

Structural elucidation of tungsten compounds containing arylamine, piperazine and morpholine fragments of pyrrole and keto-amine ligands



Guan-Xuan Chen^a, Amitabha Datta^a, Hung-Chang Hsiao^a, Chia-Her Lin^b, Jui-Hsien Huang^{a,*}

^a Department of Chemistry, National Changhua University of Education, Changhua 50058, Taiwan

^b Department of Chemistry, Chung-Yuan Christian University, Chun-Li 320, Taiwan

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ABSTRACT

Various imido tungsten derivatives incorporating bidentate pyrrole–piperazine, pyrrole–morpholine, pyrrole–imine and keto-amine precursors were synthesized. Reacting $W(=N^tBu)_2(NH^tBu)_2$ with one equivalent of the pyrrole–phenylpiperazine ligand $\{C_4H_3NH-[2-CH_2N(CH_2CH_2)_2NPh]\}$ in toluene generated $[W(=N^tBu)_2(NH^tBu)\{C_4H_3N-[2-CH_2N(CH_2CH_2)_2NPh]\}]$ (**1**). Similarly, addition of $W(=N^tBu)_2(NH^tBu)_2$ to one equivalent of the pyrrole–morpholine ligand $\{C_4H_3NH-[2-CH_2N(CH_2CH_2)_2O]\}$ in toluene afforded $[W(=N^tBu)_2(NH^tBu)\{C_4H_3N-[2-CH_2N(CH_2CH_2)_2O]\}]$ (**2**), which was converted to $[W(=N^tBu)_2\{C_4H_3N-[2-CH_2N(CH_2CH_2)_2O]\}_2(\mu_2-O)]$ (**3**) in moisture. Reacting the pyrrole–imine ligand $\{C_4H_3NH-[2-CH=N(C_6H_3-2,6-^iPr_2)]\}$ with one equivalent of $W(=N^tBu)_2(NH^tBu)_2$ in toluene gave $[W(=N^tBu)_2(NH^tBu)\{C_4H_3N-[2-CH=N(C_6H_3-2,6-^iPr_2)]\}]$ (**4**), which was transformed to $[W(=N^tBu)(NH^tBu)\{C_4H_3N-[2-CH=N(C_6H_3-2,6-^iPr_2)]\}(\mu-O)]_2$ (**5**) upon absorbing moisture. Furthermore, when one equivalent of $\{C_4H_3NH-[2-CH=NC_2H_4N(C_2H_4)_2O]\}$ reacted with $W(=N^tBu)_2(NH^tBu)_2$ in toluene, $[W(=N^tBu)_2\{C_4H_3N-[2-CH=NC_2H_4N(C_2H_4)_2O]\}_2]$ (**6**) was isolated. The tungsten keto-amine compounds $\{W(=N^tBu)_2[OCMeCHCMeN(C_6H_3-2,6-^iPr_2)]_2\}$ (**7**) and $\{W(=N^tBu)_2[OCMeCHCMeNCH_2CH_2N(CH_2CH_2)_2O]_2\}$ (**8**) were obtained by the reaction between $W(=N^tBu)_2(NH^tBu)_2$ and two equivalents of the corresponding keto-amine ligands in toluene. All the tungsten derivatives were characterized by 1H and ^{13}C NMR spectroscopy. Single crystal X-ray diffraction analysis revealed that in compounds, **1**, **3**, **5**, **6** and **7**, the central W atom belonged to either a distorted trigonal bipyramidal or an octahedral geometrical arrangement. Overall, the influence of the substituted pyrrole and keto-amine bidentate precursors on the imido tungsten derivatives were explored and structurally constructed.

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1. Introduction

Organoimido compounds [1] have been applied to catalytic and synthetic methodologies involving net [NR] transfer chemistry [2], amination [3] and aziridination [4] of olefins or the ammoxidation of propylene [5]. Organoimido ligands have also been implicated in nitrile reduction [6] and have seen increasing utility as ancillary groups to support high oxidation state metals [7]. Recent advances in metal imido chemistry have included organometallic compounds containing reactive $L_nM=NR$ ligands that can activate the C–H bonds of methane [8] or engage in cycloaddition reactions [9]. In recent years, several structural investigations on half-sandwich imido compounds of the early transition metals have been reported [10]. Organoimido ligands have been increasingly utilized as ancillary ligands [11] and recent theoretical studies [12] have

suggested that imido ligands may prove uniquely effective in promoting catalytic olefin metathesis. In this regard, tungsten imido complexes have played an important role in the development of the chemistry of W–N containing compounds [13] and, more recently, have been featured in materials chemistry research focused on the formation of tungsten nitride [14]. The four-coordinate tungsten(VI) (d^0) bis-imido, bis-amido compound $W(=N^tBu)_2(NH^tBu)_2$ was first reported by Nugent and Harlow in 1980 [15], although the chemistry owes much to the work of Wilkinson and colleagues who first isolated $Li_2[W(N^tBu)_4]$ [16] and utilized this salt to prepare other heterobimetallic imido complexes [17]. Considering group VI, several compounds containing the metal–N–pyrrolyl moiety have been reported [18]; however, the complete characterization of tungsten compounds incorporating keto-amine ligands has not yet been reported.

Herein, we describe a convenient synthetic route for the preparation of a variety of tungsten-imido compounds exhibiting bi-dentate pyrrole–piperazine, pyrrole–morpholine, pyrrole–imine

* Corresponding author. Tel.: +886 4 7232105x3512; fax: +886 4 7211190.

E-mail address: juihuang@cc.ncue.edu.tw (J.-H. Huang).

and keto-amine precursors. We investigate the influence of the substituted bidentate precursors on the electronic structures of these tungsten imido derivatives.

2. Results and discussion

2.1. Synthesis and characterization

A series of tungsten imido compounds containing bidentate substituted pyrrole and keto-amine ligands were synthesized. The synthetic procedure for reacting $W(=N^tBu)_2(NH^tBu)_2$ [15] with the substituted pyrrole ligands is depicted in Scheme 1. When $W(=N^tBu)_2(NH^tBu)_2$ was reacted with one equivalent of the pyrrole–phenylpiperazine ligand $\{C_4H_3NH-[2-CH_2N(CH_2CH_2)_2NPh]\}$ in toluene, $[W(=N^tBu)_2(NH^tBu)\{C_4H_3N-[2-CH_2N(CH_2CH_2)_2NPh]\}]$ (**1**) was generated in moderate yield, along with the elimination of one equivalent of t butyl amine. The 1H NMR spectrum of compound **1** showed the t Bu proton chemical shifts of the NH^tBu and N^tBu fragments at δ 1.29 and 1.44 ppm, respectively. Similarly, addition of $W(=N^tBu)_2(NH^tBu)_2$ and one equivalent of the pyrrole–morpholine ligand $\{C_4H_3NH-[2-CH_2N(CH_2CH_2)_2O]\}$ in toluene afforded $[W(=N^tBu)_2(NH^tBu)\{C_4H_3N-[2-CH_2N(CH_2CH_2)_2O]\}]$ (**2**), which was converted to $[W(=N^tBu)_2\{C_4H_3N-[2-CH_2N(CH_2CH_2)_2O]\}]_2(\mu_2-O)$ (**3**) after absorbing moisture. Compound **3** was recrystallized at $-20^\circ C$. The 1H NMR spectrum of **3** displayed the corresponding NH^tBu and $=N^tBu$ signals at δ 1.13 and 1.40 ppm, respectively, and the methylene fragment of the side arm substituent appeared at δ 3.91 ppm as a singlet.

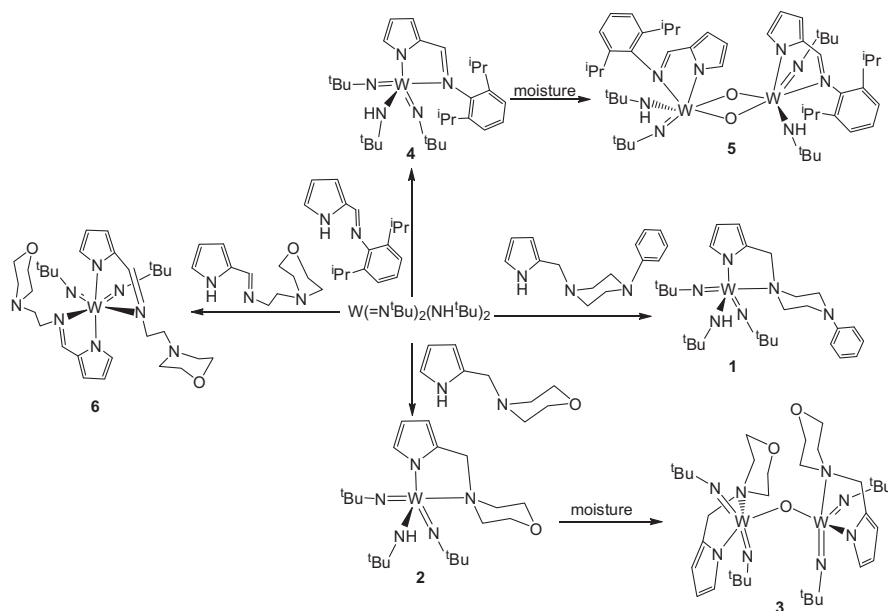
Further reaction of the pyrrole–imine ligand $\{C_4H_3NH-[2-CH=N(C_6H_3-2,6-^iPr_2)]\}$ with one equivalent of $W(=N^tBu)_2(NH^tBu)_2$ in toluene afforded a five coordinated tungsten derivative, $[W(=N^tBu)_2(NH^tBu)\{C_4H_3N-[2-CH=N(C_6H_3-2,6-^iPr_2)]\}]$ (**4**), in moderate yield. The 1H NMR spectrum of compound **4** showed two doublets (δ 1.10 and 1.30 ppm) and one septet (δ 3.44 ppm) for the methyl and methine protons of the phenyl isopropyl fragments. The methine proton of the imine $CH=N$ group showed a singlet at δ 8.04 and 161.4 ppm in the 1H and ^{13}C NMR spectra, respectively. Compound **4** was quite moisture sensitive and underwent transformation to the oxo-bridged di-tungsten compound $[W(=N^tBu)(NH^tBu)\{C_4H_3N-[2-CH=N(C_6H_3-2,6-^iPr_2)]\}(\mu-O)]_2$ (**5**).

Similarly, on reacting one or two equivalents of $\{C_4H_3NH-[2-CH=N(C_2H_4N(C_2H_4)_2O)]\}$ with $W(=N^tBu)_2(NH^tBu)_2$ in toluene, only $\{W(=N^tBu)_2\{C_4H_3N-[2-CH=N(C_2H_4N(C_2H_4)_2O)]\}_2\}$ (**6**) was isolated. The 1H NMR spectrum of **6** showed one singlet at δ 1.22 ppm for t Bu of the imido group and one singlet for $CH=N$ at δ 7.96 ppm. The ^{13}C NMR spectrum also confirmed the structure of **6**.

The tungsten keto-amine compounds $\{W(=N^tBu)_2[OCMeCHCMeN(C_6H_3-2,6-^iPr_2)]_2\}$ (**7**) and $\{W(=N^tBu)_2[OCMeCHCMeNCH_2-CH_2N(CH_2CH_2)_2O]_2\}$ (**8**) were synthesized in moderate yields by the reaction of $W(=N^tBu)_2(NH^tBu)_2$ with two equivalents of the corresponding keto-amine ligands in toluene, as shown in Scheme 2. The 1H NMR spectrum of **7** showed two singlets for the methine protons of the two keto-amine backbones at δ 5.04 and 5.46 ppm, indicating the different coordination modes of the two keto-amine ligands. The methine protons of the isopropyl fragments for the two keto-amine ligands exhibited only two septets. Unlike **7**, compound **8** showed only one methine proton signal at δ 5.12 ppm, indicating a fast fluxionality between the two different binding modes of the keto-amine fragments, which was attributed to less steric hindrance of the amine substituents.

2.2. Molecular geometries of compounds **1**, **3**, **5**, **6** and **7**

The X-ray crystal data collected for compounds **1**, **3**, **5**, **6**, and **7** are shown in Table 1, while selected bond lengths and angles are shown in Table 2. Crystals of **1** suitable for single crystal diffractometric analysis were obtained from a saturated methylene chloride solution at $-20^\circ C$. The molecular structure of compound **1** (Fig. 1) can be described as a distorted trigonal bipyramidal (TBP) geometry with a τ value of 0.595 (0 for SP; 1 for TBP) [19]. The piperazine N(2) and t Bu-imido N(4) atoms occupy the axial positions, with an N(2)–W(1)–N(4) angle of $162.74(11)^\circ$, whereas the pyrrole N(1), t Bu-imido N(6) and t Bu-amido N(5) atoms are located at equatorial positions. The tungsten to imido nitrogen atom bond lengths (W(1)–N(4), 1.753(3) Å; W(1)–N(6), 1.758(3) Å) and the W–N_{imido}–C bond angles (C(24)–N(6)–W(1), $160.3(2)^\circ$; C(16)–N(4)–W(1), $165.8(2)^\circ$) indicate the $W\equiv N$ bonding mode [20]. The W(1)–N(5) bond length (1.975(3) Å) and the W(1)–N(5)–C(20) bond angle ($138.7(2)^\circ$) represent sp^3 hybridization of



Scheme 1.

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