

中文摘要

當一具有雙配位之單陰電性配位基 (2-(dimethylaminomethyl)pyrrole (LH) 與 $WCl_4(=NPh)(Et_2O)$ 和 $W(=N^tBu)_2(NH^tBu)_2$ 反應時可分別產生 $WCl_3(=NPh)(L)$ 和 $[W(=N^tBu)_2L]_2O$ 。它們可經由核磁共振光譜及 X 光結構法來鑑定。當更進一步讓 $[W(=N^tBu)_2L]_2O$ 與少量之 H_2O 反應後可產生一鎢群 $W_4O_6(=N^tBu)_4L_4$ 而此化合物亦可經由核磁共振光譜及 X 光結構法來鑑定。

關鍵詞：雙配位、鎢群、

Abstract

The reactions of monoanionic bidentate 2-(dimethylaminomethyl)pyrrole(LH) with $WCl_4(=NPh)(Et_2O)$ and $W(=N^tBu)_2(NH^tBu)_2$ yield $WCl_3(=NPh)(L)$ and $[W(=N^tBu)_2L]_2O$, respectively. Their NMR spectroscopies and X-ray structures are characterized. Further reaction of $[W(=N^tBu)_2L]_2O$ with trace of H_2O generates a tungsten cluster, $W_4O_6(=N^tBu)_4L_4$ and the compound has been characterized by NMR spectroscopies and X-ray structure determination.

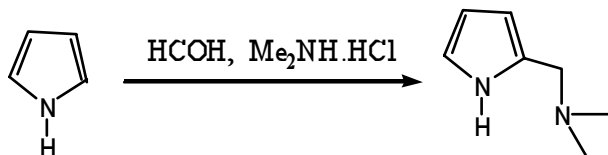
Keywords: 2-(dimethylaminomethyl)pyrrole, monoanionic, bidentate, tungsten cluster

Organoimido¹ chemistry has been investigated intensively in the past two decades and reviews surveying the organoimido chemistry have been published periodically. The reactions of organoimido complexes with monoanionic monodentate ligands have been seen very often, however, using monoanionic bidentate ligands to bind the organoimido complexes are not reported. 2-(dimethylaminomethyl)pyrrole² has been synthesized since 1947 but only very few examples of organometallic complexes containing the bidentate ligand were seen. So far only one x-ray crystal structure, CrL_3 ³, was determined. Currently we are investigating the chemistry of tungsten imido and bidentate 2-(dimethylaminomethyl)-pyrrole(LH) and here we report our latest results.

Results and Discussion

Ligand Synthesis 2-(dimethylaminomethyl)

pyrrole(LH) has been synthesized and reported by Dittermer in 1947 and here we adopted a method developed by Elsenbaumer in 1998 by using formaldehyde, dimethylamine hydrochloride, and pyrrole (Figure 1).



The white ligand, LH, can be purified *via* sublimation in *ca.* 75% yield. It decomposed at room temperature gradually to an un-identified black compound but stable at $-20\text{ }^\circ\text{C}$ even for several months. The X-ray structure of LH shows two molecules of LH are bonded together *via* hydrogen bonding.

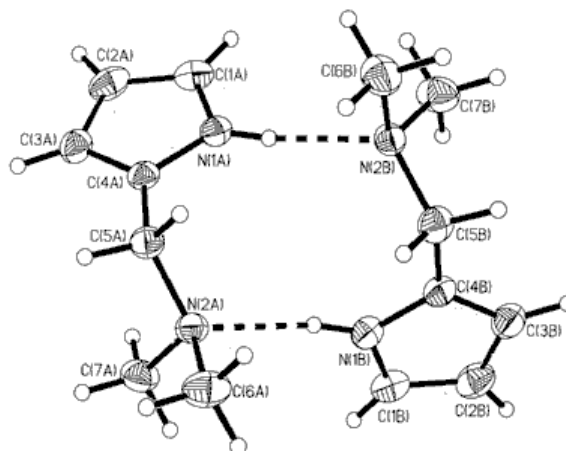
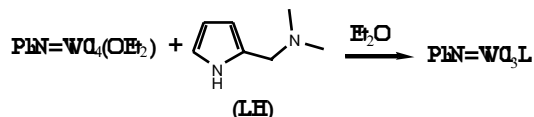


Figure 1. The ORTEP of LH, thermal ellipsoids drawn at the 50% probability, hydrogen atoms are omitted for clarity.

Reacting $WCl_4(=NPh)(Et_2O)$ and LH in Et_2O at room temperature for two hours yields $WCl_3(=NPh)(L)$ (complex 1) in 35% yield(Scheme 2).



Scheme 1

Complex 1 shows simple 1H NMR spectrum with singlet for the NMe_2 , CH_2N , and pyrrole resonances at room temperature, which is in consistent with the X-ray structure determination. ^{13}C NMR spectrum of complex 1 are also with the X-ray structure with the NMe_2 and CH_2N resonances appeared at 51.8 and 61.0 ppm respectively. Dark black single crystal was mounted for X-ray structure determination. Black cube crystal suitable for X-ray analysis were grown by cooling a concentrated ether solution of compound 1 at $-20\text{ }^\circ C$. The structure of 1 shows an six coordinated octahedral tungsten metal atom ion, which is surrounded by an phenylimido, three chloride and a monoanionic bidentate L. The ORTEP of 1 is showed in Figure 1.

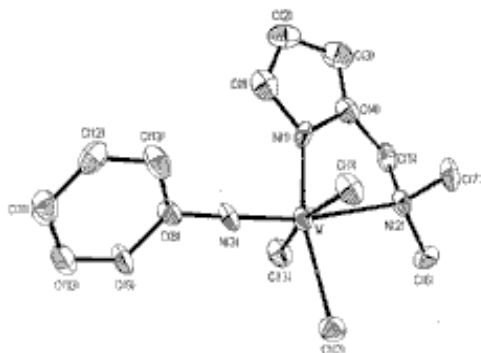
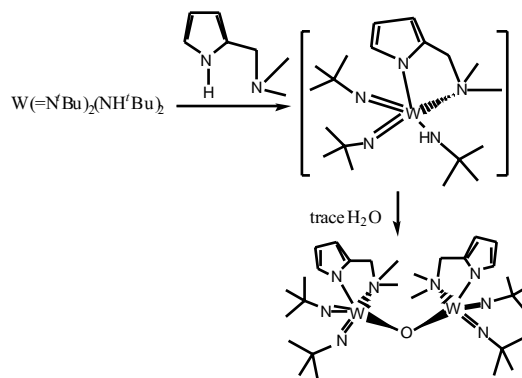


Figure 2. The ORTEP of $WCl_3(=NPh)(L)$, thermal ellipsoids draws at the 30% probability, hydrogen atoms are omitted for clarity.

The angle around the imido nitrogen of 170.5° is similar to those reported for high-valent tungsten imido complexes. The two nitrogen atoms, N(1) and N(2), of L are taking two cis positions with a constrained angle of 74.3° , while the Cl(1) and Cl(3) can be viewed as the apical atoms with Cl(1)-W-Cl(3) bond angle of 169.88° . The bond distances if W-N(1), W-N(2), and W-N(3) are 1.950(10), 2.466(8), and 1.7222(9) \AA , respectively, which are consistent with the bond distances of high valent tungsten (VI)-amido, tertiary amine, and imido ligands, respectively.

Reaction of $W(=NtBu)_2(NtBu)_2$ and 1 eq. of 1 in heptane for 24 hours yields oxo-bridged ditungsten imido complex, 2, containing monoanionic bidentate ligand, L. While the reaction was proceeded with 2 eq. of LH, no double deamination was observed. The reaction mechanism was proposed as followed.



The moisture and air sensitive pale yellow crystals of 2 were obtained from saturated toluene solution in $-20C$ and X-ray data was collected at 150K. The ORTEP structure of 2 is showed in Figure 3.

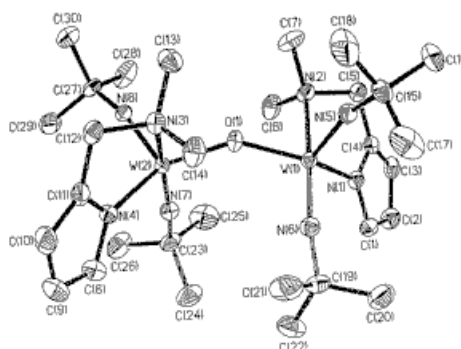
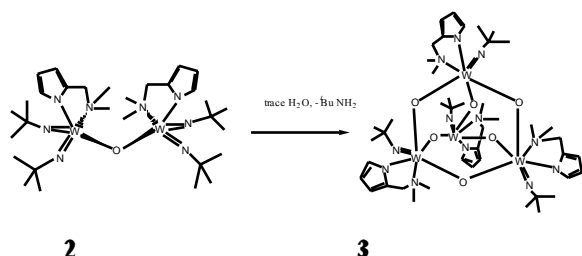


Figure 3. The ORTEP of $W_2(L)_2(N^tBu)_2(\mu-O)$. Thermal ellipsoids drawn at the 50% probability, hydrogen atoms are omitted for clarity.

2 contains a C_2 symmetry through the oxygen atom that the two trigonal planar tungsten atoms are bridged. The nitrogen of dimethyl amine and the nitrogen of one t-butylamido take the apical positions of the TBP while the oxygen atom, one t-butylamido nitrogen, and the pyrrole nitrogen form a trigonal plane. The TBP structure goes through a Berry pseudorotation which resulting one resonance for the two t-butyl groups and one resonance for the two methyl groups of the dimethyl amine. Variable temperature ¹H NMR spectra are need for monitoring the rotation.

Further reacting the oxo bridged ditungsten complex with trace amount of H₂O under nitrogen at room temperature in heptane for 12 hours yields a tungsten cluster **3**, $[W(=NtBu)]_4(\mu-O)_6$, by extruding one equiv. of t-butyl amine. **3** contains a highly symmetry of tetrahedron with the four tungsten atoms taking the apical positions.



The ¹H and ¹³C NMR spectra show the isotropic structure for the protons of the methylene and methyl

group of the bidentate ligand, **L**. Single crystals suitable for x-ray structure determination were obtained from concentrated heptane solution and * at -20 C for 24 hours. The pale yellow crystal was mounted on the x-ray diffractor and data was collected at 150 K. The ORTEP of complex **3** was showed in Figure 4. Four tungsten atoms are taking the apical positions of the cluster with each tungsten atom surrounding by one t-butylimido, one bidentate ligand, **L** and three-bridged oxygen atoms.

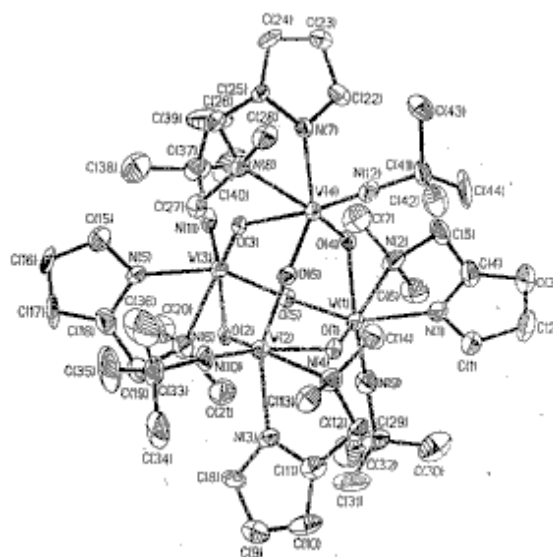


Figure 4. The ORTEP of **3**, $[W(=NtBu)]_4(\mu-O)_6$. Thermal ellipsoids drawn at the 50% probability, hydrogen atoms are omitted for clarity.

Each of the tungsten atom in the cluster can be view as a distorted octahedron with the plane of O(2), O(6), N(4), and N(3) bending toward the bridged oxygen atom O(1), presumably due to the steric effect of t-butyl imido group that opposite the O(1).

In conclusion, the organoimido compounds react with substituted pyrrrole(LH) smoothly and reaction products have been fully characterized. In continuing the NSC project, we are currently pursuing the reaction of LH with early transition metals chemistry.

References

1. (a) Nugent, W. A.; Haymore, B. L. *Coord. Chem. Rev.* **1980**, *31*, 123. (b) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*, John Wiley and Sons: New York, 1988.
2. Kim, H.; Elsenbaumer, R. L.; *Tetrahedron Letters* **1998**, *39*, 1087.
3. Drvs, H.; Schmeiber, A.; Hartung, H.; Baumeister, U. *Chem. Ber.* **1996**, *129*, 853.