1388.4): C, *34.60*; H, 5.52. Found: C, *32.91*; H, 5.34. Anal. Calcd for $W_4C_{38}O_6H_{76}$ (but with mol wt 1388.4): C, 32.87; H, 5.52. The formation of undetectable tungsten carbide during elemental analysis (combustion) is a common characteristic of alkylidyne-bridged compounds similar to III. For example, all of compounds IV (where R = *t*-Bu, $SiMe_3$, or Ph) registered low in carbon content by one carbon atom per molecule. The "missing" carbon atom is presumably the alkylidyne (μ-*C*R) carbon.

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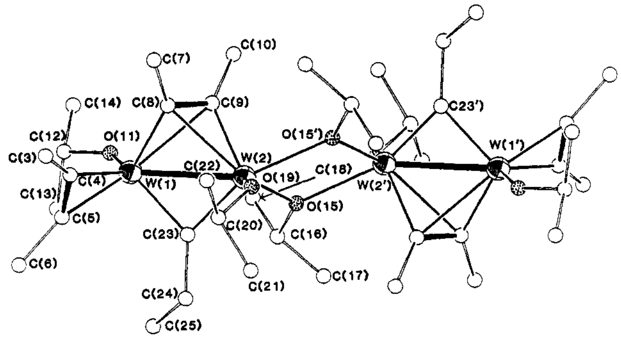
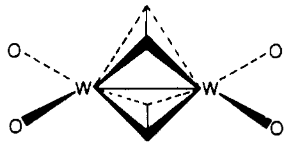


Figure 2. A ball-and-stick drawing of the $W_4(\mu\text{-}CEt)_2(\mu\text{-}C_2Me_2)_2(\eta^2\text{-}C_2Me_2)_2(O\text{-}i\text{-}Pr)_6$ molecule. Pertinent bond distances (Å) and angles (deg) are as follows: W(1)–W(2) = 2.721 (1), W(2)–W(2)′ = 3.5, W(1)–C(η^2-alkyne) = 2.03 (1) (average), W(1)–C(8) = 2.01 (1), W(1)–C(9) = 2.51 (1), W(2)–C(8) = 2.48 (1), W(2)–C(9) = 2.00 (1), W(2)–O(19) = 1.91 (1), W(2)–O(15) = 1.99 (1), W(2)–O(15)′ = 2.29 (1), W(1)–O(11) = 1.89 (1), W(1)–C(23) = 2.00 (1), W(2)–C(23) = 1.92 (1); C(3)–C(4)–C(5) = 136 (1), C(23)–W(2)–O(15)′ = 159 (1).

Compounds I are thermally unstable in the solid-state and in hydrocarbon solvents at room temperature. Thermolysis of I(n-Pr) at 50 °C in C_6D_6 for 30 h in the dark yields $W_2(\mu\text{-}C_2Me_2)_2(O\text{-}i\text{-}Pr)_4$ (IIa) and $W_4(\mu\text{-}CEt)_2(\mu\text{-}C_2Me_2)_2(\eta^2\text{-}C_2Me_2)_2(O\text{-}i\text{-}Pr)_6$ (III) in 1:2 concentration ratio, with the formal elimination of propane, propene, and i-PrOH. Compound IIa is presumably formed from a β-H elimination pathway, eq 1, whereas the formation of III requires α-CH activation. There is, of course, a problem with nomenclature in dinuclear systems since an α-hydrogen to one metal is a β-hydrogen to the other (M–M–CH) and the mechanism of hydrogen atom transfer is not known.[9]

Thermolysis of I(i-Bu) at room temperature for 2 days in C_6D_6 in the dark produces IIa as the only observable organometallic product. Compound IIa can be isolated in high yield from thermolyzed pentane solutions of I(i-Bu) as analytically pure,[8] dark brown cubes. The ^1H and $^{13}C\{^1H\}$ NMR data[10] reliably establish that IIa is an analogue of the structurally characterized compound $(t\text{-}BuO)_2W(\mu\text{-}C_2Ph_2)_2W(O\text{-}t\text{-}Bu)_2$[1] and is depicted below.



IIa

Compound III can be isolated as a yellow crystalline solid in low yield from thermolyzed solutions of I(n-Pr) by two successive, fractional crystallizations from pentane. The ^1H NMR spectrum[10] reveals three signals for the MeC≡CMe ligands in the integral ratio 1:1:2, three different O-i-Pr ligands, each having diastereotopic Me groups, and an ABX_3 spin system for the propylidyne ligand. The data are consistent with the molecular structure found in the solid-state[8] given that rotation of the $\eta^2\text{-}C_2Me_2$ ligand is fast in the NMR time scale. A ball-and-stick drawing of III is shown in Figure 2.

If the alkyne ligands are taken to occupy one coordination site at a metal, then the coordination geometry about the terminal tungsten atoms is pseudotetrahedral whereas the internal tungsten atoms are in trigonal-bipyramidal environments with the μ-alkyne moieties occupying equatorial sites. The bridging alkyne is grossly distorted[11,12] (θ = 35°) from a perpendicular position (θ = 0) as evidenced by the distances W(1)–C(8) = 2.01 (1) Å, W(1)–C(9) = 2.51 (1) Å, W(2)–C(8) = 2.48 (1) Å, and W(2)–C(9) = 2.00(1) Å. The W(1)–W(2) distance, 2.721 (1) Å, is long, indicative of a W–W single bond at most while the W(2) to W(2)′ distance, 3.5 Å, is nonbonding.

The structure of III is unprecedented, and the formation of III in the thermal decomposition of I(n-Pr) is puzzling. Formally, III is formed by a double α-CH activation process in which one H atom is used to eliminate alkane and the other i-PrOH. Bis(alkyl) complexes analogous to I typically decompose according to eq 3 to form alkyne-coupled $HW_2(\mu\text{-}CR)(\mu\text{-}C_4Me_4)(O\text{-}i\text{-}Pr)_4$ compounds (IV), where R = Ph or $SiMe_3$.[13] Conceivably, compound III

$$W_2(CH_2R)_2(\eta^2\text{-}C_2Me_2)_2(O\text{-}i\text{-}Pr)_4 \xrightarrow[\text{hexane}]{60\ ^\circ C} \underset{\text{IV}}{HW_2(\mu\text{-}CR)(\mu\text{-}C_4Me_4)(O\text{-}i\text{-}Pr)_4} + RCH_3 \quad (3)$$

could be converted to IV (R = Et) by coupling the alkyne ligands and oxidative addition of 1 equiv of i-PrOH per W_2 subunit. However, NMR tube reactions indicate that III and i-PrOH do not react at room temperature. Furthermore, when reaction 3 employing α-deuteriated CD_2Ph ligands was carried out in the presence of excess i-PrOH, no W–H formation was observed as would be required if an intermediate akin to III was involved. Thus it appears that the α-CH activation pathway is altered by the presence of the β-CH atoms.

Further work is in progress.[14]

Supplementary Material Available: Tables of fractional coordinates and isotropic thermal parameters, anisotropic thermal parameters, bond distances, and bond angles (6 pages); a listing of structure factor amplitudes (8 pages). Ordering information is given on any current masthead page.

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(9) M–M–CH interactions have been seen in both crystallographic studies and in dynamic NMR studies. E.g. as in (a) $Os_3(H)(\mu\text{-}CH)_3(CO)_{10}$: Shapley, J. R.; Calvert, R. B. *J. Am. Chem. Soc.* **1978**, *100*, 7726. (b) $Cp_2Ti(\mu\text{-}CH_3)(\mu\text{-}CH_2)Rh(COD)$: Park, J. W.; MacKenzie, P. B.; Schaefer, W. P.; Grubbs, R. H. *J. Am. Chem. Soc.* **1986**, *108*, 6402.

(10) NMR data for IIa: ^1H NMR (25 °C, C_6D_6) δ 4.58 (1 H, sept, $^3J_{HH}$ = 6.1 Hz, OCHMe$_2$), 2.67 (3 H, s, C_2Me_2), 1.22 (6 H, d, $^3J_{HH}$ = 6.1 Hz, OCHMe_2); $^{13}C\{^1H\}$ NMR (25 °C, C_6D_6) δ 165.7 (C_2Me$_2$, $^1J_{^{183}W-^{13}C}$ = 44 Hz, 24% total satellite intensity), 74.1 (OCHMe$_2$), 26.6 (OCHMe_2), 19.9 (C_2Me_2). NMR data for III: ^1H NMR (25 °C, C_6D_6) δ 5.18 (1 H, mult, μ-CCH_2Me), 4.76 (1 H, mult, μ-CCH_2Me), 4.36 (1 H, sept, $^3J_{HH}$ = 6.1 Hz, OCHMe$_2$), 3.84 (1 H, sept, $^3J_{HH}$ = 6.1 Hz, OCHMe$_2$), 3.57 (1 H, sept, $^3J_{HH}$ = 6.1 Hz, OCHMe$_2$), 3.25 (3 H, s, μ-C$_2$$Me_2$), 3.09 (3 H, s, μ-C$_2$$Me_2$), 2.96 (6 H, s, η^2-C$_2$$Me_2$), 1.89 (3 H, t, $^3J_{HH}$ = 7.4 Hz, μ-CCH$_2$$Me$), 1.06 (3 H, d, $^3J_{HH}$ = 6.1 Hz, OCHMe_2), 0.92 (3 H, d, $^3J_{HH}$ = 6.1 Hz, OCHMe_2), 0.88 (3 H, d, $^3J_{HH}$ = 6.1 Hz, OCHMe_2), 0.78 (3 H, d, $^3J_{HH}$ = 6.1 Hz, OCHMe_2), 0.49 (3 H, d, $^3J_{HH}$ = 6.1 Hz, OCHMe_2), 0.43 (3 H, d, $^3J_{HH}$ = 6.1 Hz, OCHMe_2).

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(14) We thank the Department of Energy, Office of Basic Research, Chemical Sciences Division, and the Wrubel Computing Center for support. B.W.E. is the 1986/1987 Indiana University SOHIO fellow.