J. Am. Chem. Soc. 1994, 116, 7419–7420

# Tungsten(IV) Imido Complexes from Oxidation of a Protected Zero-Valent Nitrene Precursor

Patrick C. McGowan, Scott T. Massey,
Khalil A. Abboud, and Lisa McElwee-White*

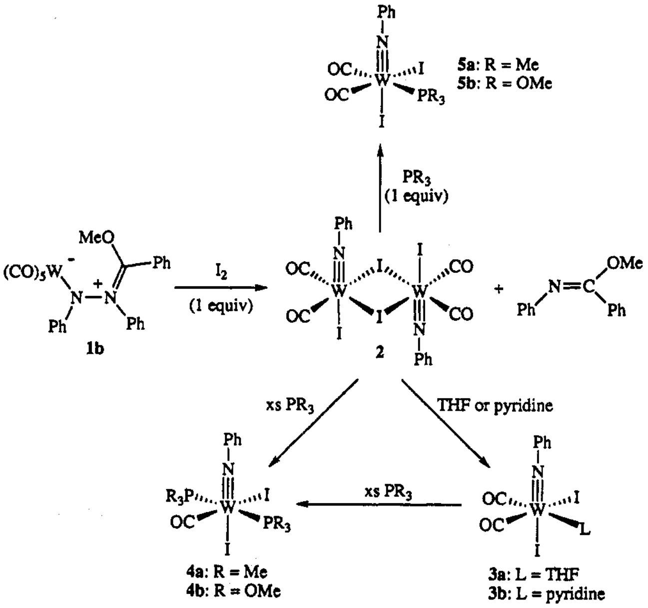
*Department of Chemistry, University of Florida*
*Gainesville, Florida 32611*

*Received April 25, 1994*

Due to discussion of their electronic structure[1,2] and their potential use as catalyst precursors,[3] $d^2$ imido complexes such as tungsten(IV) compounds have recently been of interest. Varying the electronic properties of these species by changing the ancillary ligands has been an objective of these studies. However, the use of $\pi$-acid ligands such as carbonyls has been limited by the difficulty of supporting multiple $\pi$-acceptors in a complex with few d electrons. Because filled metal d orbitals are needed for back-bonding, examples of $d^2$ imido complexes are almost entirely restricted to a single $\pi$-acid ligand.[1,2,4,5] To our knowledge, only the $Tp'W(CO)_2(NR)^+$ species contain more than one.[6] Oxidation of low-valent imido (or nitrene) species could potentially provide access to higher valent complexes with multiple carbonyl ligands, but the instability of $(CO)_5W{=}NR$ species[7,8] makes them difficult starting materials. This problem can be circumvented by using the transient zero-valent nitrene complex $(CO)_5W{=}NPh$ in a protected form. We had previously reported that the zwitterionic complexes $(CO)_5WNPhNPhC(OMe)R$ [R = Me (**1a**), Ph (**1b**)] decompose upon thermolysis or photolysis to yield $PhN{=}C(OMe)R$ and $(CO)_5W{=}NPh$.[7] We now report that **1b** is also a precursor to tungsten(IV) imido complexes bearing two carbonyls. The zwitterionic ligand of **1b** serves as a protected imido functionality during oxidation of the metal center. The imido ligand is then unmasked *in situ* after a higher oxidation state has been reached.

Treatment of the zwitterionic complex $(CO)_5WNPhNPhC(OMe)Ph$ (**1b**) with 1equiv of $I_2$ leads to formation of the highly unusual iodo-bridged tungsten(IV) imido dimer $[(CO)_2W(NPh)I_2]_2$ (**2**) and $PhN{=}C(OMe)Ph$ (Scheme 1).[9] Although solutions of **1b** decompose over the course of 3 h in the absence of oxidizing agents, disappearance of **1b** upon reaction with $I_2$ is complete in less than 5 s. Therefore, the first step of this reaction cannot be thermal decomposition of **1b** to $(CO)_5W{=}NPh$. Upon addition of iodine to zwitterion **1b**, immediate effervescence is observed, and the reaction mixture turns from black to green. An IR spectrum taken at that time shows that the zwitterion is completely consumed and $PhN{=}C(OMe)Ph$ has been formed. Since the two IR bands at 2082 and 2038 cm$^{-1}$ are consistent with a $(CO)_3W$ moiety, we postulate that the process begins with iodination of the W(0) center of zwitterion **1b**, followed by rapid cleavage of the N–N bond to form $I_2(CO)_3WNPh$.

Scheme 1



Over the course of 30 min, slow effervescence is observed as the green solution becomes red and the IR spectrum of dimer **2** grows in at the expense of the intermediate. The carbonyl stretching frequencies in the IR spectrum of **2** appear at 2069 and 2009 cm$^{-1}$. These high values are indicative of limited back-bonding from each $d^2$ metal center to its carbonyl ligands and are similar to those observed for the cationic W(IV) nitrene complex $[Tp'(CO)_2W{\equiv}NPh]^+PF_6^-$ (2079 and 2006 cm$^{-1}$).[6c] The $^1H$ NMR and $^{13}C$ NMR spectra of **2** confirm the presence of symmetry equivalent phenyl groups, with an additional signal in the $^{13}C$ NMR indicating equivalent CO ligands.

A crystal structure analysis was performed on **2**, and an ORTEP diagram appears in Figure 1. The molecule has $C_2$ symmetry, and there is half of a molecule per asymmetric unit. Each W center has an octahedral conformation, with one of the iodide ligands bridging to the other W atom. Of note in the structure are the W–N bond length of 1.756(10) Å and the angle W–N–C1 of 177.0(8)°. This short W–N bond and near linear imido ligand are suggestive of a triple bond, as expected for a W(IV) complex.

Cleavage of **2** with THF or pyridine leads to formation of the monomeric compounds $(CO)_2W(NPh)I_2L$ (**3a,b**). Due to the lability of the THF ligand, **3a** could not be isolated, but it has been spectroscopically characterized.[10] The pyridine adduct **3b** can be isolated as a crystalline green solid from a red/green

---

(1) (a) Hall, K. A.; Mayer, J. M. *J. Am. Chem. Soc.*, **1992**, *114*, 10402–10411. (b) Su, F.-M.; Bryan, J. C.; Jang, S.; Mayer, J. M. *Polyhedron* **1989**, *8*, 1261–1277.

(2) (a) Williams, D. S.; Schofield, M. H.; Schrock, R. R. *Organometallics* **1993**, *12*, 4560–4571. (b) Williams, D. S.; Schofield, M. H.; Anhaus, J. T.; Schrock, R. R. *J. Am. Chem. Soc.* **1990**, *112*, 6728–6729.

(3) (a) Johnson, L. K.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1993**, *115*, 8130–8145. (b) Johnson, L. K.; Frey, M.; Ulibarri, T. A.; Virgil, S. C.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1993**, *115*, 8167–8177.

(4) Hillhouse, G. L.; Haymore, B. L. *J. Organomet. Chem.* **1978**, *162*, C23–C26.

(5) (a) Nielson, A. J.; Ware, D. C. *Polyhedron* **1990**, *9*, 603–610. (b) Clark, G. R.; Nielson, A. J.; Rickard, C. E. F.; Ware, D. C. *J. Chem. Soc., Dalton Trans.* **1990**, 1173–1178. (c) Clark, G. R.; Nielson, A. J.; Rickard, C. E. F. *J. Chem. Soc., Chem. Commun.* **1989**, 1157–1159. (d) Clark, G. R.; Nielson, A. J.; Rickard, C. E. F.; Ware, D. C. *J. Chem. Soc., Chem. Commun.* **1989**, 343–345.

(6) (a) Powell, K. R.; Pérez, P. J.; Luan, L.; Feng, S. G.; White, P. S.; Brookhart, M.; Templeton, J. L. *Organometallics* **1994**, *13*, 1851–1864. (b) Pérez, P. J.; Luan, L.; White, P. S.; Brookhart, M.; Templeton, J. L. *J. Am. Chem. Soc.* **1992**, *114*, 7928–7929. (c) Luan, L.; Brookhart, M.; Templeton, J. L. *Organometallics* **1992**, *11*, 1433–1435. (d) Luan, L.; White, P. S.; Brookhart, M.; Templeton, J. L. *J. Am. Chem. Soc.* **1990**, *112*, 8190–8192.

(7) (a) Maxey, C. T.; Sleiman, H. F.; Massey, S. T.; McElwee-White, L. *J. Am. Chem. Soc.* **1992**, *114*, 5153–5160. (b) Arndtsen, B. A.; Sleiman, H. F.; Chang, A. K.; McElwee-White, L. *J. Am. Chem. Soc.* **1991**, *113*, 4871–4876. (c) Sleiman, H. F.; Mercer, S.; McElwee-White, L. *J. Am. Chem. Soc.* **1989**, *111*, 8007–8009. (d) Sleiman, H. F.; McElwee-White, L. *J. Am. Chem. Soc.* **1988**, *110*, 8700–8701.

(8) (a) Pilato, R. S.; Williams, G. D.; Geoffroy, G. L.; Rheingold, A. L. *Inorg. Chem.* **1988**, *27*, 3665–3668. (b) Hegedus, L. S.; Kramer, A. *Organometallics* **1984**, *3*, 1263–1267. (c) Hegedus, L. S.; Lundmark, B. R. *J. Am. Chem. Soc.* **1989**, *111*, 9194–9198. (d) Herndon, J. W.; McMullen, L. A. *J. Organomet. Chem.* **1989**, *368*, 83–101.

(9) Experimental procedure for the preparation of **2**: to a stirred solution of **1b** (0.916 g, 1.47 mmol) in $CH_2Cl_2$ (20 mL) was added 1equiv of $I_2$ (0.374 g, 1.47 mmol) in $CH_2Cl_2$. After 20–30 min, there was a gradual color change from green to red. Removal of the solvent under reduced pressure was followed by washing with $Et_2O$ (50 mL) for a period of 2 h. Filtration of the orange/brown $Et_2O$ solution left a red powder, which was recrystallized from a mixture of $CH_2Cl_2$/hexane: yield 0.362 g, 42%; IR ($CDCl_3$) 2069, 2009 cm$^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 7.70–7.20 (m); $^{13}C$ NMR ($CDCl_3$) $\delta$ 202.7 (CO), 153.4, 129.6, 129.1, 126.3 ($C_6H_5$). Anal. Calcd for $C_{16}H_{10}I_4N_2O_4W_2{\cdot}0.5\ H_2O$: C, 16.31; H, 0.94; N, 2.38. Found: C, 16.35; H, 0.86; N, 2.35.

0002-7863/94/1516-7419$04.50/0

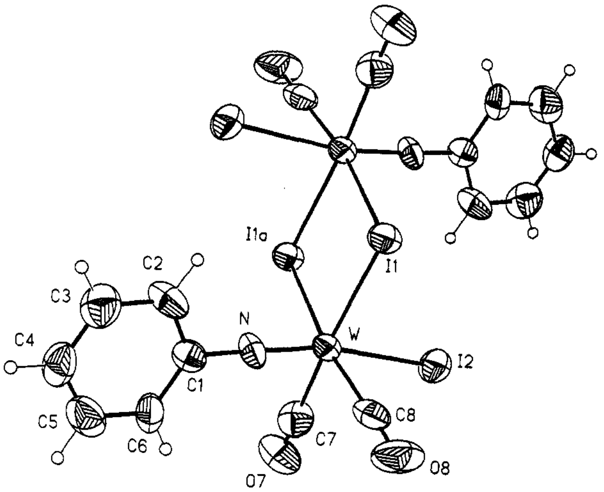


**Figure 1.** ORTEP drawing of compound **2**·$0.5H_2O$ showing the crystallographic numbering scheme. Hydrogen atoms and the partial solvent molecule are omitted. Thermal ellipsoids are drawn at the 40% probability level. Selected distances (Å) and angles (deg) are as follows: W–I1 2.826(1), W–I1a 2.829(1), W–I2 2.808(1), W–N 1.756(10), W–C7 2.051(14), W–W 4.239(1), W–N–C1 177.0(8) I1a–W–I1 82.90(3), I1–W–N 97.0(3), I2–W–N 170.0(3), I1a–W–C8 170.3(4).

dichroic toluene solution.[11] The *cis*-$W(CO)_2$ moiety of **3b** can be established by the two strong bands at 2068 and 1987 $cm^{-1}$ in its IR spectrum and the inequivalent CO signals at $\delta$ 208.3 and 207.6 in its $^{13}C$ NMR spectrum.

As shown in Scheme 1, treatment of **2** with excess $PMe_3$ or $P(OMe)_3$ leads to the replacement of the iodine bridge and displacement of one of the carbonyl ligands to yield compounds of the type $W(NPh)I_2(CO)(PR_3)_2$ (**4a,b**) in 90% yield.[12] Reaction of the pyridine adduct **3b** with excess $PR_3$ also furnishes **4a** or **4b**. The bis(phosphine) complexes are purple crystalline materials and are similar to those prepared by Mayer *et al.*[1a,b] by oxidative addition of isocyanates to $WCl_2(PMePh_2)_4$. Isolation of the intermediate monophosphine complexes has proven problematic, but $^1H$ NMR and $^{13}C$ NMR spectra of the reaction mixtures provide evidence[13] for the formation of the monophosphine compound **5a**.

There are examples of higher oxidation state tungsten imido compounds being reduced to W(IV) complexes,[1a,2,5,14] but to our knowledge no examples of oxidation of zero-valent nitrene complexes have been reported. We have now found an analogue to oxidation of $(CO)_5W{=}NPh$ in the conversion of the zero-valent zwitterion **1b** to a series of tungsten(IV) imido complexes. Protection of the highly reactive zero-valent nitrene complex as zwitterion **1b** allows oxidation of the metal center before cleavage of the N–N bond. Thus the imido ligand can be generated in a higher valent complex that is more compatible with its strongly donating nature. The iodo-bridged dimer **2**, formed upon oxidation of **1b** with $I_2$, provides a synthon for the unsaturated $(CO)_2W(NPh)I_2$ fragment through replacement of the weak iodide bridges. Further substitution of the CO groups has also been illustrated. We are currently investigating the mechanism for oxidative conversion of zwitterion **1b** to **2** as well as extensions of the chemistry of **2** to provide access to a wider variety of derivatives.

**Acknowledgment.** Funding for this work was provided by the U.S. Army Research Office and the Office of Naval Research.

**Supplementary Material Available:** Tables of crystallographic data, bond distances, bond angles, positional parameters, and anisotropic displacement parameters for **2** (7 pages); listing of observed and calculated structure factors for **2** (11 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

---

(10) Spectral data for **3a**: IR ($CHCl_3$) 2067, 1989 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 7.70–7.20 (m, $C_6H_5$), 4.71 (m, THF), 2.12 (dt, THF); $^{13}C$ NMR ($CDCl_3$) $\delta$ 212.7 (CO, $J_{WC}$ = 173.6 Hz), 207.0 (CO, $J_{WC}$ = 168.6 Hz), 153.2, 129.5, 129.2, 124.8 ($C_6H_5$), 81.1, 26.6 (THF).

(11) Spectral data for **3b**: IR ($CDCl_3$) 2068, 1987 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 9.40 (dd, 2H, $^1J_{HH}$ = 6.6 Hz, $^2J_{HH}$ = 1.6 Hz, pyr), 7.94 (tt, 1H, $^1J_{HH}$ = 7.7 Hz, $^2J_{HH}$ = 1.6 Hz, pyr), 7.51 (m, 3H, pyr and $C_6H_5$), 7.27 (m, 4H, $C_6H_5$); $^{13}C$ NMR ($CDCl_3$) $\delta$ 208.3, 207.6 (CO), 154.5, 153.1, 139.5, 129.5, 129.2, 125.7, 124.8.

(12) Spectral data for **4a**: IR ($CDCl_3$) 1957 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 7.18 (m, 5H, $C_6H_5$), 1.90 (t, 18H, $J_{PH}$ = 8.4 Hz); $^{13}C$ NMR ($CDCl_3$) $\delta$ 233.6 (CO), 154.4, 128.9, 127.0, 123.6 ($C_6H_5$), 18.5 (d, $J_{PC}$ = 31.4 Hz); $^{31}P$ NMR ($CDCl_3$) $\delta$ −38.8 ($J_{WP}$ = 281.7 Hz). Anal. Calcd. for $C_{13}H_{23}I_2NOP_2W$: C, 22.03; H, 3.27; N, 1.97. Found: C, 22.03; H, 3.32; N, 1.85.

(13) Spectral data for **5a**: $^1H$ NMR ($CDCl_3$) $\delta$ 7.27 (m, 5H, $C_6H_5$), 1.97 (d, 9H, $J_{PH}$ = 9.7 Hz). $^{13}C$ NMR ($CDCl_3$) 207.8 (d, *cis*-CO, $J_{PC}$ = 6.0 Hz), 196.8 (d, *trans*-CO, $J_{PC}$ = 64.7 Hz), 153.5, 129.1, 129.4, 124.6 ($C_6H_5$), 17.7 (d, $J_{PC}$ = 33.7 Hz).

(14) (a) Bradley, D. C.; Hursthouse, M. B.; Abdul Malik, K. M.; Nielson, A. J.; Short, R. L. *J. Chem. Soc., Dalton Trans.* **1983**, 2651–2656. (b) Green, M. L. H.; Konidaris, P. C.; Mountford, P.; Simpson, S. J. *J. Chem. Soc., Chem. Commun.* **1992**, 256–259.