

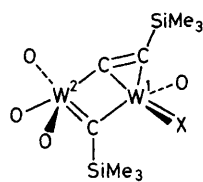
Attack of Isocyanide and Carbon Monoxide on a Bridging Alkylidyne Ligand at a Ditungsten Centre. Cleavage of the C–N and C–O Triple Bonds with Respective Formation of Tungsten–imido and -oxo Groups and Concomitant Addition of the Carbon Atom to the Bridging Alkylidyne Carbon Yielding a Bridging σ -W¹, η^2 -W² Alkynyl Ligand

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Isocyanide ligands and carbon monoxide, C \equiv X, where X = NBut^t, NC₆H₃Me₂-2,6, and O, react in hydrocarbon solvents with [(PrⁱO)₂W(μ -CSiMe₃)₂] to give compounds of formula (PrⁱO)(X=)W(μ -CSiMe₃)(μ - η^2 , η^1 -CCSiMe₃)W(OPrⁱ)₃; the compound where X = 2,6-dimethylphenylimido has been characterized by an X-ray study while that for X = O is formulated as an analogue based on i.r. and n.m.r. data.

There is current interest in the chemical reactivity of bridging alkylidyne ligands in dinuclear and polynuclear metal chemistry in part because these reactions may mimic those involved in



(1)

X = NR or O (oxo)
O = OPrⁱ

heterogeneous catalytic processes. Carbon–carbon bond formation is of particular interest with respect to polymerizations of alkenes and alkynes and Fischer–Tropsch chemistry.¹ We describe here our initial findings concerning the reactivity of a μ -CSiMe₃ ligand in the d¹–d¹ dimer [(PrⁱO)₂W(μ -CSiMe₃)₂]² with isocyanides and carbon monoxide, C \equiv X where X = NBut^t, NC₆H₃Me₂-2,6, and O, which leads to insertion of the carbon atom of the C \equiv X function into the μ -CSiMe₃ ligand with accompanying cleavage of the C–X triple bond and formation of a σ , π -CCSiMe₃ ligand.

Hydrocarbon solutions of [(PrⁱO)₂W(μ -CSiMe₃)₂] react with isocyanides RNC, where R = Bu^t and 2,6-dimethylphenyl, and carbon monoxide (1 equiv.) at room temperature to give new compounds which are formally 1 : 1

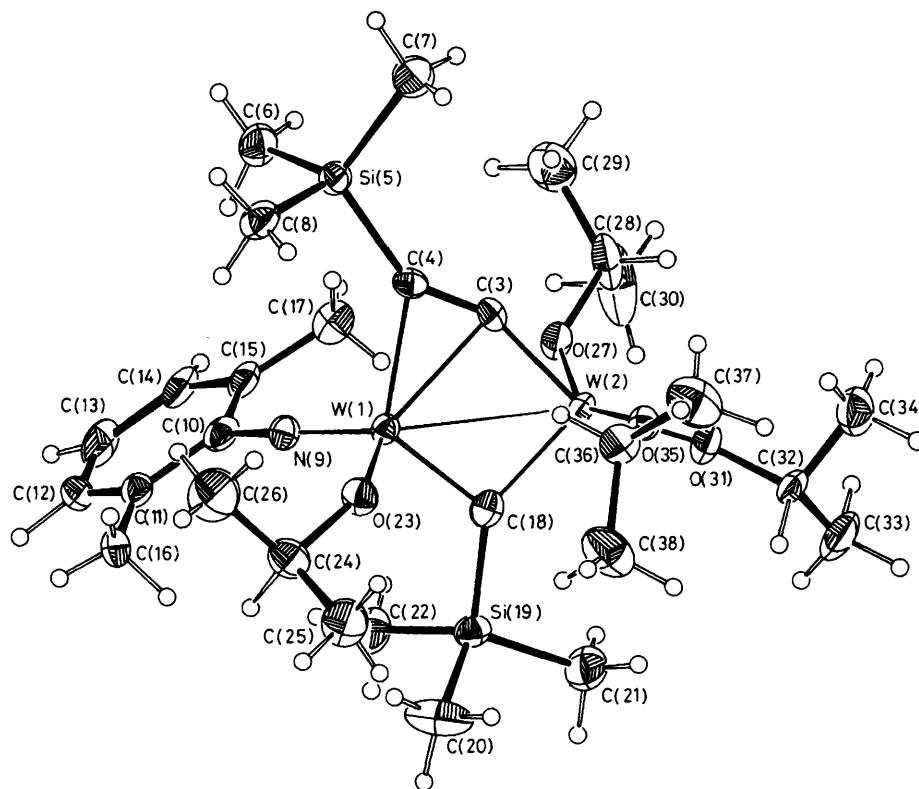


Figure 1. An ORTEP view of the (PrⁱO)(C₆H₃Me₂N)W(μ -CSiMe₃)(μ -CCSiMe₃)W(OPrⁱ)₃ molecule. Selected bond distances (Å) and angles (°) are W(1)–W(2) 2.9125(12), W(1)–O(23) 1.851(5), W(1)–N(9) 1.763(6), W(1)–C(3) 2.178(7), W(1)–C(4) 2.109(7), W(1)–C(18) 2.043(7), W(2)–O(27) 1.901(5), W(2)–O(31) 1.921(5), W(2)–O(35) 1.914(5), W(2)–C(3) 2.022(7), W(2)–C(18) 1.916(7); O(23)–W(1)–N(9) 111(1), O(23)–W(1)–C(18) 106(1), N(9)–W(1)–C(18) 103(1), Si(5)–C(4)–C(3) 148(1), W(2)–C(3)–C(4) 157(1), W(1)–C(18)–W(2) 95(1), W(1)–C(3)–W(2) 88(1). The local co-ordination environment about W(1) may be viewed as pseudotetrahedral if C(3)–C(4) are taken to occupy one site while that about W(2) is close to square-pyramidal having C(18) (the alkylidyne carbon atom) in the apical position.

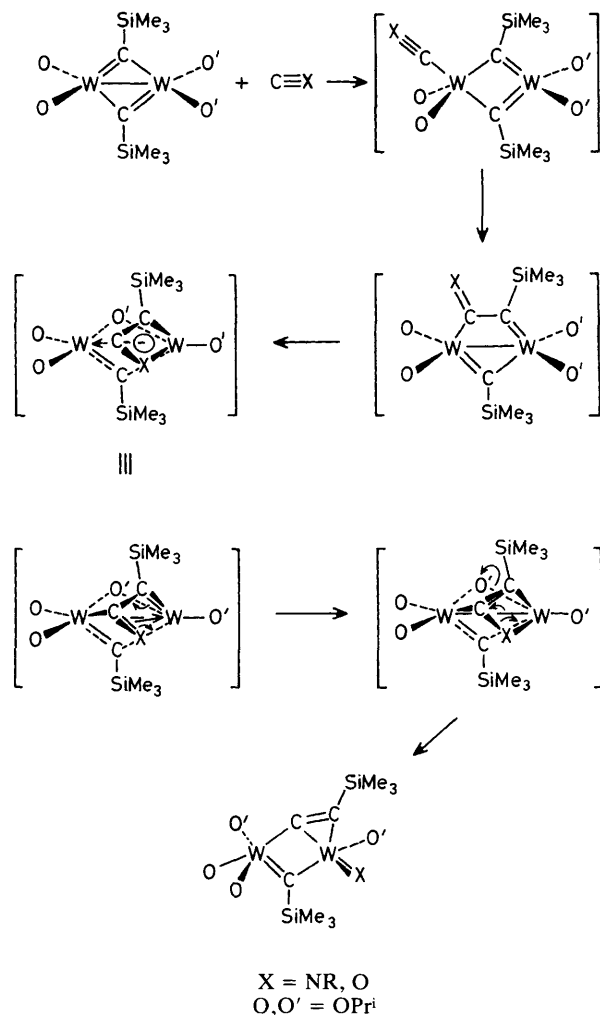
adducts.† The ^1H and $^{13}\text{C}\{^1\text{H}\}$ n.m.r. spectra of all three species are very similar.‡ Specifically the ^1H n.m.r. spectra show four types of OPr^i ligands, each containing diastereotopic methyl groups, and two types of SiMe_3 resonances. In the $^{13}\text{C}\{^1\text{H}\}$ n.m.r. spectra there are three low-field signals of particular significance. One at δ ca. 280 is assignable to a $\mu\text{-CSiMe}_3$ ligand bridging two tungsten atoms in an asymmetric manner with $J(^{183}\text{W}\text{-}^{13}\text{C})$ ca. 120 and 100 Hz. The two other low-field carbon resonances occur at δ ca. 250 and 170 with the resonances at δ ca. 250 showing a significant coupling to one tungsten atom, $J(^{183}\text{W}\text{-}^{13}\text{C})$ ca. 110 Hz. The other resonance at δ ca. 170 shows negligible coupling to ^{183}W ($I = 1/2$, 14.5% nat. abund.). In reactions involving labelled (92 g atom %) carbon monoxide, ^{13}CO , it is the resonance at δ ca. 250 which is clearly derived from carbon monoxide. Moreover there is $^{13}\text{C}\text{-}^{13}\text{C}$ coupling to the carbon signal at δ ca. 170 of 35.4 Hz. These data are entirely consistent with the formation of a new class of compounds having the formula and generic structure depicted by structure (1).

Thus far we have only been able to grow crystals of the compound where $\text{R} = 2,6\text{-dimethylphenyl}$ suitable for single

† Dry and oxygen free atmospheres (N_2) and solvents were used at all times. The new compounds are air-sensitive and are formed in essentially quantitative yield (by ^1H n.m.r. spectroscopy) based on the addition of 1 equiv. of $\text{C}\equiv\text{X}$ to $(\text{Pr}^i\text{O})_4\text{W}_2(\mu\text{-CSiMe}_3)_2$. Crystallization from hexane yields the imido compounds in >60% yield based on W . The oxo compound appears to be an oil at room temperature and yields waxy crystals from pentane at -78°C . With further added equivalents of $\text{C}\equiv\text{X}$ no reaction is observed for $\text{X} = \text{NR}$, but for $\text{X} = \text{O}$ additional products are formed.

‡ Selected spectroscopic data for (1), $(\text{Pr}^i\text{O})(\text{X}=\text{W})[\mu\text{-}\eta^2,\eta^1\text{-C}\equiv\text{C}(\text{SiMe}_3)](\mu\text{-CSiMe}_3)\text{W}(\text{OPr}^i)_3$: (1; $\text{X} = 2,6\text{-Me}_2\text{C}_6\text{H}_3\text{-N}=\text{N}$): ^1H n.m.r. ($[\text{H}_8]$ toluene, 23°C) δ 6.87 [2H, d, $J(\text{H}_{\text{para}}\text{-H}_{\text{meta}})$ 7.6 Hz, 2,6- $\text{Me}_2\text{C}_6\text{H}_3\text{-N}$], 6.73 [1H, t, $J(\text{H}_{\text{para}}\text{-H}_{\text{meta}})$ 7.6 Hz, 2,6- $\text{Me}_2\text{C}_6\text{H}_3\text{-N}$], 5.12, 4.92, 4.71, 2.84 [1H, sept, $J(\text{H-Me})$ 6.1 Hz, OCHMe_2], 2.03 [6H, s, 2,6- $\text{Me}_2\text{C}_6\text{H}_3\text{-N}$], 1.64, 1.62, 1.21, 1.18, 1.14, 1.11, 0.92, 0.77 [3H, d, $J(\text{H-Me})$ 6.1 Hz, OCHMe_2], 0.54, 0.42 [$\mu\text{-CSiMe}_3$, $\mu\text{-}\eta^2,\eta^1\text{-C}\equiv\text{C}(\text{SiMe}_3)$]; ^{13}C n.m.r. ($[\text{H}_8]$ toluene, 23°C) δ 285.0 ($\mu\text{-CSiMe}_3$), 249.1 ($\mu\text{-}\eta^2,\eta^1\text{-C}\equiv\text{C}(\text{SiMe}_3)$), 178.9 [$\mu\text{-}\eta^2,\eta^1\text{-C}\equiv\text{C}(\text{SiMe}_3)$], 154.9 (*ipso*), 132.6, 129.2, 126.9 (2,6- $\text{Me}_2\text{C}_6\text{H}_3\text{-N}$), 79.9, 78.9, 75.9, 74.6 (OCHMe_2), 27.6, 27.0, 26.5, 25.8, 25.6, 25.5, 25.3, 25.3 (OCHMe_2), 25.2 (2,6- $\text{Me}_2\text{C}_6\text{H}_3\text{-N}$), 2.9, 0.1 [$\mu\text{-CSiMe}_3$, $\mu\text{-}\eta^2,\eta^1\text{-C}\equiv\text{C}(\text{SiMe}_3)$]. (1; $\text{X} = \text{Bu}^t\text{-N}=\text{N}$): ^{13}C n.m.r. ($[\text{H}_8]$ toluene, 23°C) δ 278.6 [$\mu\text{-CSiMe}_3$, $J(^{183}\text{W}\text{-}^{13}\text{C})$ 129.5, 99.2 Hz], 250.7 [$\mu\text{-}\eta^2,\eta^1\text{-C}\equiv\text{C}(\text{SiMe}_3)$], 171.1 Hz], 171.5 [$\mu\text{-}\eta^2,\eta^1\text{-C}\equiv\text{C}(\text{SiMe}_3)$], 78.6, 78.1, 76.2, 74.7 (OCHMe_2), 66.5 ($\text{Me}_3\text{C-N}$), 32.4 ($\text{Me}_3\text{C-N}$), 27.4, 27.0, 26.8, 26.4, 25.5, 25.1, 24.7, 24.5 (OCHMe_2), 3.7, 0.7 [$\mu\text{-CSiMe}_3$, $\mu\text{-}\eta^2,\eta^1\text{-C}\equiv\text{C}(\text{SiMe}_3)$]. (1; $\text{X} = \text{O}$): ^1H n.m.r. ($[\text{H}_8]$ toluene, 23°C) δ 5.06, 4.15, 3.74, 3.28 [1H, sept, $J(\text{H-Me})$ 6.1 Hz, OCHMe_2], 1.63, 1.61, 0.99, 0.91, 0.89, 0.82, 0.76, 0.69 [3H, d, $J(\text{H-Me})$ 6.1 Hz, OCHMe_2], 0.78, 0.52 [9H, s, $\mu\text{-CSiMe}_3$, $\mu\text{-}\eta^2,\eta^1\text{-C}\equiv\text{C}(\text{SiMe}_3)$]; ^{13}C n.m.r. (C_6D_6 , 23°C) δ 277.0 ($\mu\text{-CSiMe}_3$), 245.6 [$\mu\text{-}\eta^2,\eta^1\text{-C}\equiv\text{C}(\text{SiMe}_3)$], $J(^{183}\text{W}\text{-}^{13}\text{C})$ 113 Hz], 171.8 [$\mu\text{-}\eta^2,\eta^1\text{-C}\equiv\text{C}(\text{SiMe}_3)$], 80.0, 77.6, 77.6, 76.5 (OCHMe_2), 27.4, 27.1, 26.1, 26.1, 25.9, 25.2, 25.2, 25.2 (OCHMe_2), 3.0, 0.4 [$\mu\text{-CSiMe}_3$, $\mu\text{-}\eta^2,\eta^1\text{-C}\equiv\text{C}(\text{SiMe}_3)$].

Pertinent *i.r.* data: It is noteworthy that no *i.r.* bands which can be attributed to carbonyl functionalities are observed in the complex derived from the reaction of $\text{W}_2(\mu\text{-CSiMe}_3)_2(\text{OPr}^i)_4$ and CO . The weak $\text{C}\equiv\text{C}$ stretching band for $(\text{Pr}^i\text{O})(\text{O}=\text{W})[\mu\text{-}\eta^2,\eta^1\text{-C}\equiv\text{C}(\text{SiMe}_3)](\mu\text{-CSiMe}_3)\text{W}(\text{OPr}^i)_3$ occurs at 1722 cm^{-1} , showing an expected isotopic shift (to 1690 cm^{-1}) when the compound is prepared with 92 atom % ^{13}CO . Use of regular *vs.* labelled CO^* where O^* represents 98 g atom % ^{18}O has allowed identification of $\nu(\text{W}=\text{O})$ at 945 cm^{-1} and $\nu(\text{W}=\text{O})$ at 900 cm^{-1} . It is noteworthy that the band assigned to $\nu(\text{C}=\text{C})$ is not perturbed by the ^{18}O labelling experiment.



Scheme 1. Proposed reaction pathway leading to $\text{C}\equiv\text{X}$ cleavage in the reactions between $[(\text{Pr}^i\text{O})_2\text{W}(\mu\text{-CSiMe}_3)]_2$ and $\text{C}\equiv\text{X}$, where $\text{X} = \text{NBu}^t$, $\text{NC}_6\text{H}_3\text{Me}_2\text{-2,6}$, and O . The reaction pathway is based on that established² for alkyne additions followed by C-X bond cleavage with concomitant W=X bond formation.

crystal *X-ray* work§ but this has allowed characterization and establishment of our claim in the one instance. An ORTEP view of the molecule is shown in Figure 1 which together with the structural parameters given are reconcilable with the

§ *Crystal data* for (1; $\text{X} = 2,6\text{-Me}_2\text{C}_6\text{H}_3\text{-N}=\text{N}$) at -155°C : $a = 14.169(5)$, $b = 14.343(5)$, $c = 9.807(3)$ Å, $\alpha = 102.35(2)$, $\beta = 109.29(2)$, $\gamma = 89.44(2)^\circ$, $Z = 2$, $D_c = 1.65\text{ g cm}^{-3}$ and space group $P1$. Of the 4841 unique reflections collected ($\text{Mo-K}\alpha$, $6^\circ < 2\theta < 45^\circ$), the 4221 having $F > 3\sigma(F)$ were used in the full-matrix least squares refinement. Hydrogen atoms were visible in a Fourier phased on the non-hydrogen parameters and were included in the final cycles. Non-hydrogen atoms were assigned anisotropic thermal parameters while hydrogen atoms were allowed to vary isotropically. Final residuals are $R(F) = 0.029$ and $R_w(F) = 0.031$. 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. The complete structural report is available from the Indiana University Chemistry Library only in microfiche form at a cost of \$2.50 per copy. Request IUMS Report No. 85082.

valence bond description shown in (1), bearing in mind that the W-NAr bond and the W-O bond can have triple bond character.³ The μ -CCSiMe₃ ligand can be counted as a -3 ligand with charge being partitioned as -1 to W(2) and -2 to W(1) which is η^2 -bound to the μ -CCSiMe₃ ligand. Each tungsten atom is thus in a formal oxidation state +6 and the W-W distance, 2.91 Å is non-bonding. The C(3)-C(4) distance, 1.31 Å and the ¹³C-¹³C coupling constant, 37 Hz are similar to those seen for C-C double bonds, cf. C-C 1.337(3) Å in ethylene⁴ and $J(^{13}\text{C}-^{13}\text{C})$ 35, 68, and 172 Hz for ethane, ethylene and ethyne, respectively.⁵ The bonding of the σ, π -C₂ moiety of the μ -CCSiMe₃ ligand is reminiscent of that recently found in *trans*-Pt[C₂W₂(OBU^t)₅]₂(PMe₂Ph)₂ except that in the latter compound there is a W=W bond and Pt substitutes for Si.⁶

Based on our earlier studies of the reactions involving [(Y)₂W(μ -CSiMe₃)₂] where Y = CH₂SiMe₃⁷ and OPrⁱ² with alkynes,^{2,8} allenes⁹ and diazoalkanes¹⁰ we suggest a reaction pathway shown in Scheme 1. It should be noted that whereas alkynes give stable 1,3-dimetallated allyl derivatives the analogues involving C-C bond formation with RNC and CO would be expected to be less stable and prone to C-X bond cleavage because of the thermodynamic favourability of forming the W \equiv X bond. It may be noted that compounds of formula Fe₂M(μ -CCR)(CO)₈Cp are formed¹¹ in reactions between M \equiv CR(CO)₂Cp compounds (Cp = cyclopentadienyl; M = Mo, R = Me; M = W, R = Me and *p*-tolyl) and [Et₃NH]⁺[Fe₃H(CO)₁₁]⁻. Here the μ -CCR ligand is σ -bound to M and π -bound to each Fe atom. To our knowledge this is the only previous finding which suggests that a carbonyl ligand and an alkylidyne ligand may react in the manner described herein, although the stoichiometry in the previous work was not established.

Further studies are in progress and promise to be very interesting since reactions between [(PrⁱO)₂W(μ -CSiMe₃)₂] and CO apparently give additional compounds upon addition of more than one equivalent of CO.

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