Coupling C≡C, C≡N, and W≡W Bonds. Preparation, and Crystal and Molecular Structure of Hexaneopentoxy(pyridine)[2-amido(2−)-W^1,W^1-5-amido(2−)-W^2-3,4-dimethylhexa-2,4-diene]ditungsten $W_2(OCH_2Bu^t)_6(py)(N[CMe]_4N)$

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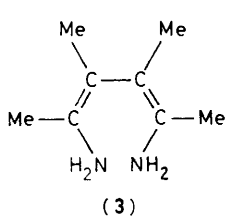
In a sequential reaction, $W_2(OCH_2Bu^t)_6(py)_2(W{\equiv}W)$ reacts in hydrocarbon solvents at room temperature with (i) but-2-yne (1 equiv.) and (ii) acetonitrile (2 equiv.) to yield $W_2(OCH_2Bu^t)_6(py)(N[CMe]_4N)(W{-}W)$, a novel dinuclear compound containing a ligand which may be considered to be the 4− anion derived from 1,4-diamino-1,2,3,4-tetramethylbuta-1,3-diene.

Dinuclear compounds of general formula $L_nM(\mu\text{-}X)ML_n$, where X = a reactive organic group (*e.g.* CR, CR_2, or C_2R_2), are of current interest with respect to C–C bond formation.[1–4] We have been exploring the reactivity of dinuclear alkoxides $(RO)_3M{\equiv}M(OR)_3$, where M = Mo and W, with small molecules such as CO, NO, O_2, and alkynes, $R'C{\equiv}CR'$ (R′ = H, Me). Alkyne adducts of formula $M_2(OR)_6L_2(\mu\text{-}C_2R'_2)$ have been isolated where L = pyridine (py), and some of these compounds have been shown to react further with alkynes forming C–C bonds as in complexes (1) and (2); the Mo_2-containing compounds have been shown to be intermediates in the catalytic cyclotrimerization of alkynes to benzenes.[5,6]

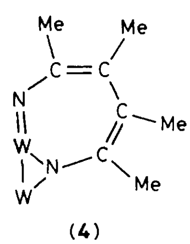
$$(py)(RO)_2M(\mu\text{-}C_4H_4)(\mu\text{-}OR)M(OR)_3$$
(1)
$$M = Mo, W;\ R = CH_2Bu^t$$
$$(RO)_3M(\mu\text{-}C_4R'_4)(\mu\text{-}OR)M(OR)_2(C_2R'_2)$$
(2)
$$M = W;\ R = CH_2Bu^t, Pr^i;\ R' = H, Me$$

As an extension of this work, we are investigating the reactivity of the $M_2(\mu\text{-}C_2R'_2)$ and $M_2(\mu\text{-}C_4R'_4)$ moieties in these compounds towards other C–C bond-forming reactions. We describe here a sequence wherein a W≡W and C≡C unit are first coupled and then two C≡N groups are added to form a novel dinuclear compound containing a ligand which may be considered to be the 4− anion derived from deprotonation of (3).

$W_2(OCH_2Bu^t)_6(py)_2(W{\equiv}W)$ and $MeC{\equiv}CMe$ (1 equiv.) react† in hydrocarbon solvents to give $W_2(OCH_2Bu^t)_6(py)_2(\mu\text{-}C_2Me_2)$ in an analogous manner to that described for the synthesis of $Mo_2(OR)_6(py)_2(\mu\text{-}C_2R_2)$ compounds. The blue crystalline compound $W_2(OCH_2Bu^t)_6(py)_2(\mu\text{-}C_2Me_2)$, when stirred for 18 h at room temperature in toluene with *ca.* 30 equiv. of $MeC{\equiv}N$, gives a dark red solution. Removing the solvent *in vacuo*, redissolving the residue in warm hexanes, and then cooling the solution to *ca.* −15 °C, produced dark red crystals‡ of the title compound, $W_2(OCH_2Bu^t)_6(py)(\mu\text{-}N[CMe]_4N)$.



(3)



(4)

An ORTEP view of the central $W_2O_6N(N[CMe]_4N)$ skeleton of this molecule is shown in Figure 1. Each tungsten atom is in a distorted octahedral geometry and shares with its neighbour a face formed by a pair of bridging OR ligands and a bridging nitrogen of the $N[CMe]_4N$ ligand.

The W–W distance, 2.617(1) Å, is approaching a typical W–W single bond distance and a comparison with the Mo–Mo distance, 2.661(2) Å, in the $Mo_2(OCH_2Bu^t)_6(py)(N_2CAr_2)_2$ molecule (Ar = *p*-tolyl) is particularly pertinent.[7] In the latter

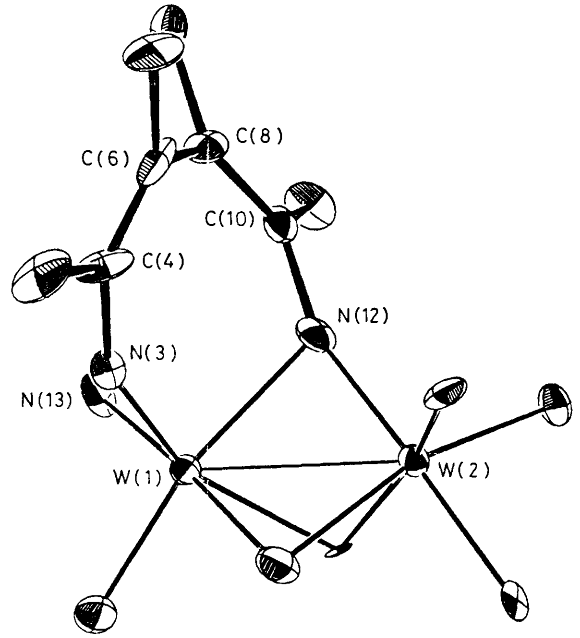


Figure 1. An ORTEP view of the central $W_2O_6N(N[CMe])_4N$ skeleton of the $W_2(OCH_2Bu^t)_6(py)(N[CMe]_4N)$ molecule emphasizing the confacial bioctahedral geometry and the nature of the novel $N[CMe]_4N$ ligand. Some distances (Å) are: W–W, 2.617(1); W(1)–N(3), 1.78(1); W(1)–N(12), 2.09(1); W(2)–N(12), 1.90(1); N(3)–C(4), 1.37(2); C(4)–C(6), 1.38(2); C(6)–C(8), 1.48(2); C(8)–C(10), 1.36(2); C(10)–N(12), 1.40(2); W(1)–N(py), 2.20(1); W–O (terminal), 1.93(2) (averaged); W–O (bridging), 2.10(3) (averaged).

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† Standard procedures for the manipulation of air-sensitive materials were used at all times. Satisfactory elemental analyses were obtained.

‡ *Crystal data* at −168 °C: a = 26.006(12), b = 17.056(7), c = 12.015(4) Å, β = 110.29(2)°, D_c = 1.467 g cm^{-3}, monoclinic, space group $P2_1/a$ with Z = 4. The structure was solved by Patterson and Fourier techniques with 6548 unique intensities collected using Mo-K_α radiation for 6° ≤ 2θ ≤ 45°. Final refinement utilized anisotropic thermal parameters for all non-hydrogen atoms and converged to R = 0.051 and R_w = 0.048. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

molecule, there are three OR bridges uniting octahedrally coordinated molybdenum atoms. The terminal N_2CAr_2 ligands may be counted as 2− ligands on the basis of Mo–N distances [1.77(1) Å averaged] together with N–N and C–C distances.[8,9] By analogous arguments, the N[CMe]$_4$N ligand can be counted as the 4− ligand formed by deprotonation of (**3**). The W–N distances are very short, comparable to those seen for terminal and bridging imido ligands (RN^{2-}),[10] and the alternating short, long, short C–C distances within the C_4 portion of the ring imply a significant contribution from the resonance structure (**4**).

$W_2(OR)_6(py)_2(\mu-C_2H_2)$ compounds, where R = Bu^t and Pr^i, similarly react with MeC≡N under mild conditions to give products of insertion into the W–C (alkyne) bond, and further studies of the reactions of these $M_2(\mu-C_2R'_2)$-containing compounds are under investigation.

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