$W_2Cl_3(NMe_2)_3(PMe_2Ph)_2$ and its Reaction with Ethyne to give $(PMe_2Ph)Cl_2W(\mu\text{-}NMe_2)(\mu\text{-}\sigma,\eta^2\text{-}CHCH_2)(\mu\text{-}\eta^2,\sigma\text{-}CH_2NMe)WCl(NMe_2)(PMe_2Ph)$: a Compound containing an Azadimetallabicyclobutane Core and a σ,π-Vinyl Ligand

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

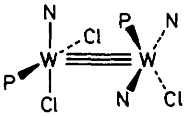
Department of Chemistry and Molecular Structure Center, Indiana University, Bloomington, Indiana 47405, U.S.A.

$W_2Cl_3(NMe_2)_3(PMe_2Ph)_2$ and ethyne (1 equiv.) react in toluene at 5 °C to give $W_2Cl_3(NMe_2)_3(PMe_2Ph)_2(C_2H_2)$ which contains a pseudo-tetrahedral $W_2(\mu\text{-}C_2H_2)$ core supported by one Cl and one NMe_2 bridging group; in toluene at room temperature a further reaction occurs to give $(PMe_2Ph)Cl_2W(\mu\text{-}NMe_2)(\mu\text{-}\sigma,\eta^2\text{-}CHCH_2)(\mu\text{-}\eta^2,\sigma\text{-}CH_2NMe)WCl(NMe_2)(PMe_2Ph)$ which is the first example of a compound containing a σ,π-vinyl ligand unsupported by carbonyl ligands and also the first example of an azadimetallabicyclobutane.

We have found that $W_2(NMe_2)_6$ and Me_3SiCl (3 equiv.) react in toluene at room temperature in the presence of PMe_2Ph to give $W_2Cl_3(NMe_2)_3(PMe_2Ph)_2$ which can be isolated as red crystals† [preparation of $W_2Cl_2(NMe_2)_4$ has previously been reported[1]]. In the solid state $W_2Cl_3(NMe_2)_3(PMe_2Ph)_2$ adopts the molecular structure shown in (1) in which two four-co-ordinate tungsten atoms are united by a W≡W bond of length 2.338(1) Å. The solution n.m.r. data are consistent with the maintenance of this type of structure in solution.

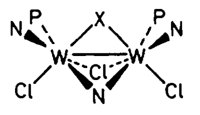
Concentrated toluene solutions of $W_2Cl_3(NMe_2)_3(PMe_2Ph)_2$ react at 5 °C with ethyne (1 equiv.) to give $W_2Cl_3(NMe_2)_3(PMe_2Ph)_2(C_2H_2)$ as a purple microcrystalline precipitate. Addition of PMe_3 (>2 equiv.) gives $W_2Cl_3(NMe_2)_3(PMe_3)_2(C_2H_2)$ by phosphine exchange and this compound, being thermally more stable (*vida infra*), can be recrystallized from toluene.† In the solid state $W_2Cl_3(NMe_2)_3(PMe_3)_2(C_2H_2)$ adopts the pseudo-confacial bioctahedral geometry shown in (2).

There is a central pseudo-tetrahedral W_2C_2 core supported by one chloro and one dimethylamido bridge: W–W = 2.667(1), C–C = 1.39(2), and W–C = 2.10(2) Å (averaged).



P = PMe_2Ph, N = NMe_2

(1)



P = PMe_3, PMe_2Ph
N = NMe_2, X = HCCH

(2)

On the basis of n.m.r. parameters the PMe_2Ph compound appears analogous to the PMe_3 compound (2)‡ and both are similar to previously characterized compounds such as $W_2(OPr^i)_6(py)_2(C_2H_2)$ (py = pyridine). However, in the

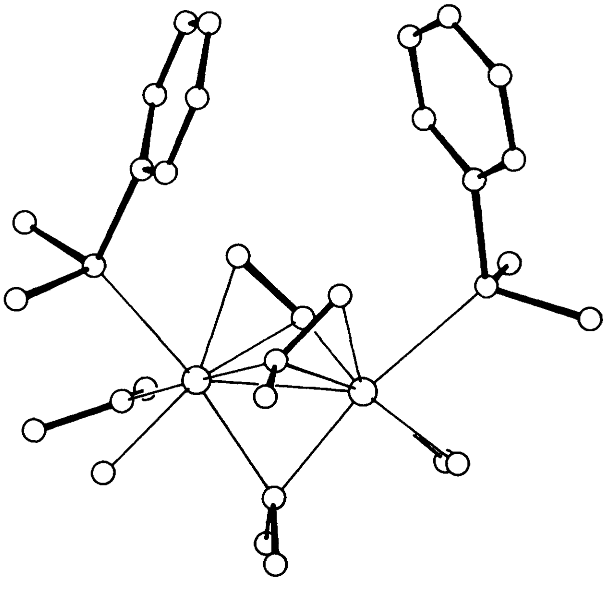


Figure 1: A view of the $W_2Cl_3(NMe_2)_2(PMe_2Ph)_2(\mu\text{-}CHCH_2)(\mu\text{-}CH_2NMe)$ molecule.

---

† All operations were carried out in dry and oxygen-free solvents and atmospheres (N_2). Satisfactory elemental analyses were obtained. *Crystal data summary:* (a) $W_2Cl_3(NMe_2)_3(PMe_2Ph)_2$ at −160 °C: triclinic, a = 11.909(3), b = 13.271(4), c = 11.551(3) Å, α = 104.76(1), β = 108.64(1), γ = 71.09(1)°, Z = 2, D_c = 1.916 g cm^{-3}, space group $P1$; $R(F)$ = 0.036 and $R_w(F)$ = 0.037. (b) $W_2Cl_3(NMe_2)_3(PMe_3)_2(C_2H_2)\cdot 1/2C_7H_8$ at −162 °C, where C_7H_8 is a toluene molecule of crystallization: monoclinic, a = 18.069(7), b = 14.108(4), c = 11.204(3) Å, β = 106.09(2)°, space group $P2/a$, Z = 4, D_c = 2.01 g cm^{-3}; $R(F)$ = 0.041 and $R_w(F)$ = 0.043, (c) $W_2Cl_3(NMe_2)_2(CH_2NMe)(CHCH_2)(PMe_2Ph)_2\cdot 1/2C_7H_8$ at −106 °C, where C_7H_8 is a toluene molecule of crystallization: triclinic, a = 16.929(7), b = 17.766(8), c = 11.108(4) Å, α = 103.31(2), β = 91.76(2), γ = 78.59(2)°, space group $P\bar{1}$; $R(F)$ = 0.0483 and $R_w(F)$ = 0.0482. The asymmetric unit contains two independent molecules (distinguished by the labels A and B in the supplementary materials). Molecule A is slightly disordered with one phenyl group of a PMe_2Ph ligand occupying the same space as the toluene of solvent. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

‡ (a) $W_2Cl_3(NMe_2)_3(PMe_2Ph)_2(C_2H_2)$: ^1H n.m.r. (CD_2Cl_2; 22 °C) δ 1.62 (d, 6H, J_{PH} 9.0 Hz, PMe_AMe_BPh), 1.91 (d, 6H, J_{PH} 8.6 Hz, PMe_AMe_BPh), 2.77 (s, 3H, μ-NMe_AMe_B), 3.01 (s, 3H, μ-NMe_AMe_B), 3.38 (s, 6H, NMe_AMe_B), 3.54 (d, 6H, J_{PH} 3.6 Hz, NMe_AMe_B), 6.57 (td, 1H, J_{PH} 7.9, J_{HH} 2.5, J_{WH} 2.2 Hz, CH_ACH_B), and 8.92 (dt, 1H, J_{PH} 2.0, J_{HH} 2.5, J_{WH} 5.3 Hz, CH_ACH_B); $^{31}P\{^1H\}$ n.m.r. (CD_2Cl_2; 22 °C) δ −7.41 (s, J_{WP} 217.5, J_{PP} 3.8 Hz); ^{13}C n.m.r. of the ^{13}CH–^{13}CH ligand (gated ^1H decoupled; CD_2Cl_2, −35 °C) δ 163.1 (J_{CC} 17.6, J_{WC} 34.9, J_{CH} 195.5 Hz) and 119.8 (J_{WC} 34.4, J_{CH} 193.7, J_{CP} 9.2 Hz).

(b) $W_2Cl_3(NMe_2)_2(CH_2NMe)(CHCH_2)(PMe_2Ph)_2$: ^1H n.m.r. (CD_2Cl_2; 22 °C) δ −1.05 (d, 1H, J_{PH} 3.9 Hz, NCH_AH_B), 0.92 (d, 1H, J_{PH} 11.5 Hz, NCH_AH_B), 1.73 (d, 3H, J_{PH} 9.0 Hz, PMe_AMe_BPh), 1.84 (d, 3H, J_{PH} 9.4 Hz, PMe_AMe_BPh), 1.86 (d, 3H, J_{PH} 8.3 Hz, $P'Me_AMe_BPh$), 2.03 (d, 3H, J_{PH} 9.4 Hz, $P'Me_AMe_BPh$), 2.23 (d, 3H, J_{PH} 2.2 Hz, NMe_AMe_B), 2.63 (s, 3H, $N'Me_AMe_B$), 3.16 (s, 3H, $N''Me$), 3.26 (poor d, 3H, NMe_AMe_B), 3.44 (s, 3H, $N'Me_AMe_B$), 4.93 (unresolved m, 1H, $CH_XCH_AH_B$), and 14.75 (tt, 1H, J_{PH} 6.5 Hz, J_{HH} 8.3 Hz, $CH_XCH_AH_B$); ^2H n.m.r. (CH_2Cl_2; 22 °C) δ 14.67 (br., 1H, $CD_XCD_AD_B$), 4.94 (br., 0.75H, $CD_XCD_AD_B$, and 1.70 (br., 0.25H, $CD_XCD_AD_B$); $^1H\{^{31}P\}$ n.m.r. (CD_2Cl_2; 22 °C) δ 4.93 (dd, J_{HH} 8.3 and 3.8 Hz) and 14.75 (t, J_{HH} 8.3 Hz); $^{31}P\{^1H\}$ n.m.r. (CD_2Cl_2; 22 °C) δ −12.28 (d, J_{pp} 2.0 Hz, PMe_2Ph) and −14.23 (d, J_{PP} 2.0 Hz, $P'Me_2PH$); ^{13}C n.m.r. of the ^{13}CH–$^{13}CH_2$ ligand (gated ^1H decoupled; CD_2Cl_2; 22 °C) δ 208.0 (J_{CH} 150, J_{CW} 83, J_{CC} 29, J_{CP} 13.6 Hz, $C_AHC_XH_2$), 75.53 (J_{CH} 149, J_{CW} unobserved, J_{CC} 29 Hz, $C_AHC_XH_2$).

present case the acetylenic carbon atoms are different, one being closer to the μ-Cl ligand and the other closer to the μ-NMe$_2$ ligand, which leads to very different chemical shifts for the W$_2$(μ-C$_2$H$_2$) carbons, Δδ ~40 p.p.m. The value of J_{CC} (18 Hz) is greatly reduced from that typical of one-bond ^{13}C–^{13}C couplings (*cf.* J_{C-C} = 35, 69, and 172 Hz for ethane, ethylene and ethyne, respectively[2]) but is comparable to that seen in W$_2$(OBu^t)$_6$(μ-C$_2$H$_2$)(CO),[3] where J_{CC} is 15.8 Hz for the W$_2$(μ-C$_2$H$_2$) moiety. These low values of J(^{13}C–^{13}C) appear to be a common feature in ditungsta-tetrahedra, W$_2$(μ-C$_2$H$_2$)-containing compounds,[3] and parallel the small ^1J(^{13}C–^{13}C) recently reported for C$_4$(OBu^t)$_4$.[4]

The compound W$_2$Cl$_3$(NMe$_2$)$_3$(PMe$_2$Ph)$_2$(C$_2$H$_2$) reacts in toluene at room temperature over a period of 24 h to give W$_2$Cl$_3$(NMe$_2$)$_2$(CH$_2$NMe)(CHCH$_2$)(PMe$_2$Ph)$_2$ which is the first example of a σ,π-vinyl dinuclear compound unsupported by carbonyl ligands[5] and the first example of an azadimetallabicyclobutane.[6] This compound can be isolated in 80% yield as a dark green crystalline material. A view of the molecular structure deduced from an *X*-ray study is shown in Figure 1. The unit cell contains two crystallographically independent molecules, one having a disordering of one of the PMe$_2$Ph ligands. The structural features of both molecules are, however, quite similar as is shown for the central W$_2$(μ-CHCH$_2$)(μ-CH$_2$NMe)(μ-NMe$_2$) skeleton in Figure 2.

A consideration of the bond distances and angles associated with the central core suggests that the μ-CH$_2$NMe ligand can be considered a 2− ligand and that the μ-σ,π-vinyl is a 3− ligand having significant contributions from the resonance forms (**3**) and (**4**).

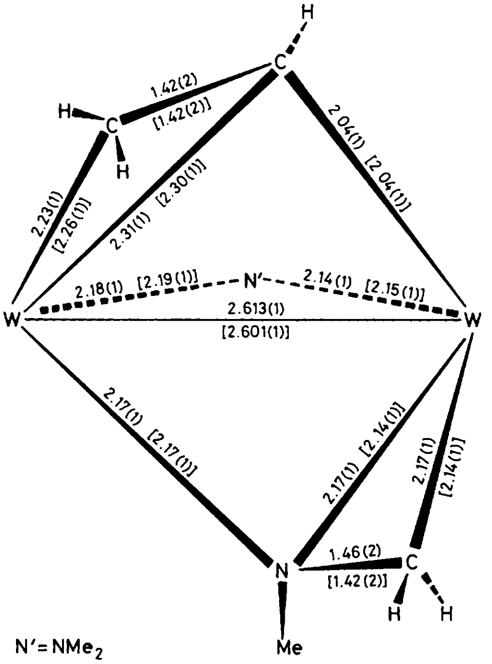
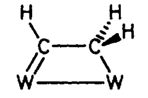
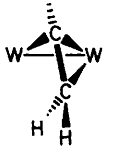


Figure 2. Pertinent bond distances (in Å) associated with the central skeleton of the W$_2$Cl$_3$(NMe$_2$)$_2$(PMe$_2$Ph$_2$)(μ-CHCH$_2$)(μ-CH$_2$NMe) molecule. The unit cell contains two crystallographically independent molecules yielding two different but similar distances as shown here, those for one molecule being given in square brackets.



(3)



(4)

The ^{13}C n.m.r. data are also indicative of the importance of the contributions from (**3**) and (**4**). The chemical shift of C$_\alpha$, 208 p.p.m., is in the region expected for an alkylidene carbon resonance, while C$_\beta$, 75 p.p.m., is where M–C alkyl carbon resonances are seen in several tungsten alkyl-containing compounds.[7] The value of ^1J(^{13}C–^{13}C) (28 Hz) in the ^{13}C n.m.r. spectrum of the labelled compound containing 92% ^{13}C atom enrichment of the vinyl ligand is also consistent with reduced C–C bond order (very small values of $^1J_{C-C}$ are seen in organic small ring systems[2]).

The reaction pathway leading to the formation of the μ-CH$_2$NMe and μ-CHCH$_2$ ligand is currently under investigation. Reactions employing C$_2$D$_2$ lead to the ligand μ-CDCHD with scrambling of H/D over both sites on C$_\beta$. Prior work has shown that protonation of M$_2$(μ-C$_2$H$_2$) compounds[5a,5b] and reactions of H$_2$Os$_3$(CO)$_{10}$ with alkynes[5d,5e] can lead to the formation of μ-CHCH$_2$ compounds and that the formation of η^2-RCH=NCH$_2$R ligands at mononuclear centres can occur in the thermolyses of dialkylamide ligands at elevated or ambient temperatures[8] (R = H or Me). In the present instance it seems likely that the hydrogen atom from a Me$_2$N ligand is transferred to the μ-C$_2$H$_2$ ligand. Quite probably this occurs by an initial β-hydrogen atom transfer to the metal and the W$_2$(μ-CH$_2$NMe) moiety seen here could prove to be an important functionality in the catalytic C–H/C–D scrambling effected by W$_2$(NMe$_2$)$_6$ in its reactions with Me$_2$ND at 160 °C recently reported by Nugent and co-workers.[9]

We thank the National Science Foundation and the Wrubel Computing Centre for financial support.

Received, 20th September 1984; Com. 1331

References

1 M. Akiyama, M. H. Chisholm, F. A. Cotton, M. W. Extine, and C. A. Murillo, *Inorg. Chem.*, 1977, **16**, 2407.

2 J. L. Marshall, 'C–C and C–H n.m.r. Couplings,' in 'Methods in Stereochemical Analysis,' Vol. 2, Verlag Chemie, 1983.

3 M. H. Chisholm, K. Folting, D. M. Hoffman, and J. C. Huffman, *J. Am. Chem. Soc.*, 1984, **106**, 6794.

4 T. Loerzer, R. Machinek, W. Luttke, L. H. Franz, K. D. Malsch, and G. Maier, *Angew. Chem., Int. Ed. Engl.*, 1983, **22**, 878.

5 For previously reported *X*-ray structural studies of the σ,π-vinyl ligand, see: (a) [(η^5-C$_5$H$_5$)$_2$Mo$_2$(CO)$_4$(CHCHPh)(H$_2$O)]$^+$[BF$_4$]$^-$: R. F. Gerlach, D. N. Duffy, and M. D. Curtis, *Organometallics*, 1983, **2**, 1172; (b) Ru$_2$(CO)$_2$(μ-H){μ-CHC(H)Me}(η-C$_5$H$_5$)$_2$: R. E. Colborn, A. F. Dyke, S. A. R. Knox, K. A. Mead, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1983, 2099; (c) [Mo$_2${OC(O)CF$_3$}(CO)$_4$(μ-CHCH$_2$)(η-C$_5$H$_5$)]: J. A. Beck, S. A. R. Knox, G. H. Riding, G. E. Taylor, and M. J. Winter, *J. Organomet. Chem.*, 1980, **202**, C49; (d) HOs$_3$(CHCH$_2$)(CO)$_{10}$: A. G. Orpen, D. Pippard, G. M. Sheldrick, and K. D. Rouse, *Acta Crystallogr., Sect. B*, 1978, **34**, 2466. (e) HOs$_3${CHC(H)Et}(CO)$_{10}$: J. J. Guy, B. E. Reichert, and G. M. Sheldrick, *ibid.*, 1976, **32**, 3319; (f) Fe$_2${μ-CHC(H)Br}(μ-Br)(CO)$_6$: C. Kruger, T. H. Tsay, F. W. Grevels, and E. Koerner von Gustorf, *Isr. J. Chem.*, 1972, **10**, 201.

6 An azametallacyclopropane has been structurally characterized containing the $\overline{\mathrm{WN(Bu^t)C}}\mathrm{Me_2}$ ligand, formed in the reaction between WMe$_6$ and excess of Bu^{t}NC: K. W. Chiu, R. A. Jones, G. Wilkinson, A. M. R. Galas, and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1981, 2088.

7 For a listing of W–C, W=C, and W≡C resonances (^{13}C), see ref. 3.

8 (a) Y. Takahashi, N. Onoyama, Y. Ishikawa, S. Motojima, and K. Sugiyama, *Chem. Lett.*, 1978, 525; (b) C. Airoldi, D. C. Bradley, and G. Vuru, *Transition Met. Chem.*, 1979, **4**, 64; (c) J. M. Mayer, C. J. Curtis, and J. E. Bercaw, *J. Am. Chem. Soc.*, 1983, **105**, 2651.

9 W. A. Nugent, D. W. Ovenall, and S. J. Holmes, *Organometallics*, 1983, **2**, 161.