Effect of competing π-donor N-bound ligands on structure and bonding. Synthesis and structure of tungsten organoimido nitrido complexes

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Tungsten organoimido nitrido compounds, $[W_2(N)(NR)_2Cl_5]_3$ (R = Et, C_6H_4Me-*p*), form in high yield in the reactions of $W(NR)Cl_4$ with $N(SiMe_3)_3$ and adopt structures in solution and the solid state consisting of chloro-bridged trimers of mononitrido-bridged di(organoimidotungsten) units with an unusual geometry that allows maximum π-donation from the imido and nitrido ligand set.

The nitride ion, N^{3-}, is a simple ligand that can be incorporated into a variety of environments in transition-metal compounds.[1–4] We have been interested in the nitrido ligand as a bridging group to link transition metals in new polynuclear, oligomeric and polymeric species.[5–9] To do so, it is necessary to establish control over bridging *versus* terminal structures in metallonitride compounds. Simple models of bonding suggest that competing π-donor ligands could be used to favor formation of nitrido-bridged structures. We report here, the synthesis and structure of two tungsten organoimido nitrido compounds, that support this idea. To our knowledge, these represent the first examples of *organo*imido nitrido transition-metal compounds, although compounds containing both the nitrido and parent imido (NH) ligand, especially clusters, are known,[10–15] and polynuclear haloimido nitrido complexes have been reported.[16,17]

$[W_2(N)(NEt)_2Cl_5]_3$ **1** and $[W_2(N)(NC_6H_4Me\text{-}p)_2Cl_5]_3$ **2** are isolated in high yield from the 2:1 reaction of the appropriate tungsten organoimido chloro compound with $N(SiMe_3)_3$.† ^1H NMR monitoring of the reaction indicates quantitative formation of **1** or **2** and $ClSiMe_3$ according to the stoichiometry in eqn. (1).

$$6\,W(NR)Cl_4(L) + 3\,N(SiMe_3)_3 \rightarrow [W_2(N)(NR)_2Cl_5]_3 + 9\,ClSiMe_3 + 6\,L \quad (1)$$

1 (R = Et L = none)
2 (R = C_6H_4Me-*p* L = OEt_2)

Compound **1** is a yellow air-sensitive solid while **2** is a purple air-sensitive solid. Single crystal X-ray diffraction studies indicate that **1** and **2** adopt solid state structures consisting of chlorobridged trimers of linear mononitrido-bridged ditungsten units (Figs. 1 and 2).‡ Solution studies indicate that the trimeric structure persists in dichloromethane. The ^1H NMR spectrum of **1** shows a single ethylimido signal with diastereotopic methylene protons consistent with the dissymmetry of the trimeric structure, and a molecular weight measurement of **2** confirms its trimeric nature in solution.§

The cyclic structures of **1** and **2** contain six approximately octahedral tungsten atoms each coordinated to one bridging nitrido ligand, one terminal organoimido ligand, and one terminal plus three bridging chloro ligands (Figs. 1 and 2). The $W–N_{nitrido}$ distances and $W–N_{nitrido}–W$ angles are consistent with tungsten–nitrogen double bonds in a W=N=W unit.[1,4] The $W–N_{imido}$ distances and $W–N_{imido}–C$ angles indicate tungsten–nitrogen triple bonds in an essentially linear W≡NR.[4,18] The W–Cl distances follow an understandable pattern, with $W–Cl_{terminal}$ distances (average 2.33 Å for **1**, 2.32 Å for **2**) shorter than $W–Cl_{bridging}$ distances that, in turn, vary with the *trans* ligand. Specifically, the $W–Cl_{bridging}$ distances increase on

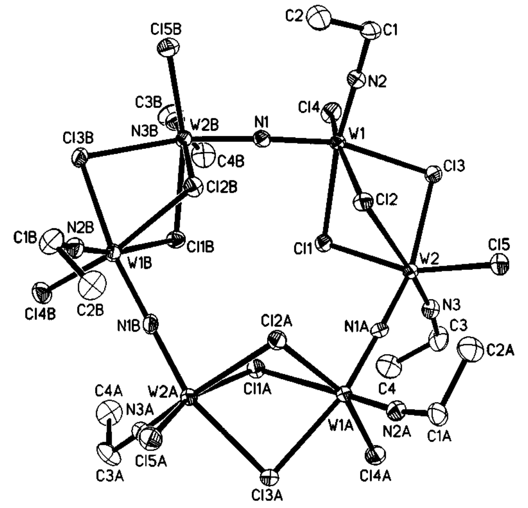

Fig. 1 Structural drawing of **1** with 50% probability thermal ellipsoids for non-hydrogen atoms. Selected bond distances (Å) and angles (°): For W=N=W, W(1)–N(1) 1.833(5), W(2B)–N(1) 1.849(5), W(1)–N(1)–W(2B) 174.5(3). For W≡NR, W(1)–N(2) 1.726(6), W(2)–N(3) 1.732(6), W(1)–N(2)–C(1) 168.6(5), W(2)–N(3)–C(3) 172.0(5). For $W–Cl_{bridging}$, W(1)–Cl(1) 2.631(2), W(1)–Cl(2) 2.443(2), W(1)–Cl(3) 2.552(2), W(2)–Cl(1) 2.452(2), W(2)–Cl(2) 2.641(2), W(2)–Cl(3) 2.546(2). For $W–Cl_{terminal}$, W(1)–Cl(4) 2.332(2), W(2)–Cl(5) 2.336(2).

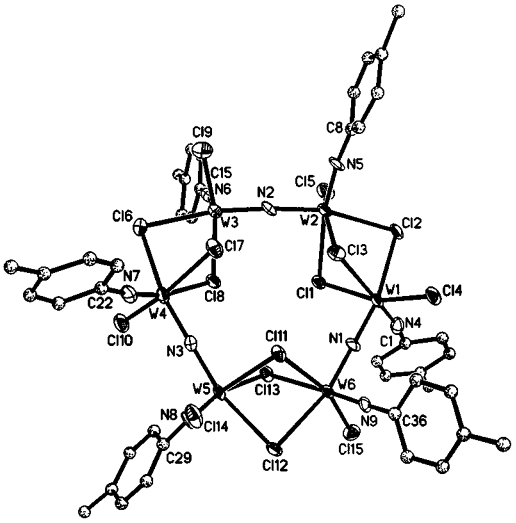

Fig. 2 Structural drawing of **2** with 50% probability thermal ellipsoids for non-hydrogen and non-carbon atoms. Selected bond distances (Å) and angles (°): For W=N=W: W(1)–N(1) 1.841(11), W(2)–N(2) 1.851(11), W(3)–N(2) 1.818(11), W(4)–N(3) 1.832(11), W(5)–N(3) 1.840(11), W(6)–N(1) 1.831(11), W(1)–N(1)–W(6) 175.3(7), W(2)–N(2)–W(3) 175.2(8), W(4)–N(3)–W(5) 175.0(8). For W≡NR: W(1)–N(4) 1.727(13), W(2)–N(5) 1.752(12), W(3)–N(6) 1.723(13), W(4)–N(7) 1.731(14), W(5)–N(8) 1.726(11), W(6)–N(9) 1.747(10), W(1)–N(4)–C(1) 167.6(10), W(2)–N(5)–C(8) 171.9(11), W(3)–N(6)–C(15) 171.0(12), W(4)–N(7)–C(22) 172.9(12), W(5)–N(8)–C(29) 176.2(10), W(6)–N(9)–C(36) 178.0(10).

going from W–Cl bonds *trans* to the terminal chloride (average 2.45 Å for **1** and **2**), to *trans* to the doubly bonded bridging nitride (average 2.55 Å for **1** and **2**), to *trans* to the triply bonded organoimido ligand (average 2.64 Å for **1**, 2.62 Å for **2**), consistent with the *trans* effects of these groups.

Of particular interest is the orientation of the two organoimido ligands in each $W_2(N)(NR)_2$ unit. The organoimido ligands are *cis* to the bridging nitrido ligand and at (RN)WW(NR) torsion angles of 105.3° for **1** and 95.2–98.9° for **2**. This nearly orthogonal orientation of the two triply bonded organoimido ligands at $W^{VI}(N)W^{VI}$ allows the complex to achieve maximum electron donation from the ligand set (each tungsten has an 18-electron count) and maximum nitrogen–tungsten π-bonding. This unusual geometry indicates that **1** and **2** may be viewed as inorganic analogs of allene with localized perpendicular π-bonds to the central atom (Fig. 3), as has also been noted for $[(\eta\text{-}C_5Me_5)W(NO)(CH_2CMe_3)](\mu\text{-}N)[(\eta\text{-}C_5Me_5)W(O)Cl]$ and $[(\eta\text{-}C_5Me_5)Mo(NO)(CH_2SiMe_3)](\mu\text{-}N)[(\eta\text{-}C_5Me_5)Mo(O)(CH_2SiMe_3)]$.[19] This is in sharp contrast with the many previously reported M=N=M compounds that are best described by delocalized three-center π-bonding.[20]

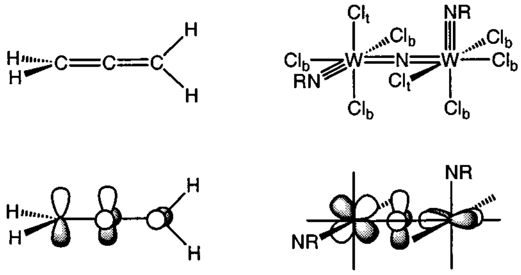

Fig. 3 Comparison of π-bonding to the central atom in allene and in the $W_2(N)(NR)_2$ unit.

Organoimido and nitrido ligands are both multiply bonding nitrogen-bound species, as terminal ligands they have similar demands for the empty π-symmetry orbitals at early transition metals, and both are capable of bridging between two or more metals. However, in a compound containing both these ligands, the nitrido should have advantages over the organoimido in a bridging position because it is sterically less demanding and a more flexible donor, able to adopt a number of different bridging structures. This is borne out by the synthesis and structures of **1** and **2**. Extension of this work to other early transition metals and the synthesis and study of 1:1:1 organoimido–nitrido–metal compounds are being explored in our laboratory.

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Notes and references

† For $[W_2(N)(NEt)_2Cl_5]_3$ **1**: a solution of $W(NEt)Cl_4$ (0.802 g, 2.17 mmol) and $N(SiMe_3)_3$ (0.250 g, 1.07 mmol) in toluene (50 mL) was stirred with heating at 90 °C under vacuum for 24 h. The solvent and volatiles were removed under reduced pressure, and the resulting solids were crystallized from dichloromethane–pentane (1:1) affording yellow crystalline **1** (0.574 g, 83%). For $[W_2(N)(NC_6H_4Me\text{-}p)_2Cl_5]_3$ **2**: a solution of $W(NC_6H_4Me\text{-}p)Cl_4\cdot Et_2O$ (2.00 g, 3.96 mmol) and $N(SiMe_3)_3$ (0.462 g, 1.98 mmol) in toluene (50 mL) was stirred with heating at 90 °C under vacuum for 24 h. The solids produced in the reaction were collected by filtration and recrystallized from dichloromethane affording purple crystalline **2** (1.32 g, 87%).

‡ *Crystal data*: for **1**: $C_{12}H_{30}Cl_{15}N_9W_6$, rhombohedral, $P\bar{3}$, $a = 21.108(2)$, $b = 21.108(2)$ Å, $c = 16.258(3)$ Å, $\alpha = \beta = 90$, $\gamma = 120°$, $Z = 6$. Intensity data were collected at 158 K on a Siemens P4 rotating-anode diffractometer *via* a 2θ–ω scan technique in the range $2.56 < \theta < 27.50°$ using Mo-Kα radiation, $\lambda = 0.71073$ Å. All 3351 data were corrected for absorption, $\mu = 17.417\ mm^{-1}$, and for Lorentz and polarization effects. The structure was solved by direct methods (SHELXTL) and refined on F^2 by full-matrix least-squares techniques. Hydrogen atoms were included using a riding model. At convergence, $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2} = 0.0765$ and GOF = 1.039 for 127 variables refined against all 3123 unique data; $R1 = \Sigma||F_o| - |F_o||/\Sigma|F_o| = 0.0266$ for those 2521 data with $F_o > 4.0\sigma(F_o)$. For **2**: $C_{42}H_{42}Cl_{15}N_9W_6$, triclinic, $P\bar{1}$, $a = 10.140(2)$, $b = 15.796(2)$, $c = 22.529(2)$ Å, $\alpha = 87.921(10)$, $\beta = 86.200(15)$, $\gamma = 78.862(14)°$, $Z = 2$. Intensity data were collected at 158 K on a Siemens P4 rotating-anode diffractometer *via* a θ–2θ scan technique in the range $4.0 < 2\theta < 55.0°$ using Mo-Kα radiation, $\lambda = 0.71073$ Å. All 17128 data were corrected for absorption, $\mu = 10.33\ mm^{-1}$, and for Lorentz and polarization effects. The structure was solved by direct methods (SHELXTL) and refined by full-matrix least-squares techniques; the quantity minimized was $\Sigma w(F_o - F_c)^2$. Hydrogen atoms were included using a riding model. Three carbon atoms in the tolyl ring attached to N(5) are disordered and were included with two components each; four carbon atoms in the tolyl ring attached to N(6) exhibited high thermal motion, however, the probable disorder could not be fit to a reasonable model.At convergence, $R_F = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.055$, $R_{wF} = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2} = 0.083$, and GOF = 2.82 for 451 variables refined against those 11817 data with $|F_o| > 6.0\sigma(|F_o|)$. CCDC 182/1369.

§ *Spectroscopic data*: for **1**: ^1H NMR (CD_2Cl_2): δ 1.56 (t, *J* 7 Hz, 3H), 6.27 (13-line non-first-order pattern at 500 MHz observation frequency, 2H). IR (neat): 2983, 2934, 2853, 1679, 1447, 1423, 1373, 1313, 1279, 1107, 1066, 1003, 949, 863, 826, 796, 613, 342, 294 cm^{-1}. For **2**: ^1H NMR (CD_2Cl_2): δ 7.42 (d, *J* 8 Hz, 2H), 7.23 (d, *J* 8 Hz, 2H), 2.87 (s, 3H). IR (neat): 2924, 2856, 1679, 1587, 1490, 1439, 1410, 1350, 1221, 1170, 1115, 1023, 1010, 954, 818, 787, 738, 645, 546, 442, 350, 295 cm^{-1}. MW calc. for $C_{42}H_{42}Cl_{15}N_9W_6$: 2307.8, found ($CH_2Cl_2$) 2403. Anal. Calc. for $C_{42}H_{42}Cl_{15}N_9W_6$: C, 21.86; H, 1.83; N, 5.46. Found: C, 22.13; H, 1.82; N, 5.43%.

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