



Reactions of $W_2(H)(OR)_7$, $W_2(OR)_6(py)_2$ and $W_4(OCH_2^cC_4H_7)_{12}$ compounds ($R = Pr^i$, CH_2Bu^t , cC_5H_9) with azobenzene, 1,2-diphenylhydrazine and 1,1-dimethylhydrazine

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Abstract—The reaction of $W_2(H)(OR)_7$, $W_2(OR)_6(py)_2$ and $W_4(OCH_2^cC_4H_7)_{12}$ compounds ($R = Pr^i$, CH_2Bu^t , cC_5H_9) in hydrocarbon solvents with azobenzene, 1,2-diphenylhydrazine and 1,1-dimethylhydrazine have been studied. The tetranuclear cluster proved to be inert while $W_2(H)(OR)_7$ was the most kinetically labile. In all cases where a reaction was observed the dinuclear center was ultimately oxidized with the formation of imido (NR^{2-}) or hydrazido (NNR_2^{2-}) ligands being formed. These were isolated as compounds of $W(6+)$ supported by four OR ligands. These products require alkoxide group scrambling and no compound from which OR groups were lost was detected. Studies of the reactions between $W_2(H)(OR)_7$ compounds and hydrazines by low-temperature NMR spectroscopy indicate the initial formation of 1:1 adducts followed by elimination of H_2 and ROH as the hydrazine is activated. The following compounds were isolated and crystallographically characterized by single crystal studies: $[W(OPr^i)_4(NPh)_2]$, $[W_3(\mu_3-H)(OPr^i)_9(NPh)(py)]$, $[W(OPr^i)_4(NPh)(py)]$ and $[W(OPr^i)_4(NNMe_2)(py)]$. The trinuclear tungsten compound is noteworthy in being a rare, if not the only, example of a 12-electron triangular metal cluster capped by a hydrido ligand. In the other structures the $W(6+)$ center is in a distorted octahedral coordination and the imido or hydrazido(2-) ligand is terminal with significant contribution from the resonance form having a $W-N$ triple bond. © 1997 Elsevier Science Ltd. All rights reserved.

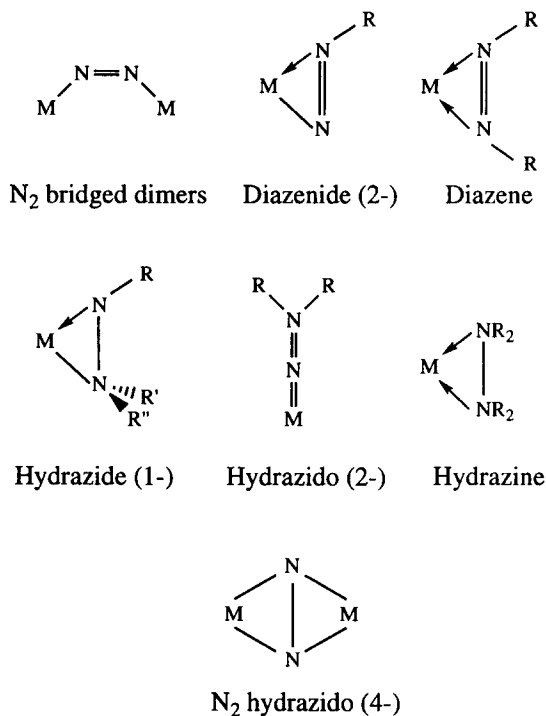
Keywords: tungsten; alkoxide; imido; hydrazido; $N-N$ bond.

Recent years have witnessed a rapid expansion in the coordination and activation of $N-N$ containing ligands at transition metal centers [1]. The desire to enhance the understanding of the pathways by which dinitrogen is reduced to ammonia is central to this rapidly expanding field of chemical research [2, 3]. [In nature reduction of N_2 by a variety of nitrogenase enzymes [4] involves an iron cofactor containing either molybdenum [5, 6] or vanadium [7]. A number of N_2 containing complexes have been prepared including N_2 -bridged dimers, diazenide (NNR), diazene ($RNNR$), hydrazide (1-) (NNR_2), hydrazido (2-)

(NNR_2) and hydrazine (R_2NNR_2), as depicted in Scheme 1 [8]. A more unique binding mode for N_2 in a transition metal complex involves a reduced hydrazido (4-) ligand, where the N_2 ligand engages in both σ - and delocalized π -bonding to the metal center [9]. This ligand is found in the $\{[(Pr^i)_2PCH_2SiMe_2]_2NZrCl\}_2(\mu-\eta^2:\eta^2-N_2)$ complex and involves a "world record" for the longest $N-N$ bond found in a dinitrogen containing complex [$N-N = 1.548(7)$ Å, compared with $N-N$ in hydrazine of 1.47 Å], while the $Zr-N$ bond (2.024 Å) is shorter than a typical single bond [9b].

A variety of W and Mo complexes coordinated to N_2 have been prepared and in several cases successful cleavage of the $N-N$ bond has been demonstrated

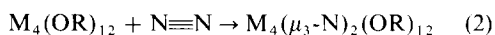
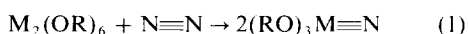
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[10], while in other systems protonation yields one of the aforementioned dinitrogen containing ligands [11]. More recently the synthetic inorganic chemist achieved catalytic reduction of dinitrogen at a transition metal center and reports of such achievements continue to progress [12].

Traditionally "low oxidation state" chemistry has dominated the study of coordination chemistry of the ligand and its reduction. However, recent advances by Schrock and co-workers have demonstrated that high-valent centers of Mo and W can also be employed to study this chemistry [13], as in the isolation of $[\text{Cp}^*\text{WMe}_3]_2(\mu\text{-N}_2)$ [14]. In addition, these workers performed detailed studies into the "protic" reduction of hydrazine and hydrazido containing monomers achieving a degree of success in elucidating possible pathways for N—N reduction.

Ditungsten and tetratungsten centers supported by alkoxide ligands have been found to cleave $\text{RC}\equiv\text{N}$, [15] $\text{RC}\equiv\text{CR}$, [16] $\text{C}\equiv\text{O}$ [17] and $\text{RN}\equiv\text{C}$ [18] bonds. Upon observation of these six electron reductions it was speculated that activation and reduction of dinitrogen should also be possible. The existence of the thermally persistent compounds $(\text{RO})_3\text{M}\equiv\text{N}$, [15] where $\text{R} = \text{Bu}^t$ and $\text{M} = \text{Mo}$ and W and $\text{Mo}_4(\mu_3\text{-N})_2(\text{OPr}^t)_{12}$ [19] led to the belief that these compounds are in fact thermodynamically stable with respect to the reactions shown in eqs (1) and (2), respectively.



The studies of the reductive cleavage of $\text{C}\equiv\text{O}$ by $\text{W}_4(\text{OCH}_2\text{R})_{12}$ compounds [17a] showed that the rate-limiting step involved uptake of CO by the $\text{W}_4(\text{OCH}_2\text{R})_{12}$ cluster ($\text{R} = \text{Bu}^t$, Pr^t , ${}^t\text{C}_6\text{H}_{11}$, and ${}^t\text{C}_5\text{H}_9$), which was slow at -30°C in hydrocarbon solvents. The problem of substrate uptake at these W_2 and W_4 alkoxide supported centers is exacerbated by the π -donor properties of the OR ligands.

In this paper the reactions of azobenzene and substituted hydrazines with the W_2 -containing alkoxides $\text{W}_2(\text{OR})_6$, where $\text{R} = {}^t\text{Pr}$ and CH_2CMe_3 , $\text{W}_2(\text{H})(\text{OR})_7$ ($\text{R} = {}^t\text{Pr}$ and ${}^t\text{C}_5\text{H}_9$) and $\text{W}_4(\text{OCH}_2{}^t\text{C}_4\text{H}_7)_{12}$ will be presented. This work was motivated by the fact that both azobenzene and hydrazines are more Lewis basic than is $\text{N}\equiv\text{N}$ and furthermore the involvement of the hydride ligand in $\text{W}_2(\text{H})(\text{OR})_7$ compounds could prove interesting as has been noted previously in its reactions with alkenes, alkynes and nitriles [20].

RESULTS AND DISCUSSION

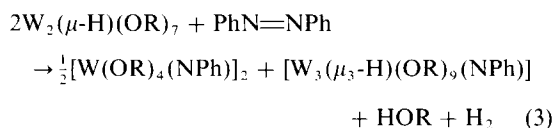
Synthesis and reactivity studies

(i) *Reactions with azobenzene. Synthesis of* $[\text{W}(\text{OR})_4(\text{NPh})]_2$ (**1**) and $\text{W}_3(\mu_3\text{-H})(\text{OR})_9(\text{NPh})\text{py}$ (**2**). Hydrocarbon solutions of $\text{W}_2(\text{H})(\text{OR})_7(\text{L})$ ($\text{R} = \text{Pr}^t$ or ${}^t\text{C}_5\text{H}_9$, $\text{L} = \text{W}_2(\text{H})(\text{OPr}^t)_7$ or HNMe_2 , respectively) react with 1 equiv. of azobenzene under ambient conditions to afford $[\text{W}(\text{OR})_4(\text{NPh})]_2$ (**1**) and $[\text{W}_3(\mu_3\text{-H})(\text{OR})_9(\text{NPh})\text{py}]$ (**2**), in a combined isolated yield of 82%. These compounds are extremely soluble in hydrocarbon solvents and form yellow-brown crystals (**1**) and small green cubes (**2**). Crystals suitable for X-ray study were obtained for $[\text{W}(\text{OR})_4(\text{NPh})]_2$ from pentane and $[\text{W}_3(\mu_3\text{-H})(\text{OR})_9(\text{NPh})\text{py}]$ from pyridine pentane (1:1). Both compounds can be stored in the solid state at room temperature for several months without decomposition.

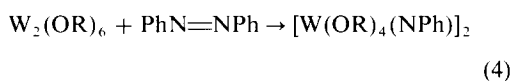
The formation of compound **1** arises from the formal reduction of azobenzene by the $\text{W}=\text{W}$ double bond, and represents a rare example of azoalkane metathesis at an early transition metal center affording a metal imido fragment [21]. However, it should be noted that azobenzene has been widely employed as a source of a phenyl imido moiety in the preparation of capped late transition metal clusters supported by π -acid ligands [22]. The reactivity reported here closely parallels early reports of alkyne bond cleavage reactions with $\text{W}_2(\text{OBu}^t)_6$ to afford monomeric $(\text{RO})_3\text{W}\equiv\text{CR}$ [15]. The presence of $\text{W}_3(\mu_3\text{-H})(\text{OR})_9(\text{NPh})\text{py}$ (**2**) can be attributed to the facile reaction of a co-generated imido-monomer with a metal-metal bonded dimer, closely resembling the formation of $\text{M}_3(\text{OR})_9(\mu_3\text{-CR})$ in the reaction of $\text{M}_2(\text{OR})_6\text{py}_2$ with alkynes [23].

The reaction of azobenzene with $[\text{W}_2(\text{H})(\text{OPr}^t)_7]_2$ has been monitored by low-temperature ${}^1\text{H}$ NMR spectroscopy to try and gain further insight into the reaction pathway. Addition of $\text{PhN}=\text{NPh}$ resulted in

the formation of $[\text{W}_2(\text{H})(\text{OPr}^i)_7(\eta^2\text{-NPhNPh})]$ prior to metathesis. Upon warming to room temperature this reaction goes to completion within 2 h, with evidence for the liberation of dihydrogen after only 10 min. The byproducts of this reaction have been identified as HOPr^i and H_2 , consistent with those shown in eq. (3).



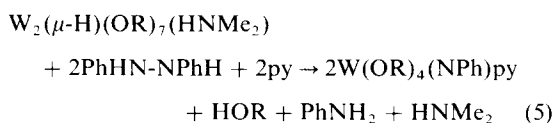
The kinetic facility with which this reaction proceeds is in contrast to the "sluggish" reactivity of $\text{W}_2(\text{OR})_6$ ($\text{R} = \text{Pr}^i$ and CH_2CMe_3) with azobenzene [eq. (4)]. This latter reaction takes 3 weeks to form a significant amount of $[\text{W}(\text{OR})_4(\text{NPh})]_2$ and in no instance was there any evidence supporting the formation of a trinuclear imido-bridged complex. It is believed that this reaction is enhanced by alcohol, either present as trace amounts of adventitious alcohol or resulting from hydrolysis of water present in solution. Other products formed during this reaction remain to be identified.



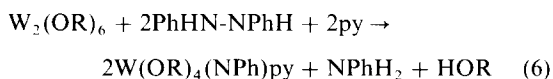
The cluster $\text{W}_4(\text{OCH}_2\text{C}_4\text{H}_7)_{12}$ was allowed to react with azobenzene at low temperatures and slowly warmed to room temperature. Although this cluster is capable of providing the electrons necessary for the reduction of azobenzene, there was no evidence for reactivity with N_2Ph_2 under conditions similar to those employed in the cleavage of CO , RCN , RNC and $\text{RC}\equiv\text{CR}$ [15–18]. In the above reaction the starting material was recovered in high yield.

Reactions with 1,2-diphenylhydrazine. Synthesis of $[\text{W}(\text{OR})_4(\text{NPh})\text{py}]$ (3). Hydrocarbon solutions of $[\text{W}_2(\text{H})(\text{OPr}^i)_7]_2$ and $\text{W}_2(\text{H})(\text{O}^i\text{C}_5\text{H}_9)_7(\text{HNMe}_2)$ react rapidly with 1,2-diphenylhydrazine to afford $[\text{W}(\text{OR})_4(\text{NPh})\text{py}]$ as the sole isolable metalloorganic product. X-ray quality crystals of **3** were obtained by cooling a 1:1 pentane:pyridine solution at -20°C overnight and its structure was determined. Compound **3** can be stored in the solid state at room temperature for several months without decomposition.

The reaction consistent with these observations is shown in **5**. Two molar equivalents of hydrazine per dimer are required for the reaction to go to completion; however, small amounts of other tungsten containing species appear as a result of ill-defined competing side reactions.



In contrast to the kinetically "sluggish" reaction of $\text{W}_2(\text{OR})_6$ [$\text{R} = \text{Pr}^i$ and CH_2CMe_3] with azobenzene, these dinuclear compounds react rapidly with 1,2-disubstituted hydrazine, resulting in high yields of $[\text{W}(\text{OR})_4(\text{NPh})\text{py}]$ as the only isolable metalloorganic products. Such disparate reactivities of azobenzene and hydrazine can be attributed to the facile coordination and N-H activation of the latter. Reaction (6) shows the proposed reaction products.

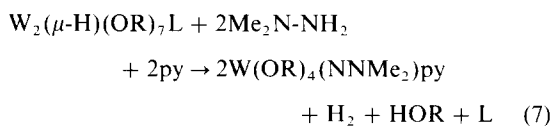


The cluster, $\text{W}_4(\text{OCH}_2\text{C}_4\text{H}_7)_{12}$, was reacted with 1,2-diphenylhydrazine at low temperatures and slowly warmed to room temperature. Again, there was no evidence for reactivity under conditions similar to those employed in the cleavage of CO , RCN , RNC and $\text{RC}\equiv\text{CR}$ [15–18].

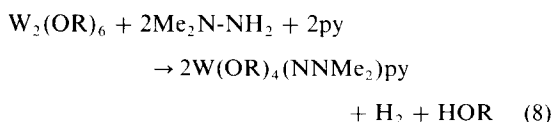
Reactions with 1,1-dimethylhydrazine. Synthesis of $[\text{W}(\text{OPr}^i)_4(\text{NNMe}_2)\text{py}]$ (4). Hydrocarbon solutions of $[\text{W}_2(\text{H})(\text{OPr}^i)_7]_2$ and $\text{W}_2(\text{H})(\text{O}^i\text{C}_5\text{H}_9)_7(\text{HNMe}_2)$ react with 1,1-dimethylhydrazine to give $[\text{W}(\text{OR})_4(\text{NNMe}_2)\text{py}]$ [$\text{R} = \text{OPr}^i$ (**4a**) or $^i\text{C}_5\text{H}_9$ (**4b**)] as the only isolable metalloorganic products. X-ray quality crystals of **4a** were obtained from solutions of pentane and pyridine (1:1) at -20°C . The X-ray crystal structure revealed **4a** to contain a hydrazido ($2-$) ($\text{N}=\text{NMe}_2$) ligand (see later). Compounds **4** can be stored in the solid state at room temperature for several months without decomposition.

In principle, at least, this reaction could lead to N-N cleavage to give dimethylamine and the imido complex, $[\text{W}(\text{OPr}^i)_4(\text{NH})]$. However, the only product isolated is the hydrazido ($2-$) species, $[\text{W}(\text{OPr}^i)_4(\text{NNMe}_2)\text{py}]$. This preference for hydrazido ($2-$) over imido ($2-$) can be accounted for by the kinetic facility of N-H activation over 1,2-migration and reductive cleavage of an η^1 -hydrazido N-N bond.

The reaction of $\text{W}_2(\mu\text{-H})(\text{OR})_7\text{L}$ requires 2 equiv. of 1,1-dimethylhydrazine to go to completion, consistent with the reaction summarized in eq. (7).



It has also been established that $[\text{W}(\text{OPr}^i)_4(\text{NNMe}_2)\text{py}]$ is the major product isolated from the reaction between $\text{W}_2(\text{OR})_6$ ($\text{R} = \text{Pr}^i$ and CH_2CMe_3) and 1,1-dimethylhydrazine, eq. (8).



This facile reactivity complements that of 1,2-diphenylhydrazine, both of which differ from the nonprotic reagent azobenzene. This difference in reactivity is believed to be due to the increase in acidity of

the N—H protons upon coordination. This facilitates further ligand transformations at the metal center, an activation pathway inaccessible to $\text{PhN}=\text{NPh}$. Schrock and coworkers have demonstrated that similar proton transfer reactions enable facile entry into hydrazido coordinated monomers [24].

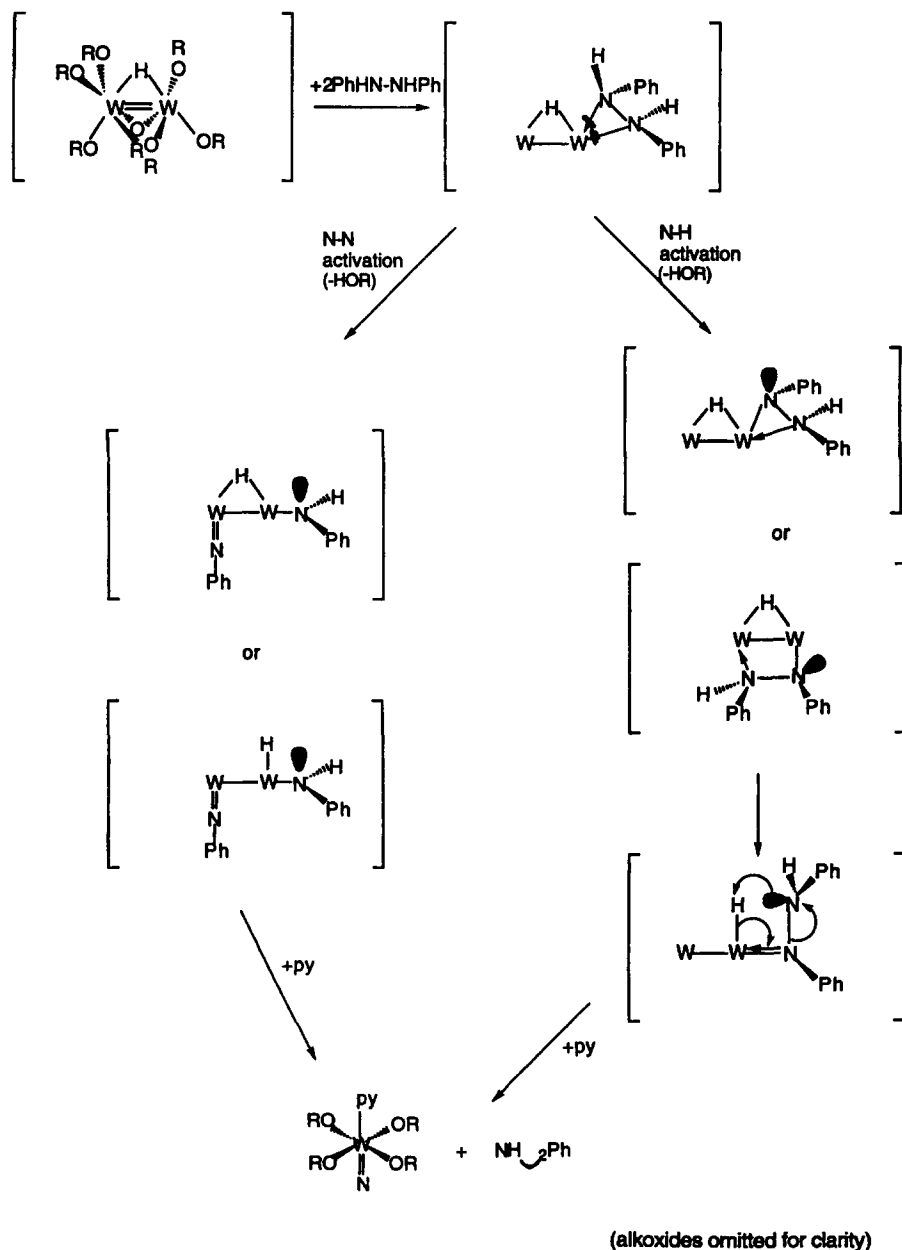
The cluster, $\text{W}_4(\text{OCH}_2\text{C}_4\text{H}_7)_{12}$, was allowed to react with 1,1-dimethylhydrazine at low temperatures and slowly warmed to room temperature. No reaction was observed and starting materials were recovered in high yields.

Reactions with phenylhydrazine. The reaction of $\text{W}_2(\mu\text{-H})(\text{OR})_7\text{L}$ complexes with PhHN_2H_2 in hydro-

carbon solutions appear to lead to a single metallocene product. This product is intensely purple and could possibly be an $\eta^2\text{-PhHN}_2\text{H}_2$ complex similar to one of the ditungsten intermediates proposed in Scheme 2 (see Conclusions). The spectroscopic data (Experimental) are, however, inconclusive and crystallization has proven to be unsuccessful.

Solid-state and molecular structures; considerations of bonding

$[\text{W}(\text{O}^i\text{Pr})_4(\text{NPh})_2]$. An ORTEP drawing of the molecule is given in Fig. 1 along with a stick drawing.



Scheme 2.

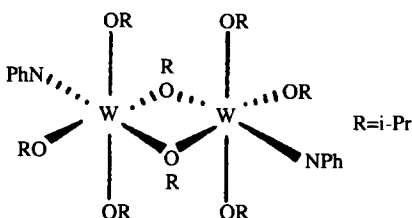
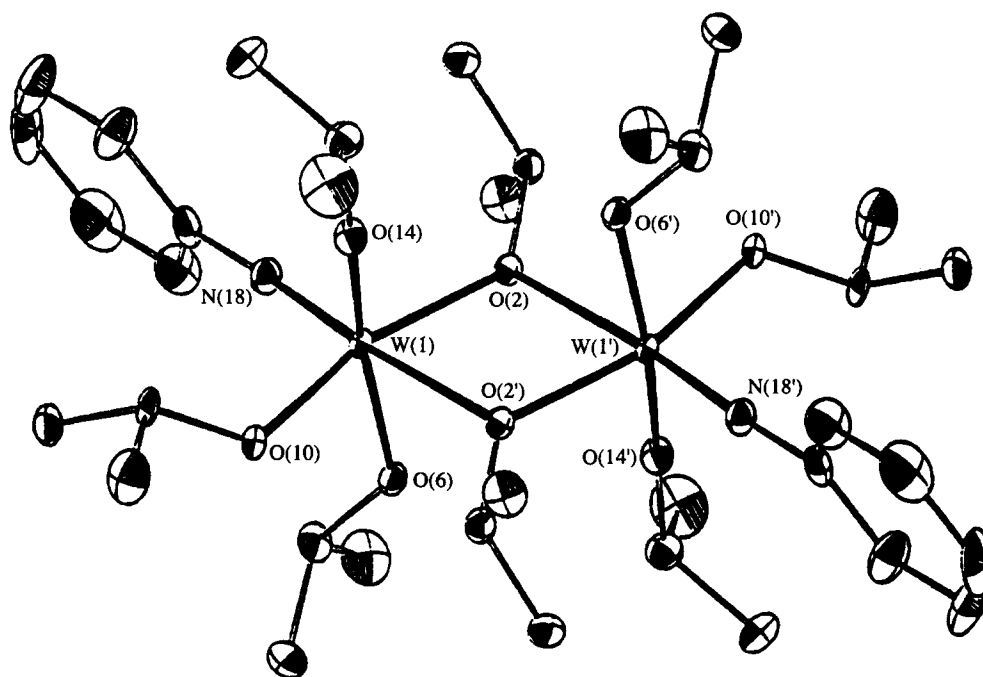


Fig. 1. ORTEP view of the $[W(OPr^i)_4(NPh)]_2$ (**1**) molecule giving the atom number scheme used in the tables (top) and a schematic drawing of the molecule (bottom). Thermal ellipsoids are of 50% probability.

Selected bond distances and angles are given in Tables 1 and 2, respectively. The molecule adopts an edge-shared bioctahedral geometry with two bridging OPr^i ligands, six terminal OPr^i ligands and two terminal imido ligands. The nonbonding $W(1)-W(1')$ distance, not included in the tables, is 3.4662(9) Å. The structure is very similar to that of $[W(OR)_4(NR')]_2$ ($R = Me$, $R' = Ph$; [25] $R = Me$ or Pr^i , $R' = NC_6H_4Me-4$ [26]). The short $W-N$ distances [$W-N = 1.755(5)$ Å] and large $W-N-C$ angles [$W-N-C(19) = 177.3^\circ$] are comparable to those observed in other tungsten phenylimido compounds, [25–28] supporting a $W-N$ bond order of three, as predicted by Nugent and Haymore [29].

Table 1. Selected bond distances (Å) for $[W(OPr^i)_4(NPh)]_2$, (**1**)

$W(1)-O(2)$	2.039(4)
$W(1)-O(6)$	1.915(4)
$W(1)-O(14)$	1.877(4)
$O(2)-C(3)$	1.464(6)
$N(18)-C(19)$	1.383(7)
$W(1)-O(2')$	2.227(4)
$W(1)-O(10)$	1.932(4)
$W(1)-N(18)$	1.755(5)
$O(6)-C(7)$	1.430(6)
$O(14)-C(15)$	1.398(7)
$O(10)-C(11)$	1.421(6)

Table 2. Selected bond angles (°) for [W(OPr^t)₄(NPh)]₂(1)

O(2)—W(1)—O(2')	71.40(16)
O(2)—W(1)—O(6)	90.46(16)
O(2)—W(1)—O(10)	160.56(15)
O(2)—W(1)—O(14)	89.97(16)
O(2)—W(1)—N(18)	100.11(18)
O(6)—W(1)—O(14)	163.44(16)
O(10)—W(1)—O(14)	88.15(17)
O(14)—W(1)—N(18)	99.07(20)
W(1')—O(2)—C(3)	121.1(3)
W(1)—O(6)—C(7)	127.2(3)
W(1)—O(14)—C(15)	169.2(4)
O(2')—W(1)—O(6)	79.81(15)
O(2')—W(1)—O(10)	89.16(15)
O(2')—W(1)—O(14)	84.65(16)
O(2)—W(1)—N(18)	170.83(18)
O(6)—W(1)—O(10)	85.95(16)
O(6)—W(1)—N(18)	97.14(19)
O(10)—W(1)—N(18)	99.29(19)
W(1)—O(2)—W(1')	108.60(16)
W(1)—O(2)—C(3)	129.4(3)
W(1)—O(10)—C(11)	126.9(3)
W(1)—N(18)—C(19)	177.3(4)

This value is within the range seen (1.61–1.77 Å) for other tungsten imido complexes [30, 31].

The bridging isopropoxide ligands are coordinated *trans* to each imido ligand, as has been observed in similar complexes [25, 26]. Three types of W—O bond distances are evident in **1**. Terminal alkoxides typically exhibit bond lengths of 1.83–1.95 Å; however, upon bridge formation a lengthening of 0.1–0.2 Å is often observed as seen for **1** [W—O(2') = 2.039(4) Å] [32]. The elongated nature of the remaining bridging W—O distance [W(1)—O(2') = 2.227(4) Å] can be attributed to its location opposite to an imido ligand with a strong *trans* influence, affording a highly asymmetric bridging alkoxide environment. In the distorted octahedral geometry of W(1), atoms O(2), O(14), O(6) and O(10) are displaced away from the imido nitrogen toward the *trans* donor ligands (the average angle subtended by N and each of the above four oxygen donors at W is 99°). This has been observed in other phenylimido and related nitrido complexes where the M—N distance is short.

W₃(μ₃-H)(OPr^t)₉(NPh)py. An ORTEP drawing of molecule **2** is given in Fig. 2(a) along with a stick drawing. Selected bond distances and angles are given in Tables 3 and 4. W₃(μ₃-H)(OPr^t)₉(NPh)py is a six-electron triangular cluster with three two-center two-electron bonds arranged to form an isosceles triangle where the angles and lengths are almost symmetrical [W(2)—W(1)—W(3) = 62.8(1), W(1)—W(2)—W(3) = 58.6(1) and W(1)—W(3)—W(2) = 58.6(1) and W(1)—W(2) = 2.6476(10), W(1)—W(3) = 2.6475(8) and W(2)—W(3) = 2.7584(9) Å].

One of the most notable features of this cluster is the presence of a bridging imido ligand

[W(1)—N(12) = 1.895(11) and W(3)—N(12) = 1.971(11) Å]. The related imido, alkylidyne and oxo capped clusters W₃(μ₃-X)(OR)₉ (X = NR, CR, O respectively) are formed from conproportionation reactions [33]. The preference of this compound to adopt an imido edge-bridged structure rather than a W₃(μ₃-NR) pseudo-tetrahedral geometry may reflect a nonredox condensation reaction pathway for its formation.

A second unique feature of this cluster involves the hydride ligand, that was not located crystallographically and was placed in an idealized position capping the W₃ triangle. A side view of molecule **2** is given in Fig. 2(b) and shows the vacant site in which the hydride ligand caps one face of the trinuclear unit. The location of the hydride site was acceptable to the XHYDEX program, [34] the μ₃-H group providing a significantly lower potential energy minimum relative to the alternative solutions of placing it bridging two metal atoms or terminal on W(1).

All three W—W bonds contain bridging ligands, two alkoxide and one imido, of which the latter is planar in nature [sum of the angles at N(12) = 359°], reflecting its σ,π-donor characteristics. All three tungsten atoms are formally W^{IV}; however, the coordination environment of each of these differs. In the absence of M—M bonding W(1) is five-coordinate, with severely distorted square-pyramidal coordination, while W(2) and W(3) are six-coordinate distorted octahedrons. All three tungsten atoms are attached to the capping hydride ligand (average W—H = 1.95 Å). W(1) has two terminal alkoxide ligands, one bridging alkoxide and one bridging imido ligand. The average L—W—L angle around W(1) is 107.1°. The two terminal oxygens [O(19) and O(23)] are distorted away from the bridging imido group (average N—W—O angle = 85.4°). W(2) has three terminal and two bridging alkoxide ligands. The average angle involving W(2) and its ligands is 106.7°. The equatorial sites are nearly planar, with the average angle of the *trans*-O—W—O planar groups equal to 172°. W(3) has two terminal and one bridging alkoxide ligand, one terminal pyridine molecule and one bridging imido group. The average angle involving W(3) and its ligands is 105.8°. The terminal oxygen, O(43), and the hydride ligand occupy the axial sites of the octahedron. The equatorial sites are nearly planar, with the angles of O(8)—W(3)—O(39) and N(12)—W(3)—N(47) equal to 160.3 and 173.9°, respectively.

The three bridging groups lie below the plane of the triangle. The average distance between the tungsten centers and the bridging alkoxide is 2.05 Å, while the average to the terminal alkoxides is 1.94 Å. The coordination sphere of W(3) is completed by the presence of a weakly bound pyridine molecule [W(3)—N(47) = 2.276(11) Å]. The imido ligand bridges unsymmetrically [W(1)—N(12) = 1.895(11) and W(3)—N(12) = 1.971(11) Å]. The shorter W—N bonding distance is consistent with the lower coord-

dination number and intrinsic electronic unsaturation of the W(1) center in comparison to W(2) and W(3). Although N(12) is planar, the angles at the imido nitrogen differ: W(3)—N(12)—C(13) = 145.5(9) and W(1)—N(12)—C(13) = 127.9(9)°. In a similar manner the W(1)—W(2) edge is asymmetrically bridged by alkoxide O(4) [W(1)—O(4) = 1.988(10) and

W(2)—O(4) = 2.104(9) Å] with the shorter W—O bond being associated with the coordinatively unsaturated W(1). In contrast, O(8) symmetrically bridges W(2) and W(3) [W(2)—O(8) = 2.065(9), W(3)—O(8) = 2.030(9) Å], a consequence of the similar coordination environments for these two metal sites.

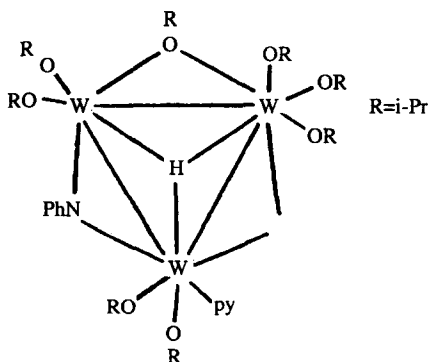
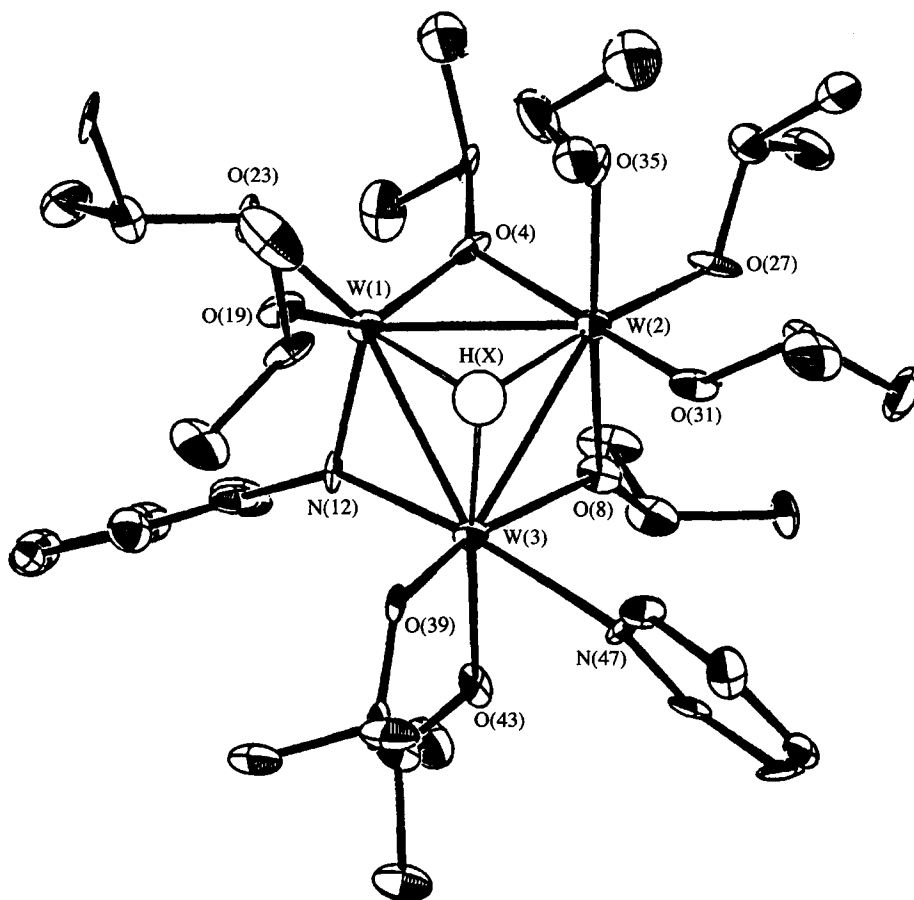
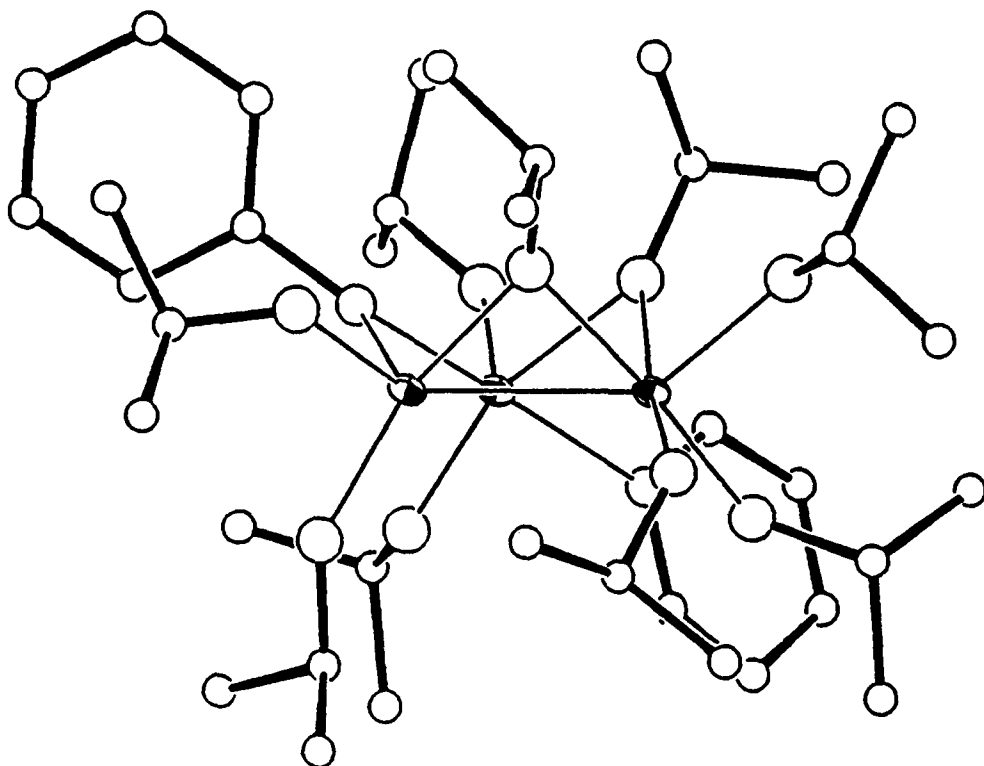


Fig. 2. (a) ORTEP view of the $W_3(\mu_3\text{-H})(\text{OPr})_9(\text{NPh})\text{py}$ (**2**) molecule giving the atom number scheme used in the tables (top) and a schematic drawing of the molecule (bottom). Thermal ellipsoids are of 50% probability. (b) Side view of the $W_3(\mu_3\text{-H})(\text{OPr})_9(\text{NPh})\text{py}$ (**2**) molecule. Note how the hydride ligand can cap the vacant site on the lower face of the molecule.

Fig. 2. *Continued.*Table 3. Selected bond distances (Å) for $W_3(\mu_3\text{-H})(\text{OPr})_9(\text{NPh})\text{py}$ (2)

W(1)—W(2)	2.6476(10)
W(1)—O(4)	1.988(10)
W(1)—O(23)	1.894(9)
W(2)—W(3)	2.7584(9)
W(2)—O(8)	2.065(9)
W(2)—O(31)	1.915(10)
W(3)—O(8)	2.030(9)
W(3)—O(43)	1.896(9)
W(3)—N(47)	2.276(11)
O(8)—C(9)	1.456(17)
O(23)—C(24)	1.421(16)
O(31)—C(32)	1.423(18)
O(39)—C(40)	1.417(17)
N(12)—C(13)	1.456(18)
N(47)—C(52)	1.363(19)
W(1)—W(3)	2.6475(8)
W(1)—O(19)	1.982(9)
W(1)—N(12)	1.895(11)
W(2)—O(4)	2.104(9)
W(2)—O(27)	1.975(10)
W(2)—O(35)	1.944(9)
W(3)—O(39)	1.983(10)
W(3)—N(12)	1.971(11)
O(4)—C(5)	1.458(16)
O(19)—C(20)	1.372(18)
O(27)—C(28)	1.417(17)
O(35)—C(36)	1.424(20)
O(43)—C(44)	1.422(17)
N(47)—C(48)	1.319(18)

$W(\text{OPr})_4(\text{NPh})\text{py}$. An ORTEP drawing of molecule **3** is given in Fig. 3 along with a stick drawing. Selected bond distances and angles are given in Tables 5 and 6. W(1) adopts a pseudo-octahedral geometry with a *trans*-arrangement of the imido and pyridine ligands. W(1) is located above the plane defined by O(2), O(4), O(10) and O(14) and can more appropriately be described as a square pyramid lightly stabilized by coordination of pyridine. This distortion is reflected in N(18)—W(1)—O, the four angles which average 99.5° , thereby minimizing the unfavorable interaction of ligand lone-pair electrons. The short W—N(18) bond distance [1.77(2) Å] and large W—N(18)—C(19) angle [W—N(18)—C(19) = $170(1)^\circ$] are close to those found in complex **1** and other high valent imido compounds [25–28]. The imido ligand exerts a strong *trans* influence on the pyridine ligand, resulting in a weak dative interaction with the metal center [W—N(25) = 2.41(2) Å]. This structure is very similar to that of $[\text{W}(\text{NPh})(\text{OCMe}_3)_3\text{Cl}(\text{NH}_2\text{CMe}_3)]$ [25] and the proposed structure of $[\text{W}(\text{NPh})(\text{OCMe}_3)_4]$ [35].

$[\text{W}(\text{OPr})_4(\text{NNMe}_2)\text{py}]$. An ORTEP drawing of molecule **4** is given in Fig. 4 along with a stick drawing. Selected bond distances and angles are given in Tables 7 and 8. The tungsten atom adopts a pseudo-octahedral geometry with O(8), O(12), O(16) and O(20) defining a square plane. W(1) is raised above this plane away from the hydrazido ligand in a manner similar to that observed for **1** and **3**. The average angle subtended at tungsten defined by the hydrazido

Table 4. Selected bond angles (°) for $W_3(\mu_3-H)(OPr^i)_5(NPh)py$ (2)

W(2)—W(1)—W(3)	62.790(23)
W(2)—W(1)—O(19)	132.22(27)
W(3)—W(1)—N(12)	101.6(3)
W(3)—W(1)—O(19)	147.5(3)
W(3)—W(1)—N(12)	48.0(3)
O(4)—W(1)—O(23)	146.5(4)
O(19)—W(1)—O(23)	87.8(4)
O(23)—W(1)—N(12)	113.2(4)
W(1)—W(2)—O(4)	47.79(28)
W(1)—W(2)—O(27)	136.0(3)
W(1)—W(2)—O(35)	91.88(28)
W(3)—W(2)—O(8)	47.11(26)
W(3)—W(2)—O(31)	90.62(28)
O(4)—W(2)—O(8)	89.3(4)
O(4)—W(2)—O(31)	173.6(4)
O(8)—W(2)—O(27)	83.8(4)
O(8)—W(2)—O(35)	170.4(4)
O(27)—W(2)—O(35)	87.4(4)
W(1)—W(3)—W(2)	58.606(23)
W(1)—W(3)—O(39)	138.29(26)
W(1)—W(3)—N(12)	45.6(3)
W(2)—W(3)—O(8)	48.21(25)
W(2)—W(3)—O(43)	125.5(3)
W(2)—W(3)—N(47)	90.1(3)
O(8)—W(3)—O(43)	160.3(4)
O(8)—W(3)—N(47)	81.7(4)
O(39)—W(3)—N(12)	93.8(4)
O(43)—W(3)—N(12)	97.5(4)
N(12)—W(3)—N(47)	173.9(4)
W(1)—O(4)—C(5)	141.1(8)
W(2)—O(8)—W(3)	84.7(3)
W(3)—O(8)—C(9)	134.4(9)
W(1)—O(23)—C(24)	138.1(9)
W(2)—W(1)—O(4)	51.62(26)
W(2)—W(1)—O(23)	120.7(3)
W(3)—W(1)—O(4)	95.44(25)
W(3)—W(1)—O(23)	109.08(28)
O(4)—W(1)—O(19)	82.9(4)
O(4)—W(1)—N(12)	100.1(4)
O(19)—W(1)—N(12)	100.1(4)
W(1)—W(2)—W(3)	58.604(23)
W(1)—W(2)—O(8)	91.66(28)
W(1)—W(2)—O(31)	127.7(3)
W(3)—W(2)—O(4)	89.62(26)
W(3)—W(2)—O(27)	130.93(26)
W(3)—W(2)—O(35)	141.3(3)
O(4)—W(2)—O(27)	88.3(4)
O(4)—W(2)—O(35)	86.5(4)
O(8)—W(2)—O(31)	95.6(4)
O(27)—W(2)—O(31)	96.4(4)
O(31)—W(2)—O(35)	89.3(4)
W(1)—W(3)—O(8)	92.47(26)
W(1)—W(3)—O(43)	97.84(26)
W(1)—W(3)—N(47)	139.8(3)
W(2)—W(3)—O(39)	134.9(3)
W(2)—W(3)—N(12)	95.9(3)
O(8)—W(3)—O(39)	86.7(4)
O(8)—W(3)—N(12)	101.7(4)
O(39)—W(3)—O(43)	96.5(4)
O(39)—W(3)—N(47)	81.3(4)
O(43)—W(3)—N(47)	79.6(4)
W(1)—O(4)—W(2)	80.6(3)

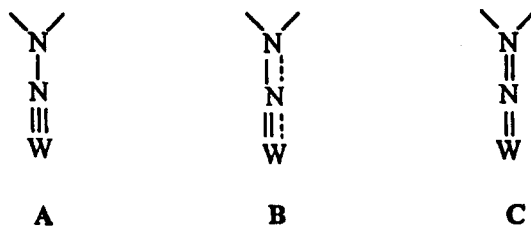
Table 4—continued

W(2)—O(4)—C(5)	137.6(8)
W(2)—O(8)—C(9)	140.3(8)
W(1)—O(19)—C(20)	128.3(8)
W(2)—O(27)—C(28)	131.0(9)
W(2)—O(31)—C(32)	129.1(8)
W(3)—O(39)—C(40)	137.1(9)
W(1)—N(12)—W(3)	86.4(4)
W(3)—N(12)—C(13)	145.5(9)
W(3)—N(47)—C(52)	120.5(9)
O(4)—C(5)—C(6)	108.8(11)
C(6)—C(5)—C(7)	112.9(12)
O(8)—C(9)—C(11)	110.4(13)
N(12)—C(13)—C(14)	117.2(12)
W(2)—O(35)—C(36)	133.3(9)
W(3)—O(43)—C(44)	132.5(9)
W(1)—N(12)—C(13)	127.9(9)
W(3)—N(47)—C(48)	122.7(10)
C(48)—N(47)—C(52)	116.8(12)
O(4)—C(5)—C(7)	108.0(12)
O(8)—C(9)—C(10)	109.2(12)
C(10)—C(9)—C(11)	113.4(13)
N(12)—C(13)—C(18)	122.1(14)

nitrogen and alkoxide oxygens is 99° , while the tungsten is raised a distance of 0.32 \AA out of the mean plane defined by the four oxygen atoms.

The elongated tungsten-pyridine bond length [$W-N = 2.397(17) \text{ \AA}$] reflects the powerful *trans* influence exerted by the hydrazido ($2-$) ligand. This bond lengthening is statistically similar to that observed in the imido supported compound $W(NPh)(OPr^i)_4py$. The $W-N-N$ linkage of the hydrazido ($2-$) moiety displays an almost linear geometry, $171.0(16)^\circ$, while the $W-N$ bond length [$1.765(14) \text{ \AA}$] and the $N-N$ bond length [$1.355(25) \text{ \AA}$] indicate an extensive electronic delocalization throughout the framework. Nugent and Haymore have reported that the range of $N-N$ bond lengths of $1.26-1.37 \text{ \AA}$ corresponds to bond orders of $1.9-1.3$, respectively [29]. By this criterion, a $N-N$ bond order of ~ 1.3 for the hydrazido ligand and a $W-N$ bond order of less than three can be assigned for the $W(NNMe_2)(OR)_4py$ compound.

There are three possible structural descriptions for the hydrazido ligand (**A-C**). For two similar systems the depictions have been discussed. [36] The structure of $[ReCl_2(NH_3)(N_2HPh)(PMe_2Ph)_2]^+$ is best described by **A** [$Re-N(1) = 1.75(1)$, $N(1)-N(2) = 1.28(2) \text{ \AA}$; $Re-N(1)-N(2) = 172(1)^\circ$] [37a]. The structure of $[WCl(NNH_2)(diphos)_2]^+$ [diphos = 1,2-bis(diphenylphosphino)ethane]; $W-N(1) = 1.73(1)$, $N(1)-N(2) = 1.37(2) \text{ \AA}$; $W-N(1)-N(2) = 171(1)^\circ$] [37b] has been described by **C**. The most appropriate description of the hydrazido ligand in $W(OPr^i)_4(NNMe_2)py$ would be expressed by **B**, an intermediate between **A** and **C**.



NMR and other spectroscopic studies

$[\text{W}(\text{OPr}^i)_4(\text{NPh})]_2$. The room-temperature ^1H NMR spectrum of **1** consists of a single isopropoxide resonance, suggestive of a dynamic process that exchanges all the alkoxide ligands. The low-temperature (-80°C) ^1H NMR spectrum showed isopropoxide resonances in the ratio 2:1:1 and four methyl resonances; reflecting the diastereotopic nature of the methyl groups of the *trans* axial isopropoxide ligands. This low-temperature spectrum is consistent with the solid-state structure.

Errington and coworkers have reported similar observations, performing detailed studies of the dynamic exchange properties in dimers with the general formula $[\text{W}(\text{E})(\text{OR})_4]_2$ ($\text{E} = \text{O}$, NPh and $\text{OR} = \text{OMe}$, OEt , OPr^i , and OBu^t).^[26] For both $\text{E} = \text{O}$ and NPh steric congestion favors rapid $\text{M}-\text{OR}$ bond rupture to generate species of type **E**. However, in the oxo-alkoxide dimers, the *trans* effect and steric properties combine to facilitate further $\text{W}-\text{O}$ bond cleavage to give a monomer dimer equi-

Table 5. Selected bond distances (\AA) for $\text{W}(\text{OPr}^i)_4(\text{NPh})\text{py}$ (**3**)

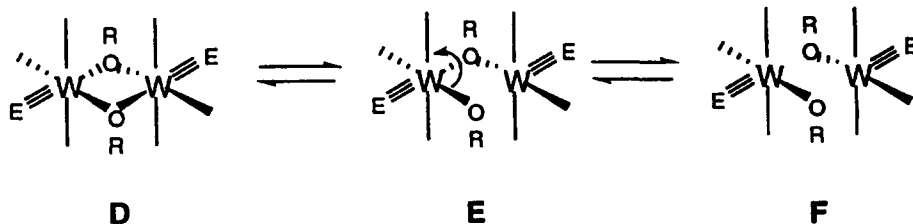
W(1)—O(2)	1.944(17)
W(1)—O(10)	1.970(17)
W(1)—N(18)	1.772(22)
O(2)—C(3)	1.37(3)
O(10)—C(11)	1.43(3)
N(18)—C(19)	1.45(3)
N(25)—C(30)	1.33(3)
W(1)—O(6)	1.977(16)
W(1)—O(14)	1.912(16)
W(1)—N(25)	2.415(22)
O(6)—C(7)	1.39(3)
O(14)—C(15)	1.354(27)
N(25)—C(26)	1.35(3)

Table 6. Selected bond angles ($^\circ$) for $\text{W}(\text{OPr}^i)_4(\text{NPh})\text{py}$ (**3**)

O(2)—W(1)—O(6)	88.4(7)
O(2)—W(1)—O(14)	94.0(7)
O(2)—W(1)—N(25)	80.2(7)
O(6)—W(1)—O(14)	159.8(7)
O(6)—W(1)—N(25)	82.0(7)
O(10)—W(1)—N(18)	103.4(9)
O(14)—W(1)—N(18)	101.0(9)
N(18)—W(1)—N(25)	174.7(9)
W(1)—O(6)—C(7)	123.9(15)
W(1)—O(14)—C(15)	131.3(14)
W(1)—N(25)—C(26)	119.6(17)
C(26)—N(25)—C(30)	121.7(23)
O(2)—C(3)—C(5)	112.4(21)
N(18)—C(19)—C(24)	112.2(25)
N(25)—C(26)—C(27)	119.8(24)
O(2)—W(1)—O(10)	161.7(7)
O(2)—W(1)—N(18)	94.6(8)
O(6)—W(1)—O(10)	85.7(7)
O(6)—W(1)—N(18)	98.8(9)
O(10)—W(1)—O(14)	85.7(7)
O(10)—W(1)—N(25)	81.8(7)
O(14)—W(1)—N(25)	78.7(7)
W(1)—O(2)—C(3)	132.5(15)
W(1)—O(10)—C(11)	132.4(14)
W(1)—N(18)—C(19)	169.5(19)
W(1)—N(25)—C(30)	118.7(17)
O(2)—C(3)—C(4)	106.8(20)
N(18)—C(19)—C(20)	122.8(24)
N(25)—C(30)—C(29)	118.3(24)

librium, $\text{D} \rightleftharpoons \text{F}$. In the case of imido-alkoxides, the weaker *trans* effect of the NPh ligand favors rotation before bond dissociation and intramolecular site exchange is observed.^[26]

$\text{W}_3(\mu_3\text{-H})(\text{OPr}^i)_6(\text{NPh})\text{py}$. The $(\mu_3\text{-H})$ ligand of **2** could arise from either: (a) alkoxide degradation to $(\mu\text{-H})$ and ketone [38] or (b) from the original hydride



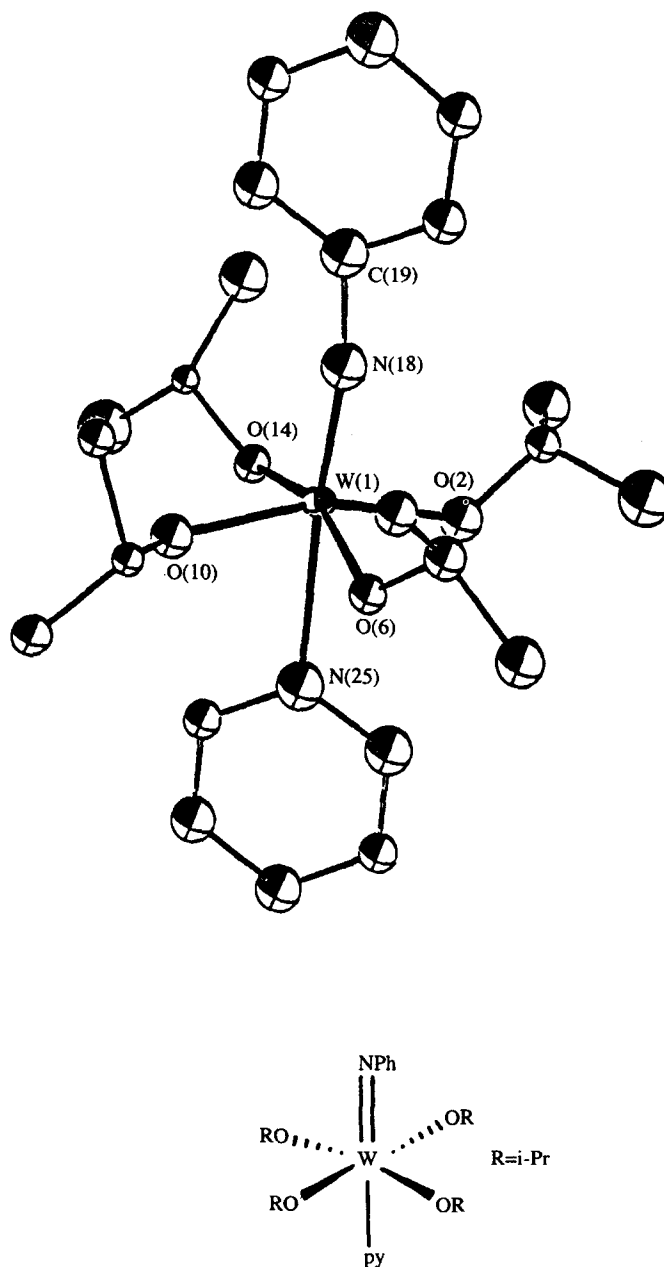


Fig. 3. ORTEP view of the $W(OPr)_4(NPh)py$ (**3**) molecule giving the atom number scheme used in the tables (top) and a schematic drawing of the molecule (bottom). Thermal ellipsoids are of 50% probability.

of $W_2(H)(OR)_7$, the latter being favored in the absence of acetone. In the reaction of $[W_2(\mu-H)(OPr-d_7)_7]_2$ and azobenzene the hydride signal was observed at 4.86 ppm in benzene- d_6 . Satellites due to tungsten coupling were not observed. A tentative assignment of its stretching vibration at 1587 cm^{-1} in its IR spectrum is consistent with a previously reported $Mo_4(\mu_3-H)(\mu_2-H)_2(OBu^t)_7(HNMe_2)$ cluster [39].

Reactions with 1,2-diphenylhydrazine. The progress of the reaction between $[W_2(H)(OPr^i)_7]_2$ and 1,2-diphenylhydrazine was monitored by 1H NMR spectroscopy and $[W(NPh)(OPr^i)_4]$ was identified as the

only metalloorganic species formed. The absence of $[W_3(\mu_3-H)(OPr^i)_9(NPh)]$ is consistent with a different pathway for reduction of the N—N bond. GC-MS analysis of the reaction mixture identified aniline and isopropanol as byproducts. During the course of the reaction a low concentration of a second hydride-containing complex was observed ($\delta = 12.47$ ppm, $^1J_{183W-1H} = 77.8$ Hz, 28%), that persisted during the course of the reaction as monitored by 1H NMR spectroscopy. This hydridic intermediate has not been observed by 1H NMR spectroscopy in the reactions of $[W_2(D)(OPr^i)_7]_2$ with 1,2-diphenylhydrazine, sug-

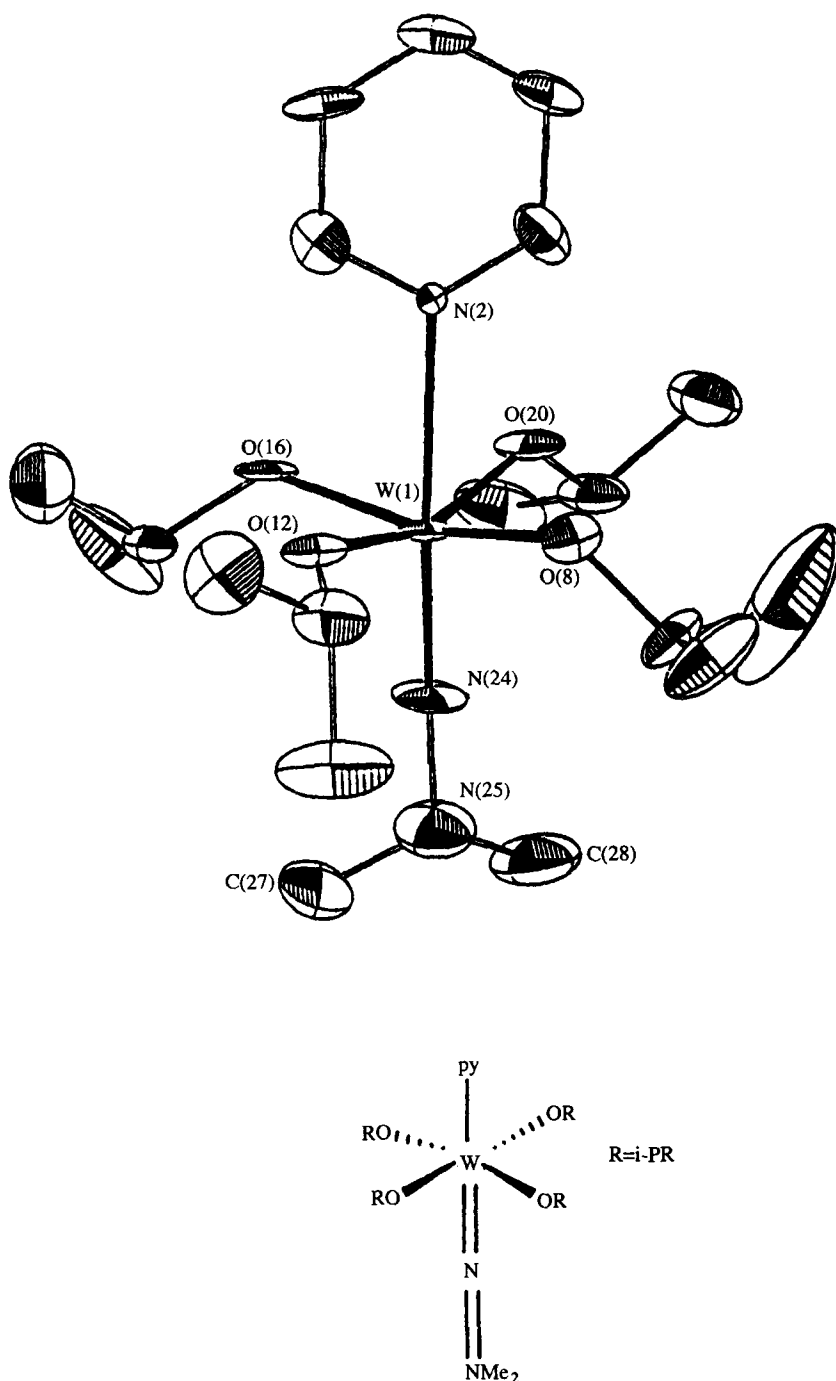


Fig. 4. ORTEP view of the $W(OPr)_4(NNMe_3)py$ (**4**) molecule giving the atom number scheme used in the tables (top) and a schematic drawing of the molecule (bottom). Thermal ellipsoids are of 50% probability.

gesting that this hydride intermediate corresponds to the η^2 -hydrazine adduct. A possible mechanism for the reaction that follows may involve N—H activation and formation of either a hydrazido (1-) or a (2-) ligand, shown in Scheme 2 (see Conclusions). Here it is acknowledged that two possible structural arrangements exist for the hydrazido ligand, one of which contains the hydrazido ligand bound to one tungsten

atom with accidental equivalent coupling, the second involving a bridging N_2 fragment. All attempts to isolate this intermediate in large scale reactions have been unsuccessful.

This type of reaction pathway has recently been observed [40]. The reaction of 1,2-diphenylhydrazine and $[(ArO)_2Zr(Me)_2]$ ($ArO = 2,6$ -di-*tert*-butylphenoxide) initially leads to the formation of

Table 7. Selected bond distances (Å) for $W(OPr)_4(NNMe_2)py$ (**4**)

W(1)—O(8)	1.944(15)
W(1)—O(16)	1.947(14)
W(1)—N(2)	2.397(17)
O(8)—C(9)	1.431(25)
O(16)—C(17)	1.398(24)
N(2)—C(3)	1.326(27)
N(24)—N(25)	1.355(25)
N(25)—C(27)	1.37(3)
W(1)—O(12)	1.945(15)
W(1)—O(20)	1.928(15)
W(1)—N(24)	1.765(14)
O(12)—C(13)	1.42(3)
O(20)—C(21)	1.425(26)
N(2)—C(7)	1.309(26)
N(25)—C(26)	1.37(3)

Table 8. Selected bond angles (°) for $W(OPr)_4(NNMe_2)py$ (**4**)

O(8)—W(1)—O(12)	86.9(6)
O(8)—W(1)—O(20)	92.1(6)
O(8)—W(1)—N(24)	100.7(7)
O(12)—W(1)—O(20)	160.1(5)
O(12)—W(1)—N(24)	102.6(7)
O(16)—W(1)—N(2)	82.5(6)
O(20)—W(1)—N(2)	77.9(6)
N(2)—W(1)—N(24)	175.0(7)
W(1)—O(12)—C(13)	132.8(15)
W(1)—O(20)—C(21)	133.9(12)
W(1)—N(2)—C(7)	117.4(15)
W(1)—N(24)—N(25)	171.0(16)
N(24)—N(25)—C(27)	113.9(21)
O(8)—W(1)—O(16)	160.9(6)
O(8)—W(1)—N(2)	80.0(6)
O(12)—W(1)—O(16)	83.2(6)
O(12)—W(1)—N(2)	82.3(6)
O(16)—W(1)—O(20)	91.6(6)
O(16)—W(1)—N(24)	97.4(6)
O(20)—W(1)—N(24)	97.1(7)
W(1)—O(8)—C(9)	129.7(13)
W(1)—O(16)—C(17)	128.7(12)
W(1)—N(2)—C(3)	117.6(14)
C(3)—N(2)—C(7)	124.7(20)
N(24)—N(25)—C(26)	112.9(21)
C(26)—N(25)—C(27)	123.2(25)

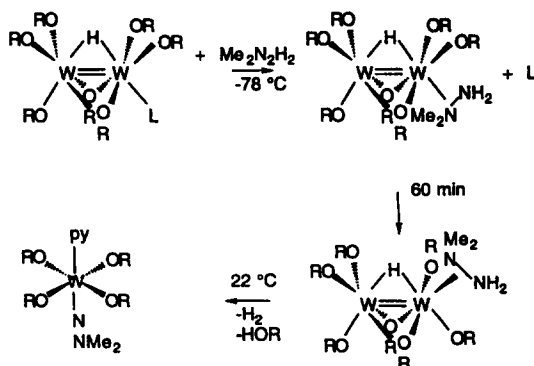
$[(ArO)_2Zr(Me)(\eta^2-PhNNHPh)]$ and 1 equiv. of methane. Upon addition of 4-pyrrolidinopyridine (py'), methane and an η^2 -azobenzene complex are formed, $[(ArO)_2Zr(\eta^2-PhNNHPh)(py')_2]$. $[(ArO)_2Zr(\eta^2-PhNNHPh)(py')_2]$ slowly converts to the imido complex $[(ArO)_2Zr(NPh)(py')_2]$ at ambient conditions.

Symmetric 1,2-disubstituted hydrazines $NHRNHR$ ($R = Me, Ph, etc.$) have been cleaved to form the imido complexes $Re(NMe)Cl_3(PPh_3)$ [41] and $[TaCl_2(NH_2Ph)]_2(\mu-Cl)_2(\mu-NPh)$ [42]. Thus, facile cleavage of the N—N bond in hydrazine and sub-

stituted hydrazines followed by complex reactions have ample precedent.

Several mechanistic possibilities have previously been considered for the reduction of hydrazine at a d^2 -tungsten center, including N—H activation of an η^2 -hydrazine to yield the hydrazido ($1-$) hydride intermediate as in $[Cp^*WMe_3H(\eta^2-NHNH_2)]$, followed by 1,2-hydride migration to N_β and formation of the imido complex $[Cp^*WMe_3(NH)]$ [13]. A more direct route has been addressed which involved 1,2-migration of hydrogen from N_α to N_β in the η^1 -hydrazine intermediate $[Cp^*WMe_3(\eta^1-H_2NNH_2)]$. This route was considered to be less favorable as a consequence of the spacial arrangement of the lone pair. Other possibilities considered by Schrock and coworkers include α -hydrogen transfer in the higher oxidation state bis-amido complex $[WCp^*Me_3(NH_2)_2]$, a reaction that currently has precedent in the formation of high valent zirconium imido complexes [43].

Reactions with 1,1-dimethylhydrazine. The spectroscopic properties of **4a** and **4b** are complementary, indicative of similar structures. In the NMR tube reaction of $[W_2(\mu-D)(OPr')_7]_2$ and 1,1-dimethylhydrazine the molecular hydrogen signal revealed no coupling to deuterium, indicating that the hydride ligand is lost as $DOPr'$. Low-temperature 1H NMR studies of the reaction between $[W_2(H)(OPr')_7]_2$ and 1,1-dimethylhydrazine (toluene- d_8 — $-60^\circ C$) revealed rapid formation of an adduct with four distinct isopropoxide resonances in the ratio 2 : 2 : 2 : 1. After 1 h at $-60^\circ C$ the kinetic product rearranged to a new species with seven distinct isopropoxide signals. It is believed that the kinetic product results from addition of hydrazine *trans* to the hydride ligand and that this subsequently rearranges to the *cis* isomer [44,45]. These observations are shown in Scheme 3. Similar observations have been noted in the reaction of $W_2(H)(OR)_7L$ with ethyne [20]. Most notable were the distinctive spectroscopic features of these adducts, displaying vastly different $^1J_{^{183}W-^1H}$ values for the *cis* and *trans* isomers (*trans*: $^1J_{^{183}W-^1H} = 56$ and 82 Hz; *cis*: $^1J_{^{183}W-^1H} = 79$ and 102 Hz) [20]. Based upon these and previous observations a *trans* configuration has been assigned to the kinetic isomer with the smaller $^1J_{^{183}W-^1H}$ coup-



Scheme 3.

ling constants ($^1J_{\text{W} \cdots \text{H}} = 58$ and 148 Hz), while that with larger $^1J_{\text{W} \cdots \text{H}}$ values (97 and 158 Hz) to an isomer with a *cis* arrangement of the bridging hydride and terminal hydrazine ligands. These species do not persist in solution; upon gradual warming to room temperature there is a rapid formation of $[\text{W}(\text{OPr}^i)_4(\text{NNMe}_2)\text{py}]$, isopropanol and dihydrogen.

The IR spectrum of **4a** shows a band at 1605 cm^{-1} , the region associated with the $\nu(\text{N}=\text{N})$ stretching of hydrazido (2-) ligands [$\nu(\text{N}=\text{N}) = 1604 \text{ cm}^{-1}$ for **4b**]. Carrillo and coworkers have recently reported structural and spectroscopic data for high valent molybdenum hydrazido (2-) complexes that support these observations [46].

Concluding remarks

It has been shown that the doubly bonded complexes ($[\text{W}_2(\text{H})(\text{OPr}^i)_7]_2$ and $\text{W}_2(\text{H})(\text{O}^i\text{C}_5\text{H}_9)_7(\text{HNMe}_2)$) reductively cleave the N—N bonds in azobenzene and 1,2-diphenylhydrazine to yield high valent imido tungsten containing complexes and the corresponding substituted amines. The nature of this N_2 substrate activation depends upon the degree of substitution at nitrogen. 1,2-Disubstituted hydrazines are cleaved readily while 1,1-disubstituted hydrazines preferentially form hydrazido (2-) complexes. Also, whereas $\text{W}_2(\mu\text{-H})(\text{OR})_7\text{L}$ complexes readily activate azobenzene, analogous reactions with $\text{W}_2(\text{OR})_6$ are extremely "sluggish" (*ca* 3 weeks). In contrast, reactions between $\text{W}_2(\text{OR})_6$ and 1,2-diphenylhydrazine are complete within a day. These differences in reactivity are intriguing and lead us to believe that related reactions with other multiply bonded W—W and Mo—Mo dinuclear complexes should be fruitful.

In the reactions involving hydrazine, the path of the reaction can be affected by a number of factors following initial adduct formation. These include the readily available tungsten–tungsten bonding electrons for reduction and the favorable thermodynamic formation of a tungsten–nitrogen triple bond by N—H activation and generation of η^1 - or η^2 -hydrazido (1-) intermediates (Scheme 2). In all cases we have isolated products of $\text{W}(6+)$ supported by four alkoxide ligands and in this regard none of our products is formed in a stoichiometric reaction. Sacrificial alkoxide scrambling occurs, analogous to that commonly observed in metal carbonyl chemistry and we have not observed the alkoxide deficient tungsten containing products.

EXPERIMENTAL

General procedures

All solvents were dried, degassed and stored over 4 Å molecular sieves under N_2 . All synthetic and handling procedures were carried out in a purified N_2 atmosphere using Schlenk or drybox techniques.

Azobenzene, 1,1-dimethylhydrazine and 1,2-diphenylhydrazine were obtained from commercial sources and used without further purification. $[\text{W}_2(\mu\text{-H})(\text{OPr}^i)_7]_2$ and $\text{W}_2(\mu\text{-H})(\text{O}^i\text{C}_5\text{H}_9)_7(\text{HNMe}_2)$ were prepared as described previously [47].

Synthesis and NMR studies

Reaction of $[\text{W}_2(\text{H})(\text{OPr}^i)_7]_2$ with azobenzene. $[\text{W}_2(\text{H})(\text{OPr}^i)_7]_2$ (0.200 g, 0.128 mmol) and azobenzene (0.035 g, 0.192 mmol) were placed in a 50 cm^3 Schlenk flask equipped with a Teflon®-coated stir bar and pentane (20 cm^3) was added *via* cannula. The solution was allowed to stir overnight at room temperature. After *ca* 18 h the solvent was reduced *in vacuo* to 1 cm^3 . After cooling overnight at -20°C , yellow plates of $[\text{W}(\text{OPr}^i)_4(\text{NPh})]_2$ had formed and were isolated for crystallographic structure determination. Addition of approximately 1 cm^3 of pyridine led to the formation of small green crystals of $[\text{W}_3(\mu_3\text{-H})(\text{OPr}^i)_9(\text{NPh})\text{py}]$, resulting in an overall combined isolated yield of 78% of $[\text{W}_3(\mu_3\text{-H})(\text{OPr}^i)_9(\text{NPh})\text{py}]$ and $[\text{W}(\text{OPr}^i)_4(\text{NPh})\text{py}]$ based on tungsten.

$[\text{W}(\text{OPr}^i)_4(\text{NPh})]_2$. ^1H NMR (300 MHz, 22°C , benzene- d_6 , δ): Ph: 7.10 (d, 2H), 7.08 (s, 1H), 6.69 (m, 2H); $\text{OCH}(\text{CH}_3)_2$: 5.03 (m, br, 4H); $\text{OCH}(\text{CH}_3)_2$: 1.34 (d, 24H).

$\text{W}_3(\mu_3\text{-H})(\text{OPr}^i)_9(\text{NPh})\text{py}$. ^1H NMR (300 MHz, 22°C , benzene- d_6 , δ): Ph: 7.72 (d, 2H), 7.35 (d, 1H); 7.15 (m, br, 2H); $\text{OCH}(\text{CH}_3)_2$: 5.20 (s, 1H), 5.08 (s, br, 6H), 4.89 (s, 1H), 4.64 (s, 1H); $\text{OCH}(\text{CH}_3)_2$: 1.68 (d, 6H), 1.52 (d, 18H), 1.40 (d, 6H), 1.31 (d, 6H), 1.22 (d, 6H), 1.10 (d, 6H), 1.02 (d, 6H). [For spectroscopic data and elemental analysis of $\text{W}(\text{OPr}^i)_4(\text{NPh})\text{py}$, see reactions with 1,2-diphenylhydrazine.]

Due to difficulties in obtaining either material in 100% pure form, the following data correspond to the mixture of both $[\text{W}(\text{OPr}^i)_4(\text{NPh})]_2$ and $\text{W}_3(\mu_3\text{-H})(\text{OPr}^i)_9(\text{NPh})$, grown from pyridine:

^1H NMR (300 MHz, 22°C , benzene- d_6 , δ): py: 8.94 (s, br), 7.08 (m), 6.90 (t), 6.65 (m); Ph: 7.23 (m, 2H), 7.18 (m, 1H), 7.13 (m, br, 2H); $\text{OCH}(\text{CH}_3)_2$: 5.26 (sep, H), 5.13 (sep, br, H); $\text{OCH}(\text{CH}_3)_2$: 1.39 (d, H), 1.38 (d, H), 1.33 (d, H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, 22°C , benzene- d_6 , δ): 131.00, 122.25, 79.22, 77.10, 74.07, 28.45, 27.28, 26.57, 26.10, 25.95, 25.66, 25.00, 24.87.

IR (cm^{-1}): 2968 (m, br), 1586 (w), 1485 (m), 1366 (m) 1325 (w), 1163 (m), 1111 (s), 968 (s), 841 (m), 758 (w), 690 (w), 598 (m), 459 (w).

Elemental analysis: Found: C, 39.8; H, 6.0; N, 2.8. Calc. For $[\text{W}(\text{OPr}^i)_4(\text{NPh})\text{py} \cdot \text{W}_3(\mu_3\text{-H})(\text{OPr}^i)_9(\text{NPh})\text{py}]$: Found: C, 39.4; H, 6.1; N, 3.0%.

Low-temperature reaction of $[\text{W}_2(\text{H})(\text{OPr}^i)_7]_2$ and azobenzene. $[\text{W}_2(\text{H})(\text{OPr}^i)_7]_2$ (0.01 g, 0.006 mmol) and azobenzene (0.003 g, 0.02 mmol) were placed in an extended NMR tube. The sample was cooled to -78°C and cold toluene- d_8 was added. The tube was

sealed with a torch and kept cold. The sample was placed in a pre-cooled NMR spectrometer and the reaction was monitored over a period of 5 h while slowly raising the temperature. One product was initially observed in the low-temperature spectrum, which rapidly rearranged to a second. The latter did not change until the temperature was raised. Reaction of this hydride complex was not observed until 23°C. After 3.5 h, the growth of H₂ was observed in the ¹H NMR spectrum. At 4 h new resonances corresponding to [W(OPrⁱ)₄(NPh)]₂ and W₃(μ₃-H)(OPrⁱ)₉(NPh) were observed in the phenyl, methine and methyl regions.

¹H NMR (300 MHz, -15°C, toluene-*d*₈, δ): Ph: 7.72 (d), 7.35 (d), 7.15 (m, br), 7.10 (d), 7.08 (s), 6.69 (m); OCH(CH₃)₂: 5.6–4.6 (br overlapping sep); H₂: 4.46; OCH(CH₃)₂: 2.4 (d), 1.32 (d), 1.8–1.0 (overlapping d).

¹H NMR (300 MHz, -35°C, toluene-*d*₈, δ): Ph: 7.72 (d), 7.35 (d), 7.15 (m, br), 7.10 (d), 7.08 (s), 6.69 (m); OCH(CH₃)₂: 6.0 (sep, br), 5.6–4.6 (br overlapping sep); H₂: 4.46; OCH(CH₃)₂: 2.4 (d), 1.32 (d), 1.8–1.0 (overlapping d).

¹H NMR (300 MHz, -35°C, toluene-*d*₈, δ): Ph: 7.72 (d), 7.35 (d), 7.15 (m, br), 7.10 (d), 7.08 (s), 6.69 (m); OCH(CH₃)₂: 6.0 (sep, br), 5.6–4.6 (br overlapping sep); H₂: 4.46; OCH(CH₃)₂: 2.4 (d), 1.32 (d), 1.8–1.0 (overlapping d).

Room-temperature reaction of [W₂(H)(OPrⁱ)₇]₂ and azobenzene. [W₂(H)(OPrⁱ)₇]₂ (0.01 g, 0.006 mmol) and azobenzene (0.003 g, 0.02 mmol) were placed in a J. Young® tube. Benzene-*d*₆ was added to the NMR tube and the tube was shaken until the solution was homogeneous. ¹H NMR spectra were obtained over a period of 3 h. At 8 min, H₂ was observed in the ¹H NMR spectrum, as well as significant changes in the phenyl, methine and methyl regions. The reaction was complete after 2 h.

Reaction of W₂(OPrⁱ)₆(py)₂ with azobenzene. W₂(OPrⁱ)₆(py)₂ (0.209 g, 0.247 mmol) and azobenzene (0.140 g, 0.768 mmol) were placed in a 50 cm³ Schlenk flask equipped with a Teflon®-coated stir bar and pentane (20 cm³) was added *via* cannula. The solution was allowed to stir at room temperature. After *ca* 18 h the solvent was reduced *in vacuo* to 1 cm³. After cooling overnight at -20°C, yellow plates of W(OPrⁱ)₄(NPh)py had formed and were isolated in 68% yield.

¹H NMR (300 MHz, 22°C, benzene-*d*₆, δ): py: 8.99 (s, br), 7.08 (m), 6.90 (t), 6.66 (m); Ph: 7.23 (m, 2H), 7.18 (d, 1H), 7.13 (m, br, 2H); OCH(CH₃)₂: 5.26 (sep, 4H); OCH(CH₃)₂: 1.40 (d, 24H).

Reaction of W₂(H)(O^cC₅H₉)₇(HNMe₂) with azobenzene. W₂(H)(O^cC₅H₉)₇(HNMe₂) (0.200 g, 0.198 mmol) and azobenzene (0.050 g, 0.274 mmol) were placed in a 50 cm³ Schlenk flask equipped with a Teflon®-coated stir bar and pentane (20 cm³) was added *via* cannula. The solution was allowed to stir overnight at room temperature. After *ca* 18 h the solvent was reduced *in vacuo* to 1 cm³, pyridine (1 cm³) was added to the flask and, after cooling overnight

at -20°C, brown-yellow plates had formed and a mixture of W(O^cC₅H₉)₄(NPh)py and W₃(μ₃-H)(O^cC₅H₉)₉(NPh)py was isolated in 74% yield based on tungsten.

¹H NMR (300 MHz, 22°C, benzene-*d*₆, δ): Ph: 7.29 (d, *ortho*, 2H), 7.21 (t, *meta*, 2H), 6.71 (m, *para*, 1H); O^cC₅H₉, CH: 5.44 (s, br, 4H); O^cC₅H₉, CH₂: 2.32 (s, br), 1.96 (s, br), 1.84 (s, br), 1.59 (s, br) (due to broadness of the signals accurate integrals were not obtained).

¹³C {¹H} NMR (126 MHz, 22°C, benzene-*d*₆, δ): 150.00, 136.74, 127.30, 125.29, 123.28, 87.04, 36.51, 35.38, 23.92.

IR (cm⁻¹): 2955 (m br), 1601 (m), 1581 (w), 1483 (w), 1444 (w), 1367 (s), 1334 (m), 1263 (w), 1217 (m), 1167 (m), 1072 (m), 999 (s br), 935 (m), 858 (m), 758 (m), 692 (s), 630 (w), 528 (w).

Elemental analysis: Found: C, 49.9; H, 6.5; N, 3.7. Calc. For [W(O^cC₅H₉)₄(NPh)py · W₃(μ₃-H)(O^cC₅H₉)₉(NPh)py · 2py]: C, 49.7; H, 6.4; N, 3.6%.

¹H NMR (300 MHz, 22°C, benzene-*d*₆, δ): py: 9.08 (s, br), 6.68 (m, br); Ph: 7.36 (d, *ortho*, 2H), 7.24 (t, *meta*, 2H), 6.87 (m, *para*, 1H); O^cC₅H₉, CH: 5.56 (s, br, 4H); O^cC₅H₉, CH₂: 2.04–1.50 (br overlapping m).

Reaction of [W₂(H)(OPrⁱ)₇]₂ with 1,2-diphenylhydrazine. [W₂(H)(OPrⁱ)₇]₂ (0.200 g, 0.128 mmol) and 1,2-diphenylhydrazine (0.080 g, 0.434 mmol) were placed in a 50 cm³ Schlenk flask equipped with a Teflon®-coated stir bar and pentane (20 cm³) was added *via* cannula. The solution was stirred overnight at room temperature. After *ca* 18 h the solvent was reduced *in vacuo* to 1 cm³ and pyridine (1 cm³) was added to the solution. After cooling overnight at -20°C, yellow plates formed and were isolated in 68% yield based on tungsten.

¹H NMR (300 MHz, 22°C, benzene-*d*₆, δ): py: 8.98 (s, br), 6.93 (t), 6.68 (m); Ph: 7.31 (d, 2H), 7.25 (s, 1H), 6.80 (t, 2H); OCH(CH₃)₂: 5.26 (sep, 4H); OC(CH₃)₂: 1.41 (d, 24H).

¹³C {¹H} NMR (126 MHz, 22°C, benzene-*d*₆, δ): 150.00, 136.07, 135.96, 129.44, 127.30, 125.27, 123.31, 119.93, 112.68, 76.94, 76.32, 26.19, 24.91.

IR (cm⁻¹): 2965 (m br), 2926 (w br), 1603 (w), 1561 (m), 1485 (s), 1445 (m), 1383 (s), 1324 (m), 1215 (m), 1163 (m), 1115 (s), 1070 (w), 1006 (m), 974 (s), 841 (m), 762 (m), 694 (m), 590 (s).

Elemental analysis: Found: C, 48.2; H, 6.0; N, 5.5. Calc. For W(OPrⁱ)₄(NPh)py: C, 49.2; H, 6.5; N, 5.8%.

Low-temperature reaction of [W₂(H)(OPrⁱ)₇]₂ and 1,2-diphenylhydrazine. [W₂(H)(OPrⁱ)₇]₂ (0.02 g, 0.013 mmol) and 1,2-diphenylhydrazine (0.01 g, 0.05 mmol) were placed in an extended NMR tube. The sample was cooled to -78°C and cold toluene-*d*₈ was added. The tube was sealed with a torch and kept cold. The sample was placed in a pre-cooled NMR spectrometer and the reaction was monitored over a period of 5 h while slowly raising the temperature. One product was initially observed in the low-temperature spectrum, that rapidly rearranged to a second and did not change until the temperature was raised. Reaction of this

hydride complex was not observed until 23°C. After 3.25 h (30 min at 23°C) the growth of H₂, aniline and a new species containing a hydride ligand was observed in the ¹H NMR spectrum. At this temperature the reaction continued, and signals corresponding to [W(OPrⁱ)₄(NPh)]₂ were observed in the phenyl, methine and methyl regions.

¹H NMR (300 MHz, -15°C, toluene-*d*₈, δ): H: 12.1 (1 *J*_{W-H} = 77.8 Hz); Ph: 7.5–7.0 (br) 6.42 (d); OCH(CH₃)₂: 5.8–4.4 (br overlapping sep); PhNH₂: 3.5 (s, br); OCH(CH₃)₂: 1.25 (d), 1.32 (d), 1.47 (d).

¹H NMR (300 MHz, -35°C, toluene-*d*₈, δ): H: 12.1 (1 *J*_{W-H} = 77.8 Hz); Ph: 7.5–7.0 (br), 6.42 (d); OCH(CH₃)₂: 6.0–4.4 (br overlapping sep); PhNH₂: 3.5 (s, br); OCH(CH₃)₂: 2.0–0.9 (br overlapping d). The same data were obtained at -65%.

Room temperature reaction of [W₂(H)(OPrⁱ)₇]₂ and 1,2-diphenylhydrazine. [W₂(H)(OPrⁱ)₇]₂ (0.02 g, 0.013 mmol) and 1,2-diphenylhydrazine (0.01 g, 0.05 mmol) were placed in a J. Young tube. Benzene-*d*₆ was added to the NMR tube and the tube was shaken until the solution was homogeneous. ¹H NMR spectra were obtained over a period of 3 h. At 10 min. H₂, aniline and a new hydride containing species were observed in the ¹H NMR spectrum, as well as significant changes in the phenyl, methine and methyl regions. The reaction was complete after 2 h.

¹H NMR (300 MHz, 22°C, benzene-*d*₆, δ): 12.47 (s, *J*_{W-H} = 78 Hz); Ph: 7.95 (d), 7.43 (t), 7.31 (d), 7.25 (s), 650 (t); OCH(CH₃)₂: 5.26 (sep), 5.00 (sep); NH₂Ph: 3.23 (s, br); OCH(CH₃)₂: 1.47–1.20 (overlapping d).

Reaction of W₂(OPrⁱ)₆py₂ with 1,2-diphenylhydrazine. W₂(OPrⁱ)₆py₂ (0.200 g, 0.237 mmol) and 1,2-diphenylhydrazine (0.080 g, 0.434 mmol) were placed in a 50 cm³ Schlenk flask equipped with a Teflon®-coated stir bar and pentane (20 cm³) was added *via* cannula. The solution was allowed to stir overnight at room temperature. After *ca* 18 h the solvent was reduced *in vacuo* to 1 cm³ and pyridine (1 cm³) was added to the solution. After further cooling at -20°C, yellow plates of W(OPrⁱ)₄(NPh)py formed and were isolated in 20% yield based on tungsten.

¹H NMR (300 MHz, 22°C, benzene-*d*₆, δ): py: 8.68 (s, br), 6.93 (t), 6.63 (m); Ph: 7.31 (d, 2H), 7.25 (s, 1H), 6.80 (t, 2H); OCH(CH₃)₂: 5.26 (sep, 4H); OCH(CH₃)₂: 1.41 (d, 24H).

Reaction of W₂(OCH₂CMe₃)₆ with 1,2-diphenylhydrazine. W₂(OCH₂CMe₃)₆ (0.200 g, 0.225 mmol) and 1,2-diphenylhydrazine (0.160 g, 0.868 mmol) were placed in a 50 cm³ Schlenk flask equipped with a Teflon®-coated stir bar and pentane (20 cm³) was added *via* cannula. The solution was allowed to stir overnight at room temperature. After *ca* 18 h the solvent was reduced *in vacuo* to 1 cm³ and pyridine (1 cm³) was added to the solution. After further cooling at -20°C, yellow plates of W(OCH₂CMe₃)₄(NPh)py formed and were isolated in 59% yield based on tungsten.

¹H NMR (300 MHz, 22°C, benzene-*d*₆, δ): py: 8.55

(s, br), 6.68 (t), 6.63 (m), Ph: 7.41 (d, 2H), 7.15 (s, 1H), 6.02 (t, 2H); OCH₂CMe₃: 4.63 (s, 8H); OCH₂C(CH₃)₃: 1.05 (s, 32H).

Reactions of W₄(OCH₂^cC₄H₇)₁₂. (i) 1,2-Diphenylhydrazine. W₄(OCH₂^cC₄H₇)₁₂ (0.200 g, 0.112 mmol) and 1,2-diphenylhydrazine (0.160 g, 0.868 mmol) were placed in a 50 cm³ Schlenk flask equipped with a Teflon®-coated stir bar and pentane (20 cm³) was added *via* cannula. The solution was allowed to stir overnight at room temperature. After *ca* 18 h the solvent was reduced *in vacuo* to 1 cm³ and pyridine (1 cm³) was added to the solution. After cooling overnight at -20°C, brown cubes had formed and were isolated in 81% yield based on tungsten. The ¹H NMR spectroscopic data were consistent with starting material. (ii) Azobenzene. In a similar reaction, W₄(OCH₂^cC₄H₇)₁₂ was found to be unreactive toward azobenzene.

Reaction of W₂(H)(O^cC₅H₉)₇(HNMe₂) with 1,2-diphenylhydrazine. W₂(H)(O^cC₅H₉)₇(HNMe₂) (0.200 g, 0.198 mmol) and 1,2-diphenylhydrazine (0.080 g, 0.434 mmol) were placed in a 50 cm³ Schlenk flask equipped with a Teflon®-coated stir bar and pentane (20 cm³) was added *via* cannula. The solution was allowed to stir overnight at room temperature. After *ca* 18 h the solvent was reduced *in vacuo* to 1 cm³ and pyridine (1 cm³) was added to the solution. After cooling overnight at -20°C, yellow plates of W(O^cC₅H₉)₄(NPh)py had formed and were isolated in 85% yield based on tungsten.

¹H NMR (300 MHz, 22°C, benzene-*d*₆, δ): py: 8.81 (s, br, 2H), 6.73 (t, 1H), 6.63 (t, 2H); Ph: 8.02 (d, 2H), 7.08 (s, 1H), 6.91 (m, 2H); O^cC₅H₉, CH: 5.42 (s, br, 4H), 4.71 (s); O^cC₅H₉, CH₂: 2.07–1.50 (br overlapping m, 32H).

¹³C {¹H} NMR (126 MHz, 22°C, benzene-*d*₆, δ): 149.86, 136.24, 131.00, 129.43, 123.46, 123.28, 119.94, 112.67, 87.24, 35.87, 35.46, 23.86.

IR (cm⁻¹): 3328 (m), 2961 (m), 2845 (w), 1603 (m), 1583 (w), 1483 (m), 1447 (w), 1339 (w), 1262 (w), 1219 (w), 1169 (m), 1073 (s), 1018 (s), 939 (w), 802 (s), 752 (m), 693 (m), 540 (w), 434 (w).

Elemental analysis: Found: C, 51.9; H, 5.9; N, 5.9. Calc. for [W(O^cC₅H₉)₄(NPh)py]: C, 53.6; H, 6.7; N, 4.0%.

Reaction of [W₂(H)(OPrⁱ)₇]₂ with 1,1-dimethylhydrazine. [W₂(H)(OPrⁱ)₇]₂ (0.200 g, 0.128 mmol) was placed in a 50 cm³ Schlenk flask equipped with a Teflon®-coated stir bar and pentane (20 cm³) was added *via* cannula. 1,1-Dimethylhydrazine (0.1 cm³, 1.32 mmol) was added *via* syringe. The solution was allowed to stir overnight at room temperature. After *ca* 18 h the solvent was reduced *in vacuo* to 1 cm³ and pyridine (1 cm³) was added to the solution. After cooling overnight at -20°C, orange crystals of W(OPrⁱ)₄(NNMe₂)py had formed and were isolated in 82% yield based on tungsten.

¹H NMR (300 MHz, 22°C, toluene-*d*₈, δ): py: 9.25 (s, br, 2H), 6.85 (t, 1H), 6.64 (t, 2H); OCH(CH₃)₂:

5.10 (sep, br, 4H); NN(CH₃)₂: 3.00 (s, 6H); OCH(CH₃)₂: 1.39 (d, 24H).

IR (cm⁻¹): 2963 (m, br), 2924 (m, br), 2860 (m, br), 1606 (m), 1483 (w), 1448 (m), 1380 (m), 1325 (m), 1261 (w), 1217 (w), 1163 (m), 1120 (s), 1072 (w), 1041 (w), 974 (s), 897 (w), 839 (m), 758 (m), 688 (m), 634 (w), 582 (s), 455 (w).

Elemental analysis: Found: C, 40.1; H, 6.5; N, 7.2. Calc. for W(OPr^t)₄(NNMe₂)py: C, 40.9; H, 7.0; N, 7.5%.

Low-temperature reaction of [W₂(H)(OPr^t)₇]₂ and 1,1-dimethylhydrazine. [W₂(H)(OPr^t)₇]₂ (0.02 g, 0.013 mmol) was dissolved in toluene-*d*₈ in a J. Young tube. The sample was frozen, evacuated and 1,1-dimethylhydrazine (0.05 mmol) was added from a calibrated gas manifold. The tube was warmed to -78°C and placed in a pre-cooled NMR spectrometer and the reaction was monitored over a period of 5 h while slowly raising the temperature. One product was initially observed in the low-temperature spectrum, which rapidly rearranged to a second. The latter did not change until the temperature was raised. Reaction of this hydride complex was not observed until 23°C. After 3.5 h the growth of H₂ was observed in the ¹H NMR spectrum.

¹H NMR (300 MHz, -65°C, toluene-*d*₈, δ): *trans*-μ-H: 10.87 (s, ¹J_{183W-1H} = 148.2, 58.3 Hz, 14% each); OCH(CH₃)₂: 5.86–4.36 (br overlapping sep); OCH(CH₃)₂: 1.0–2.0 (br overlapping d, 24H).

The sample set for 30 min and a second spectrum was obtained: ¹H NMR (300 MHz, -65°C, toluene-*d*₈, δ): μ-H: 7.86 (s, ¹J_{183W-1H} = 158.3 and 96.8 Hz, 14% each); OCH(CH₃)₂: 5.91, 5.36, 5.14, 5.03, 4.84, 4.42, 3.75 (br overlapping sep); OCH(CH₃)₂: 1.0–2.0 (br overlapping d, 24H).

¹H NMR (300 MHz, -40°C, toluene-*d*₈, δ): μ-H: 7.86 (s, ¹J_{183W-1H} = 158.3 and 96.8 Hz, 14%); OCH(CH₃)₂: 5.23, 5.02, 4.84, 4.42, 3.75 (br overlapping sep); OCH(CH₃)₂: 1.0–2.0 (br overlapping d, 24H).

¹H NMR (300 MHz, 22°C, toluene-*d*₈, δ): μ-H: 7.86 (s, ¹J_{183W-1H} = 158.3 and 96.8 Hz, 14%); OCH(CH₃)₂: 5.10 (sep), 4.96 (sep), 3.05 (sep); NN(CH₃)₂: 2.87 (s); OCH(CH₃)₂: 1.37 (d), 0.95 (d).

Room temperature reaction of [W₂(H)(OPr^t)₇]₂ and 1,1-dimethylhydrazine. [W₂(H)(OPr^t)₇]₂ (0.02 g, 0.013 mmol) and 1,1-dimethylhydrazine (0.04 cm³, 0.05 mmol) were placed in a J. Young tube. Benzene-*d*₆ was added to the NMR tube and the tube shaken until the solution was homogeneous. ¹H NMR spectra were obtained over a period of 3 h. At 10 min, H₂ was observed in the ¹H NMR spectrum, as well as significant changes in the methine and methyl regions, corresponding to the formation of W(OPr^t)₄(NNMe₂). The reaction was complete after 2 h.

Reaction of W₂(OPr^t)₆py₂ with 1,1-dimethylhydrazine. W₂(OPr^t)₆py₂ (0.200 g, 0.237 mmol) was placed in a 50 cm³ Schlenk flask equipped with a Teflon[®]-coated stir bar and pentane (20 cm³) was added *via* cannula. 1,1-Dimethylhydrazine (0.5 cm³,

0.658 mmol) was added *via* syringe. The solution was allowed to stir overnight at room temperature. After *ca* 18 h the solvent was reduced *in vacuo* to 1 cm³ and pyridine (1 cm³) was added to the solution. After cooling overnight at -20°C, orange crystals of W(OPr^t)₄(NNMe₂)py had formed and were isolated in 20% yield based on tungsten.

¹H NMR (300 MHz, 22°C, benzene-*d*₆, δ): py: 9.25 (s, br, 2H), 6.85 (t, 1H), 6.64 (t, 2H); OCH(CH₃)₂: 5.10 (sep, br, 4H); NN(CH₃)₂: 3.00 (s, 6H); OCH(CH₃)₂: 1.39 (d, 24H).

Reaction of W₂(H)(O^cC₅H₉)₇(HNMe₂) with 1,1-dimethylhydrazine. W₂(H)(O^cC₅H₉)₇(HNMe₂) (0.200 g, 0.198 mmol) was placed in a 50 cm³ Schlenk flask equipped with a Teflon[®]-coated stir bar and pentane (20 cm³) was added *via* cannula. 1,1-Dimethylhydrazine (0.6 cm³, 0.790 mmol) was added *via* syringe. The solution was allowed to stir overnight at room temperature. After *ca* 18 h the solvent was reduced *in vacuo* to 1 cm³ and pyridine (1 cm³) was added to the solution. After cooling overnight at -20°C, brown crystals of W(O^cC₅H₉)₄(NNMe₂)py had formed and were isolated in 56% yield based on tungsten.

¹H NMR (300 MHz, 22°C, benzene-*d*₆, δ): py: 8.81 (s, br, 2H), 6.91 (t, br, 1H), 6.66 (t, br, 2H); O^cC₅H₉, CH: 5.55 (m, br, 1H), 5.46 (m, br, 2H), 5.37 (m, br, 1H); NN(CH₃)₂: 3.05 (s, 6H); O^cC₅H₉, CH₂: 2.20–1.50 (br overlapping m, 32H).

¹³C {¹H} NMR (126 MHz, 22°C, benzene-*d*₆, δ): 150.00, 123.23, 87.04, 86.32, 46.79, 36.47, 35.56, 35.48, 35.38, 24.05, 23.91.

IR (cm⁻¹): 2957 (s, br), 2866 (m), 1604 (m), 1468 (w), 1446 (m), 1334 (m), 1261 (w), 1217 (w), 1169 (m), 1072 (m), 1005 (s), 937 (m), 893 (w), 864 (m), 758 (w), 692 (m), 602 (w), 538 (m).

Elemental analysis: Found: C, 48.7; H, 6.5; N, 6.2. Calc. For W(O^cC₅H₉)₄(NNMe₂)py: C, 49.0; H, 7.2; N, 6.4%.

Crystallographic studies

General operating procedures and listings of programs have been given previously [48]. A summary of crystal data is given in Table 9. Atomic coordinates have been deposited with the Cambridge Crystallographic Data Centre.

[W(OPr^t)₄(NPh)]₂ (1). A crystal of suitable size was mounted in a nitrogen atmosphere glove bag using silicone grease. The crystal was then transferred to a goniostat where it was cooled to -172°C for characterization and data collection. A selective search of a limited hemisphere of reciprocal space revealed no symmetry among the observed intensities. An initial choice of space group *P* $\bar{1}$ was later proven correct by the successful solution of the structure. Following complete intensity data collection and correction for absorption, data processing gave a unique set of 4775 intensities and a residual of 0.026 for the averaging of

Table 9. Summary of crystal data for $[\text{W}(\text{OPr})_4(\text{NPh})_2]$ (**1**), $\text{W}_3(\mu_3\text{-H})(\text{OPr})_9(\text{NPh})(\text{py})$ (**2**), $\text{W}(\text{OPr})_4(\text{NPh})\text{py}$ (**3**) and $\text{W}(\text{OPr})_4(\text{NNMe}_2)\text{py}$ (**4**)

Compound	1	2	3	4
Empirical formula	$\text{W}_2\text{O}_8\text{N}_2\text{C}_{36}\text{H}_{66}$	$\text{W}_3\text{O}_9\text{N}_2\text{C}_{38}\text{H}_{74}\text{C}_5\text{H}_5\text{N}$	$\text{W}_1\text{O}_4\text{N}_2\text{C}_{23}\text{H}_{38}\text{N}_1\text{C}_5\text{H}_5$	$\text{W}_1\text{O}_4\text{N}_3\text{C}_{19}\text{H}_{39}$
Color of crystal	Yellow	Dark purple	Yellow	Colorless
Space group	$P\bar{1}$	$P2_1/c$	$C2/c$	$P2_1/n$
Temperature ($^\circ\text{C}$)	-172	-169	-171	-95
Z (molecule/cell)	1	4	8	4
Molecular weight	1022.629	1332.65	669.517	557.23
$R1(F)$	0.0352	0.0566	0.0747	0.0732
$Rw(F)$	0.0346	0.0545	0.0764	0.0737
a (\AA)	10.347(2)	11.565(2)	35.102(7)	9.262(3)
b (\AA)	12.141(2)	18.232(3)	9.797(2)	19.521(7)
c (\AA)	10.020(2)	23.650(5)	27.200(5)	13.885(4)
α ($^\circ$)	99.18(1)	—	—	—
β ($^\circ$)	116.90(1)	90.23(1)	113.26(1)	104.00(1)
γ ($^\circ$)	103.99(1)	—	—	—

796 of these which had been measured more than once. Four standards ($-4\ 0\ 0$, $0\ 4\ 0$, $2\ -1\ -1$, and $0\ 0\ -5$) measured every 300 data showed no significant trends.

The structure was solved by initially locating the tungsten position from a Patterson map (SHELXS-86). The positions of the remaining nonhydrogen atoms in the asymmetric unit were obtained from subsequent iterations of least-squares refinement and difference-Fourier calculation. Hydrogens were included in fixed calculated positions with thermal parameters fixed at one plus the isotropic thermal parameter of the atom to which they were bonded.

In the final cycles of refinement, the non-hydrogen atoms were varied with anisotropic thermal parameters to give a final $R(F) = 0.0352$ for the 218 total variables using all of the unique data. Data having $F < 3\sigma(F)$ were given zero weight. The largest peak in the final difference map was a tungsten residual of 2.5 and the deepest hole was $-1.6\ \text{e}\ \text{\AA}^{-3}$.

The center of the molecule lies at a crystallographic center of symmetry. Symmetry related atoms are indicated with primes in the tables and figures. The non-bonded $\text{W}(1)\text{---}\text{W}(1)'$ distance, not included in the tables, is $3.4662(9)\ \text{\AA}$.

$\text{W}_3(\mu\text{-H})(\text{OPr})_9(\text{NPh})(\text{py})\text{:C}_5\text{H}_5\text{N}$, **2**: $\text{C}_6\text{H}_5\text{N}$. A small, dark purple crystal was selected from the bulk sample using inert atmosphere handling techniques. The crystal was attached to a glass fiber using silicone grease and was transferred to the goniostat where it was cooled to -169°C for characterization and data collection. A systematic search of selected ranges of reciprocal space yielded a set of reflections, which exhibited $2/m$ diffraction symmetry. Following complete data collection the systematic extinction of $h0l$ for $l = 2n + 1$ and of $0k0$ for $k = 2n + 1$ uniquely defined the space group as $P2_1/c$ (no. 14). Unit cell dimensions were determined by a least-squares fit of the setting angles for 60 carefully centered reflections

having two theta values between 20 and 36° . A total of 8761 reflections (including standards and space group extinctions) was collected. Data processing gave a unique set of 6551 reflections and a residual of 0.059 for the averaging of 1753 reflections measured more than once. Plots of the four standard reflections ($1\ 0\ -10$, $0\ 6\ 0$, $-5\ 0\ 0$, $-3\ 4\ -5$) measured every 300 reflections showed no significant trends. A correction for absorption was made.

The structure was solved using MULTAN-78. The W atoms were located in the best solution. The remaining non-hydrogen atoms were located in successive iterations of least-squares refinement and difference-Fourier calculations. A disorder was observed in one of the OR groups [at $0(35)$]. Four positions were observed for the two carbon atoms. The occupancy of the four carbon atoms [C(36), C(37) and C(59), C(60)] was refined initially and then fixed. Hydrogen-atom positions were introduced in calculated idealized positions, except on the disordered atoms and the solvent molecule. The full matrix least-squares refinement was completed using anisotropic thermal parameters on the nonhydrogen atoms (except for the disordered ones). The final $R(F)$ was 0.0566. The number of variables was 512 (including the scale factor and an overall isotropic extinction parameter). The full unique data set was used for the refinement, reflections having $F < 3.0\sigma(F)$ were given zero weight.

The asymmetric unit contains one full molecule and one molecule of pyridine solvent. The pyridine solvent molecule was assumed to be disordered, i.e. the position of the nitrogen atom was not obvious and the six atoms were refined using carbon scattering factors.

The final difference map contained several peaks of ca $2.0\ \text{e}\ \text{\AA}^{-3}$ in the vicinity of the W atoms.

$\text{W}(\text{OPr})_4(\text{NPh})(\text{py})$ (**3**). A small well formed crystal was cleaved from a larger crystal and affixed to the end of a glass fiber using silicone grease. The mounted

sample was then transferred to the goniostat where it was cooled in a gaseous nitrogen cooling system for characterization and data collection. The first crystals examined indicated that a catastrophic phase transition was occurring when the crystals were cooled. Several crystals were examined at different temperatures to determine the approximate temperature of the phase transition (*ca* -120 to -130°C) and the crystal studied was mounted at -95°C . Standard inert atmosphere handling techniques were used throughout the investigation.

A systematic search of a limited hemisphere of reciprocal space located a set of reflections with monoclinic symmetry and systematic absences corresponding to the unique space group $P2_1/n$. Subsequent solution and refinement of the structure confirmed this to be the proper space group.

Data were collected using a standard moving crystal moving detector technique with fixed background counts at each extreme of the scan. Data were corrected for Lorentz and polarization terms and equivalent data averaged. The structure was solved by direct methods (SHELXL-PC) and Fourier techniques. An absorption correction was made based on an analytical technique, approximating the faces with Miller indices assigned to the cleaved faces. The residuals did not markedly decrease when atoms were allowed to vary anisotropically, and the ellipsoids indicate that the absorption correction is not as accurate as desired. No attempt was made to refine hydrogen atoms and they were placed in fixed idealized positions for the final refinement.

A final difference Fourier was essentially featureless, although there were several peaks of intensity 1.8 – $2.8\text{ e } \text{\AA}^{-3}$ at the tungsten site. The largest peak aside from these was $0.71\text{ e } \text{\AA}^{-3}$.

$\text{W(OPr)}_4(\text{NNMe}_2)(\text{py})$ (**4**). A small yellow crystal was selected from the bulk sample using inert atmosphere handling techniques. The crystal was attached to a glass fiber using silicone grease and was transferred to the goniostat where it was cooled to -171°C for characterization and data collection. A systematic search of selected ranges of reciprocal space yielded a set of reflections which exhibited $2/m$ diffraction symmetry. Following complete data collection the systematic extinction of hkl for $h+k=2n+1$, $00l$ for $l=2n+1$ and of $0k0$ for $k=2n+1$ limited the choice of possible space groups to $C2/c$ (no. 15) or Cc (no. 9). Unit-cell dimensions were determined by a least-squares fit of the setting angles for 62 carefully centered reflections having two theta values between 22 and 28° . A total of 10,724 reflections (including standards and some space group extinctions) were collected. Data processing gave a unique set of 5638 reflections and a residual of 0.066 for the averaging of 2180 reflections measured more than once. Plots of the four standard reflections ($0\ 0\ 6$, $12\ 0\ -2$, $13\ 3\ -5$, $3\ 3\ -3$) measured every 300 reflections showed no significant trends. A correction for absorption was made.

The structure was solved using SHELXS-86. Two W atoms were located in the best solution. The non-hydrogen atoms around W(1) were readily located. After some initial difficulty in locating nonhydrogen atoms around the second W atom it was realized that the asymmetric unit contains 1.5 molecules of the W complex, with W(31) disordered around a two-fold axis at $0, y, 0.25$. The disorder is of the type where the outer ligand atoms are the same while the inner atoms W, O and N are disordered. Full-matrix least-squares refinement was completed using anisotropic thermal parameters on the tungsten atoms and isotropic thermal parameters on the non-hydrogen atoms. Atom N(43) was refined using 50% carbon and 50% nitrogen scattering factor. Hydrogen atoms were introduced in calculated fixed positions on the undisordered molecule only. In addition to the 1.5 molecules of W complex the asymmetric unit was found to contain one molecule of pyridine [atoms N(49) through C(54)]. The final $R(F)$ was 0.0747 using 3492 reflections considered observed by the criterion $I > 3.0\sigma(I)$. The total number of variables was 228, including the scale factor and an overall isotropic extinction parameter.

The final difference map contained several peaks of about $1.8\text{ e } \text{\AA}^{-3}$ in the vicinity of the W atoms. In the tables and figures atoms related by the two-fold axis symmetry are indicated by '.

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