COMMUNICATION

A NOVEL SYNTHESIS OF ORGANOIMIDO
COMPLEX BY TRANSAMINATION REACTION. X-RAY
CRYSTAL STRUCTURE OF A BIS-
(ISOPROPYLIMIDO) COMPLEX OF TUNGSTEN(VI),
 $[\text{W}(\mu\text{-NPr}^i)(\text{NPr}^i)(\text{NHPr}^i)_2]_2$

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Abstract—The bis(isopropylimido) complex $[\text{W}(\mu\text{-NPr}^i)(\text{NPr}^i)(\text{NHPr}^i)_2]_2$ was synthesized by reacting $\text{W}_2(\text{NBu}^i)_2(\text{NHBu}^i)_2$ with excess Pr^iNH_2 . The complex, characterized by X-ray crystallography, is a dimer of distorted trigonal bipyramids sharing an edge defined by the unsymmetrical bridging imido ligands. Exchange between the bridging and the terminal imido ligands were observed on the NMR timescale, $\Delta G^\ddagger = 14.5 \pm 1.0 \text{ kcal mol}^{-1}$. An equilibration process is proposed to account for the fluxional behaviour.

Organoimido complexes of transition metals are chemically and structurally interesting.¹ Potentially, they may be employed as homogeneous olefin metathesis catalysts and precursors to metal nitride thin films.^{2,3} Transamination reactions between primary amines and dialkylamido complexes have been used to prepare organoimido complexes.⁴ On the other hand, to our knowledge, preparing

organoimido complexes by transamination reactions between primary amines and organoimido complexes is not known. Here, we report the first example of an organoimido complex, $[\text{W}(\mu\text{-NPr}^i)(\text{NPr}^i)(\text{NHPr}^i)_2]_2$, prepared by this route.

Reaction of $\text{W}(\text{NBu}^i)_2(\text{NHBu}^i)_2$ with excess Pr^iNH_2 in hexane generated the air-sensitive orange solid $[\text{W}(\mu\text{-NPr}^i)(\text{NPr}^i)(\text{NHPr}^i)_2]_2$ in excellent yield. X-ray quality crystals were recrystallized from hexane solutions at -15°C . The molecular structure of $[\text{W}(\mu\text{-NPr}^i)(\text{NPr}^i)(\text{NHPr}^i)_2]_2$, deter-

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Fig. 1. Molecular structure of $[\text{W}(\mu\text{-NPr}^i)(\text{NPr}^i)(\text{NHPr}^i)_2]_2$. Important bond lengths (Å) and bond angles ($^\circ$): $\text{W}-\text{N}(1) = 2.245(4)$, $\text{W}-\text{N}(1') = 1.884(4)$, $\text{W}-\text{N}(2) = 1.975(4)$, $\text{W}-\text{N}(3) = 1.740(4)$, $\text{W}-\text{N}(4) = 1.971(4)$; $\text{N}(1)-\text{W}-\text{N}(1') = 80.9(2)$, $\text{N}(1')-\text{W}-\text{N}(2) = 114.4(2)$, $\text{N}(1')-\text{W}-\text{N}(3) = 106.9(2)$, $\text{N}(1')-\text{W}-\text{N}(4) = 113.7(2)$, $\text{N}(1)-\text{W}-\text{N}(2) = 80.1(2)$, $\text{N}(1)-\text{W}-\text{N}(3) = 172.2(2)$, $\text{N}(1)-\text{W}-\text{N}(4) = 79.4(2)$, $\text{N}(2)-\text{W}-\text{N}(3) = 97.0(2)$, $\text{N}(2)-\text{W}-\text{N}(4) = 123.2(2)$, $\text{N}(3)-\text{W}-\text{N}(4) = 96.4(2)$, $\text{W}-\text{N}(1)-\text{W}' = 99.1(2)$, $\text{W}-\text{N}(1)-\text{C}(1) = 123.9(3)$, $\text{W}-\text{N}(1')-\text{C}(1') = 137.0(3)$, $\text{W}-\text{N}(2)-\text{C}(4) = 133.6(3)$, $\text{W}-\text{N}(3)-\text{C}(7) = 174.5(4)$, $\text{W}-\text{N}(4)-\text{C}(10) = 132.8(3)$.

mined by X-ray diffraction and shown in Fig. 1, is consistent with the NMR data obtained at 0°C .^{†§} The complex is a dimer of distorted trigonal bipyramids sharing the edge defined by the very unsymmetrical bridging imido $\text{N}(1)$ and $\text{N}(1')$ atoms

[†]NMR data for $[\text{W}(\mu\text{-NPr}^i)(\text{NPr}^i)(\text{NHPr}^i)_2]_2$: ^1H (300 MHz, toluene- d_8 , 0°C , chemical shifts in ppm, coupling constants in Hz): 1.44 (d, 12 H, $-\text{N}_a\text{HCHMe}_2$, J_{HH}^3 8.4), 1.45 (d, 12 H, $-\text{N}_b\text{HCHMe}_2$, J_{HH}^3 8.6), 1.57 (d, 12 H, $=\text{NCHMe}_2(\text{terminal})$, J_{HH}^3 6.4), 1.70 (d, 12 H, $=\text{NCHMe}_2(\text{bridging})$, J_{HH}^3 6.2), 4.34 (m, 4 H, $-\text{N}_{ab}\text{HCHMe}_2$), 4.65 [m, 2 H, $=\text{NCHMe}_2(\text{terminal})$, J_{HH}^3 6.4], 5.15 [m, 2 H, $=\text{NCHMe}_2(\text{bridging})$, J_{HH}^3 6.2]. $^{13}\text{C}-\{^1\text{H}\}$ (75 MHz, toluene- d_8 , 0°C , chemical shifts in ppm, coupling constants in Hz): 26.83 [$=\text{NCH}-\text{Me}_2(\text{terminal})$], 30.16 ($-\text{N}_a\text{HCHMe}_2$), 30.57 ($-\text{N}_b\text{HCHMe}_2$), 31.75 [$=\text{NCHMe}_2(\text{bridging})$], 60.12 ($-\text{N}_{ab}\text{HCHMe}_2$), 61.59 [$=\text{NCHMe}_2(\text{bridging})$], 62.21 [$=\text{NCHMe}_2(\text{terminal})$, J_{WC}^2 23.9].

Assignment of the chemical shifts was assisted by 2D $^{13}\text{C}/^1\text{H}$ correlation spectroscopy. The ^{13}C chemical shift at 61.59 ppm was assigned to the *ipso*-carbons of the bridging imido ligands because there was no obvious coupling to the tungsten atoms. The peak at 62.21 ppm was assigned to the *ipso*-carbons of the terminal imido ligands because a coupling to the tungsten atoms of 23.9 Hz was observed.¹⁰

$[\text{W}-\text{N}(1) = 2.245(4) \text{ Å}$, $\text{W}-\text{N}(1') = 1.884(4) \text{ Å}$]. W , $\text{N}(1)$, $\text{C}(1)$, $\text{N}(3)$ and $\text{C}(7)$ atoms and their symmetric counterparts define a pseudo mirror plane bisecting the molecule if the methyl groups are ignored. An analogous structure has been observed for $[\text{W}(\mu\text{-NBu}^i)(\text{NBu}^i)\text{Me}_2]_2$.⁶ The axial positions of the trigonal bipyramids are occupied by linear terminal imido groups [$\text{W}-\text{N}(3) = 1.740(4) \text{ Å}$, $\text{W}-\text{N}(3)-\text{C}(7) = 174.5(4)^\circ$] and the bridging imido groups with the long $\text{W}-\text{N}$ bond, while the equatorial positions are occupied by the amido groups [$\text{W}-\text{N}(2) = 1.975(4) \text{ Å}$, $\text{W}-\text{N}(4) = 1.971(4) \text{ Å}$] and the bridging imido groups with the short $\text{W}-\text{N}$ bond. Apparently, having short $\text{W}-(\mu\text{-N})$ bonds *cis* to the terminal imido ligands are necessary for the complex to maximize the $\text{W}-\text{N}$ π -interactions and to enhance its stability. The metal-imido bond lengths are comparable to other tungsten dimers with both terminal and bridging imido ligands, such as $[\text{W}(\mu\text{-NBu}^i)(\text{NBu}^i)\text{Me}_2]_2$ and $[\text{W}(\mu\text{-NPh})(\text{NBu}^i)\text{Cl}_2(\text{NH}_2\text{Bu}^i)]_2$.^{6,7} The metal-amido bond lengths are close to the values of complexes containing $\text{W}-\text{NMe}_2$ bonds.⁸

Exchange between the terminal and the bridging imido groups and between the amido groups of $[\text{W}(\mu\text{-NPr}^i)(\text{NPr}^i)(\text{NHPr}^i)_2]_2$ was observed by variable temperature NMR studies. Since the estimated barriers of exchange, $\Delta G^\ddagger$, are within $14.5 \pm 1.0 \text{ kcal mol}^{-1}$ for both, we propose a single mechanism in Scheme 1 to account for the equilibration. The mechanism involves dissociation of a long $\text{W}-(\mu\text{-N})$ bond initially so that one of the trigonal bipyramid fragments is freed to undergo Berry pseudo-rotation and both imido ligands are allowed to occupy the equatorial positions.⁹ The remaining long $\text{W}-(\mu\text{-N})$ bond is now at the third equatorial site and rotation about this bond exchanges the positions of the imido ligands and the amido

[§]Crystal data for $[\text{W}(\mu\text{-NPr}^i)(\text{NPr}^i)(\text{NHPr}^i)_2]_2$: $\text{C}_{24}\text{H}_{60}\text{N}_8\text{W}_2$, $M = 828.5$, triclinic, space group $P\bar{1}$, $a = 9.942(3)$, $b = 10.133(5)$, $c = 10.179(3) \text{ Å}$, $\alpha = 67.76(3)$, $\beta = 68.72(2)$, $\gamma = 83.61(3)^\circ$, $V = 884.0(6) \text{ Å}^3$, $Z = 1$, $D_c = 1.560 \text{ g cm}^{-3}$, $\lambda(\text{Mo-K}\alpha) = 0.7107 \text{ Å}$, $F(000) = 408$, $\mu = 66.77 \text{ cm}^{-1}$. CAD4 diffractometer with graphite-monochromated $\text{Mo-K}\alpha$ radiation. Ψ scan absorption correction was made (T_{max} & T_{min} , 0.73 & 1.00, respectively). 2298 unique reflections were measured and 2172 reflections with $I > 2\sigma(I)$ were used in the refinement. The refinement of the positional and anisotropic thermal parameters (155 variables) for all non-hydrogen atoms converged to $R = 0.018$ and $R_w = 0.019$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

Scheme 1. Proposed equilibration process of bridging and terminal imido ligands, and amido ligands of $[\text{W}(\mu\text{-NPr})(\text{NPr})(\text{NHPr})_2]_2$. $\text{N}_1, \text{N}_3 = \text{NPr}^i$, $\text{N}_2, \text{N}_4 = \text{NHPr}^i$. (i) $\text{W}'\text{-N}_1'$ bond dissociation, (ii) Berry pseudorotation about W, (iii) rotation about $\text{W}\text{-N}_1$, (iv) Berry pseudo rotation about W, (v) $\text{W}'\text{-N}_3$ bond formation.

ligands. Repeating the Berry pseudorotation then forming a long $\text{W}-(\mu\text{-N})$ bond completes the exchange mechanism. The molecule was thermally unstable at temperatures exceeding 30°C and elimination of isopropylamine, probably from the amido ligands, $=\text{NHPr}^i$, to form imido ligands, $=\text{NPr}^i$, was observed. An analogous transformation of bisamido complex to imido-amine complex was reported before.³⁰ The products, probably oligomers of $\text{W}(\text{NPr})_3$, and other transamination reactions involving primary amines and organoimido complexes are under investigation.

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