6050 *Inorg. Chem.* **1994,** *33,* 6050−6056

Nitrene Transfer to Trimethylphosphine from Cationic Tungsten Tosylnitrene Complexes $[Tp'(CO)_2W(NTs)][X]$

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Received April 13, 1994[⊗]

Reaction of $Tp'(CO)_3WH$ (Tp′ = hydridotris(3,5-dimethyl-1-pyrazolyl)borate) with tosyl azide in THF at reflux affords the amido complex $Tp'(CO)_2W(N(H)Ts)$ (**1**). Crystals of **1** are monoclinic, space group $P2_1/n$, with cell parameters $a = 12.4855(11)$ Å, $b = 20.5976(16)$ Å, $c = 12.7311(11)$ Å, $\beta = 96.510(10)°$, $V = 3253.0(5)$ Å^3, and $D_{calcd} = 1.591$ g cm^{-3} for $Z = 4$. Least-squares refinement led to final R and R_w values of 0.038 and 0.046, respectively. Complex **1** undergoes oxidation by silver triflate or iodine to give the imido complexes $[Tp'(CO)_2W(NTs)]X$ (X = OTf, **2a**; X = I_3, **2b**). The single crystal X-ray structure of **2b** is also reported (orthorhombic, space group $Pcab$, $a = 15.1764(16)$ Å, $b = 16.8890(14)$ Å, $c = 26.909(3)$ Å, $V = 6897.2(13)$ Å^3, and $D_{calcd} = 2.094$ g cm^{-3} for $Z = 8$; $R = 0.044$, $R_w = 0.052$). The cationic nitrene complex **2** reacts with $LiBH_4$ to regenerate the amido compound **1**. Addition of trimethylphosphine to solutions of **2** leads to the formation of three species: the phosphinimine $TsN{=}PMe_3$ (**3**) and two tungsten complexes, $[Tp'(CO)_2W(PMe_3)_2][X]$ (X = OTf, **4a**; X = I_3, **4b**) and $[Tp'(CO)(PMe_3)W(NTs)][X]$ (X = OTf, **5a**; X = I_3, **5b**). Complex **5b** undergoes substitution by iodide to produce the tungsten monocarbonyl $Tp'(CO)IW(NTs)$ (**6**).

Introduction

The extensive use of transition-metal oxo complexes in olefin epoxidation processes[1,2] stands in contrast to the limited number of metal-mediated nitrene transfer reactions that have been reported to date. Sharpless' oxyamination[3] of olefins through osmium imido complexes was the first example of such transformations. Iron and manganese[4] porphyrin derivatives have been found to promote alkene aziridination in a catalytic manner, presumably through the intermediacy of nitrene complexes. Among copper(I) species used in asymmetric aziridination of olefins,[5] high enantioselectivities have been reported by Evans[5b] and Jacobsen[5a] using respectively chiral bis(oxazoline)- and (diimine)copper complexes as the catalytic species. Cytochrome P-450 models[6] have also been employed as catalysts for nitrene transfer reactions. More recently, Holm[7] has reported NTs group transfer from the fully characterized complex $Mo(O)(NTs)(Et_2dtc)_2$ (Ts = tosyl, $SO_2C_6H_4CH_3$; dtc, dithiocarbamate) to phosphines yielding the corresponding phosphinimines $NTs{=}PR_3$. Related products were obtained by McElwee-White upon photolysis of $(CO)_5W{=}C(OCH_3)CH_3$ in the presence of azobenzene and PPh_3.[8] In this case a nitrene intermediate of composition $(CO)_5W{=}NPh$ has been proposed but not detected. This transient species displays ambiphilic behavior. Bergman has reported[9] an imido-bridged iridium complex ($Cp^*Ir(\mu\text{-}NPh)IrCp^*$) capable of generating phosphinimines by reaction with PPh_3. Only in a few cases has the metal−imido complex responsible for nitrene transfer been isolated and characterized.

We have recently reported the synthesis and chemical properties of a series of low-valent tungsten amido complexes of type $Tp'(CO)_2W(N(R)R')$[10] (Tp′ = hydridotris(3,5-dimethyl-1-pyrazolyl)borate). These species are susceptible to oxidation processes when R = H to produce the corresponding $[Tp'(CO)_2W(NR')]^+$ imido complexes (eq 1). These compounds

$$Tp'(CO)_2W(N(H)R') \xrightarrow{[Ph_3C][PF_6]} [Tp'(CO)_2W(NR')][PF_6] \qquad (1)$$

contain strong π-acid ligands in the coordination sphere which should impart electrophilic character to the imidic nitrogen. In this contribution we report the preparation, isolation, and full characterization, including X-ray studies, of low-valent tungsten imido complexes which transfer the NR group to trimethylphosphine to form the corresponding phosphinimine.

Results and Discussion

$Tp'(CO)_2W(N(H)Ts)$ (1). When the tricarbonyl hydride complex $Tp'(CO)_3WH$[11] and tosyl azide TsN_3 are heated in

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[⊗] Abstract published in *Advance ACS Abstracts,* October 15, 1994.

(1) (a) Nugent, W. A.; Mayer, J. M. *Metal Ligand Multiple Bonds*; Wiley-Interscience: New York, 1988. (b) Woo, K. C. *Chem. Rev.* **1993**, *93*, 1125.

(2) Atagi, L. M.; Dier, D. E.; McAlister, D. R.; Mayer, J. M. *J. Am. Chem. Soc.* **1991**, *113*, 870 and references cited therein.

(3) Patrick, D. W.; Truesdale, L. K.; Biller, S. A.; Sharpless, K. B. *J. Org. Chem.* **1978**, *43*, 2628.

(4) (a) Groves, J. T.; Takahashi, T. *J. Am. Chem. Soc.* **1983**, *105*, 2073. (b) Mahy, J.-P.; Battioni, P.; Mansuy, D. *J. Am. Chem. Soc.* **1986**, *108*, 1079. (c) Mansuy, D.; Mahy, J.-P.; Dureault, A.; Bedi, G.; Battioni, P. *J. Chem. Soc., Chem. Commun.* **1984**, 1161.

(5) (a) Li, Z.; Conser, K. R.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1993**, *115*, 5326. (b) Evans, D. A.; Faul, M. M.; Bilodeau, M. T.; Anderson, B. A.; Barnes, D. M. *J. Am. Chem. Soc.* **1993**, *115*, 5328. (c) Lowental, R. E.; Abiko, A.; Masamune, S. *Tetrahedron Lett.* **1990**, *31*, 6005. (d) Pérez, P. J.; Brookhart, M.; Templeton, J. L. *Organometallics* **1993**, *12*, 261.

(6) (a) Svastits, E. W.; Dawson, J. H.; Breslow, R.; Gellman, S. H. *J. Am. Chem. Soc.* **1985**, *107*, 6427. (b) Breslow, R.; Gellman, S. H. *J. Am. Chem. Soc.* **1983**, *105*, 6728. (c) Breslow, R.; Gellman, S. H. *J. Chem. Soc., Chem. Commun.* **1982**, 1400.

(7) Harlan, E. W.; Holm, R. H. *J. Am. Chem. Soc.* **1990**, *112*, 186.

(8) (a) Arndtsen, B. A.; Sleiman, H. F.; Chang, A. K.; McElwee-White, L. *J. Am. Chem. Soc.* **1991**, *113*, 4871. (b) Sleiman, H. F.; Mercer, S.; McElwee-White, L. *J. Am. Chem. Soc.* **1989**, *111*, 8007.

(9) Dobbs, D. A.; Bergman, R. H. *J. Am. Chem. Soc.* **1993**, *115*, 3836.

(10) (a) Luan, L.; White, P. S.; Brookhart, M.; Templeton, J. L. *J. Am. Chem. Soc.* **1990**, *112*, 8190. (b) Pérez, P. J.; Luan, L.; White, P. S.; Brookhart, M.; Templeton, J. L. *J. Am. Chem. Soc.* **1992**, *114*, 7928. (c) Luan, L.; Brookhart, M.; Templeton, J. L. *Organometallics* **1992**, *11*, 1433.

(11) Caffyn, A. J. M.; Feng, S. G.; Dierdorf, A.; Gamble, A. S.; Eldredge, P. A.; Vossen, M. R.; White, P. S.; Templeton, J. L. *Organometallics* **1991**, *10*, 2842.

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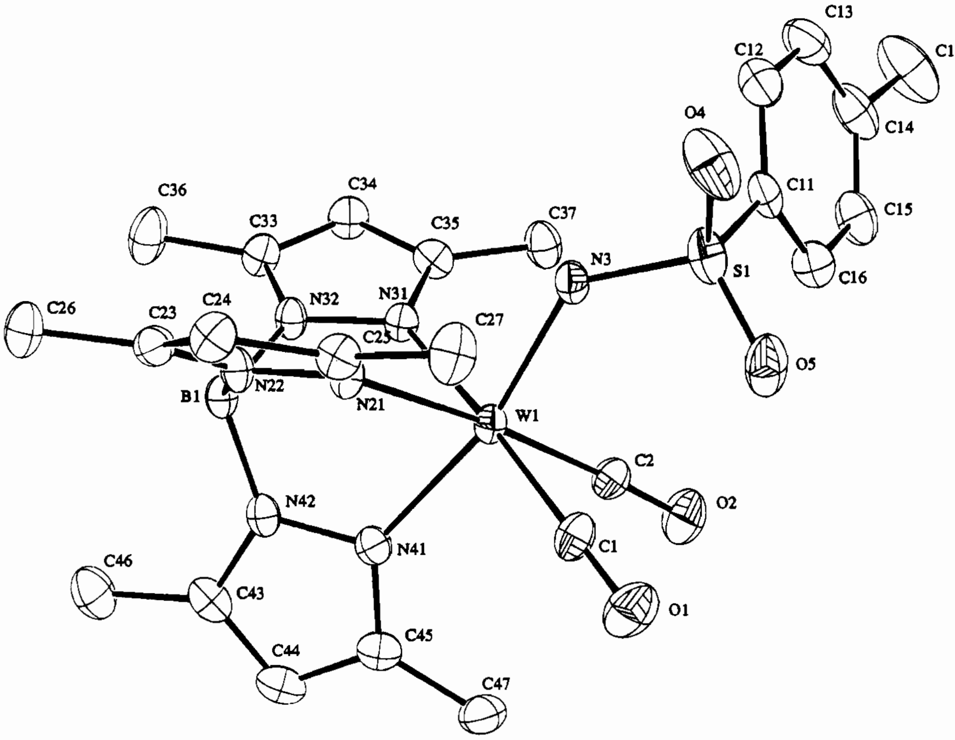


Figure 1. ORTEP diagram of Tp'(CO)$_2$W(N(H)Ts) (**1**), showing a 50% probability level of the ellipsoids.

THFfor several hours, a smooth reaction (eq 2) takes place.

$$\text{Tp'(CO)}_3\text{WH} + \text{TsN}_3 \longrightarrow \text{Tp'(CO)}_2\text{W(N(H)Ts)} + \text{CO} + \text{N}_2 \quad (2)$$

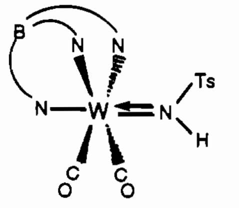
Monitoring the reaction solution by infrared spectroscopy reveals the gradual disappearance of the three ν(CO) absorptions associated with Tp'(CO)$_3$WH (1993, 1905, 1869 cm^{-1}), while two new absorptions appear at 1943 and 1826 cm^{-1}. After solvent removal and washing with hexanes the tosylamido complex **1** can be isolated as air stable yellow crystals in 75% yield. Spectroscopic and analytical data for this complex indicate that it is a tungsten(II) amido complex of composition Tp′(CO)$_2$W(N(H)Ts) (Ts = tosyl, SO$_2$C$_6$H$_4$Me). The ^{1}H NMR spectrum of **1** shows a low-field resonance at 14.4 ppm that can be assigned to the amidic proton, N*H*Ts. A typical 2:1 pattern of pyrazole resonances is also observed in both the ^{1}H and the ^{13}C NMR spectra (see Experimental Section). This indicates the existence of a plane of symmetry in **1**. In accord with the presence of a molecular mirror plane only a single resonance is observed for the two carbonyl groups in the ^{13}C-{^{1}H} NMR spectrum (248.3 ppm, 2 *C*O, $J_{\text{W-C}}$ = 168 Hz).

Table 1. Crystal and Refinement Data for Complexes **1** and **2b**

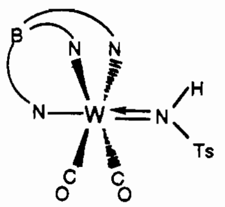
	Tp′(CO)$_2$W(N(H)Ts)·THF	[Tp′(CO)$_2$W(NTs)]I$_3$
formula	BC$_{28}$H$_{38}$N$_7$O$_5$SW	BC$_{24}$H$_{29}$I$_3$N$_7$O$_4$SW
mol wt	779.36	1086.96
space group	$P2_1/n$	P_{cab}
a (Å)	12.4855(1)	15.1764(16)
b (Å)	20.5976(16)	16.8890(14)
c (Å)	12.7311(11)	26.909(3)
β (deg)	96.510(10)	
Z	4	8
V (Å^3)	3253.0(5)	6897.2(13)
T (°C)	20	20
ϱ_{calcd} (g cm^{-3})	1.591	2.094
μ, mm^{-1}	3.72	6.18
λ (Å)	0.709 30	0.709 30
R_F[a]	0.038	0.044
R_W[b]	0.046	0.052

[a] $R_F = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = [\Sigma(w(F_o - F_c)^2)/\Sigma(wF_o^2)]^{1/2}$.

For amido complexes such as **1** there are two possible isomers, *syn* and *anti*, depending on the position of the tosyl group relative to the equatorial pyrazole rings of the Tp′ ligand. In the related species Tp′(CO)$_2$W(N(H)Ph) both conformers are in equilibrium, and the *anti* isomer is the major species in solution.[10a] Only one isomer was observed in the NMR spectrum of Tp′(CO)$_2$W(N(H)^{t}Bu), presumably reflecting severe steric interactions between the bulky *tert*-butyl group near the pyrazole rings of the Tp′ ligand (the cone angle for Tp′ is 225°).[12] For complex **1** we have no evidence of a second isomer. Considering the steric requirements of the tosyl group we propose the *anti* geometry for Tp′(CO)$_2$W(N(H)Ts) in solution.



syn-**1**



anti-**1**

We have carried out a single crystal X-ray study of Tp′-(CO)$_2$W(N(H)Ts), **1**, and an ORTEP drawing is shown in Figure 1. Data collection parameters, selected bond distances and angles and atomic coordinates are shown in Tables 1–3, respectively. A slightly distorted octahedral geometry is adopted by **1** in the solid state. The 2.000(5) Å W(1)–N(3) distance falls in the typical range for a W–N double bond[1] (A W–N distance of 1.956(5) Å was previously found for Tp′(CO)$_2$W-(NMe$_2$)).[10b] The W(1)–N(3)–S(1) angle of 132.9(3)° suggests approximately sp^2 hybridization for the nitrogen atom. The tosyl group occupies a position distal to the pyrazole rings, i.e., the *anti* position. The WNS fragment lies in the molecular mirror plane in order to optimize the metal–nitrogen π-bonding (Figure

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(12) Gorrel, I. B.; Parkin, G. *Inorg. Chem.* **1990**, *29*, 2452.

Table 2. Selected Bond Distances (Å) and Angles (deg) for $Tp'(CO)_2W(N(H)Ts)$, **1**

W(1)−C(1)	1.987(7)	W(1)−C(2)	1.950(6)
W(1)−N(3)	2.000(5)	W(1)−N(21)	2.220(5)
W(1)−N(31)	2.204(5)	W(1)−N(41)	2.151(5)
S(1)−N(3)	1.641(5)	C(1)−O(1)	1.158(8)
C(2)−O(2)	1.156(8)		

C(1)−W(1)−C(2)	74.1(3)	C(1)−W(1)−N(3)	96.72(25)
C(1)−W(1)−N(21)	98.08(23)	C(1)−W(1)−N(31)	174.55(23)
C(1)−W(1)−N(41)	93.73(24)	C(2)−W(1)−N(3)	94.57(25)
C(2)−W(1)−N(21)	172.08(23)	C(2)−W(1)−N(31)	103.05(23)
C(2)−W(1)−N(41)	96.12(24)	N(3)−W(1)−N(21)	87.60(20)
N(3)−W(1)−N(31)	88.10(20)	N(3)−W(1)−N(41)	166.76(20)
N(21)−W(1)−N(31)	84.62(18)	N(21)−W(1)−N(41)	82.88(19)
N(31)−W(1)−N(41)	81.88(19)	N(3)−S(1)−O(4)	108.1(3)
N(3)−S(1)−O(5)	108.7(3)	N(3)−S(1)−C(11)	105.7(3)
W(1)−C(1)−O(1)	174.5(6)	W(1)−C(2)−O(2)	171.1(6)
W(1)−N(3)−S(1)	132.9(3)		

Table 3. Selected Atomic Parameters *x*, *y*, *z* and B_{iso} Values ($Å^2$) for $Tp'(CO)_2W(N(H)Ts)THF$

	x	*y*	*z*	B_{iso}
W(1)	0.219464(20)	0.115593(11)	0.134432(19)	2.483(10)
S(1)	0.11350(15)	0.22511(9)	0.28634(15)	3.73(8)
C(1)	0.3066(6)	0.1935(3)	0.1087(5)	3.3(3)
O(1)	0.3524(5)	0.23940(25)	0.0861(5)	5.1(3)
C(2)	0.1313(6)	0.1668(3)	0.0287(5)	3.2(3)
O(2)	0.0896(5)	0.2031(3)	−0.0321(4)	5.2(3)
N(3)	0.1514(4)	0.1517(3)	0.2567(4)	2.96(23)
O(4)	0.1396(5)	0.2343(3)	0.3983(4)	5.9(3)
O(5)	0.1533(4)	0.27016(23)	0.2147(5)	5.0(3)
C(11)	−0.0296(5)	0.2255(3)	0.2603(6)	3.4(3)
C(12)	−0.0914(6)	0.2072(4)	0.3359(6)	4.3(3)
C(13)	−0.2033(7)	0.2103(4)	0.3162(7)	4.9(4)
C(14)	−0.2516(6)	0.2327(4)	0.2198(7)	5.0(4)
C(15)	−0.1884(6)	0.2489(4)	0.1429(6)	4.7(4)
C(16)	−0.0758(6)	0.2462(4)	0.1617(6)	3.8(3)
C(17)	−0.3739(8)	0.2418(6)	0.1995(9)	7.8(6)
B(1)	0.2948(6)	−0.0381(3)	0.1553(6)	2.7(3)
N(21)	0.3382(4)	0.06660(23)	0.2513(4)	2.64(21)
N(22)	0.3564(4)	0.00126(25)	0.2449(4)	2.72(21)
C(23)	0.4377(5)	−0.0163(3)	0.3194(5)	2.9(3)
C(24)	0.4728(5)	0.0381(3)	0.3735(5)	3.2(3)
C(25)	0.4097(5)	0.0894(3)	0.3305(5)	3.0(3)
C(26)	0.4734(6)	−0.0856(4)	0.3339(6)	3.9(3)
C(27)	0.4124(6)	0.1594(3)	0.3631(6)	3.9(3)
C(36)	0.1270(7)	−0.1501(4)	0.1853(7)	5.2(4)
C(37)	−0.0665(6)	0.0678(4)	0.1270(6)	3.9(3)
N(31)	0.1226(4)	0.02704(23)	0.1468(4)	2.62(21)
N(32)	0.1723(4)	−0.03256(23)	0.1622(4)	2.72(22)
C(33)	0.0979(5)	−0.0792(3)	0.1689(5)	3.3(3)
C(34)	−0.0014(5)	−0.0502(3)	0.1591(6)	3.5(3)
C(35)	0.0158(5)	0.0156(3)	0.1450(5)	3.1(3)
N(41)	0.2938(4)	0.05639(25)	0.0238(4)	2.83(22)
N(42)	0.3191(4)	−0.00865(24)	0.0490(4)	2.73(21)
C(43)	0.3634(5)	−0.0361(3)	−0.0304(6)	3.5(3)
C(44)	0.3675(6)	0.0095(4)	−0.1090(5)	4.0(3)
C(45)	0.3249(5)	0.0652(3)	−0.0737(5)	3.3(3)
C(46)	0.3982(7)	−0.1061(4)	−0.0280(7)	4.9(4)
C(47)	0.3118(7)	0.1284(4)	−0.1302(6)	4.4(3)
O(51)	0.3747(8)	0.5619(4)	0.0562(6)	9.6(5)
C(52)	0.3408(15)	0.5823(7)	−0.0461(10)	12.2(11)
C(53)	0.3089(14)	0.5251(10)	−0.1088(10)	13.5(13)
C(54)	0.3183(13)	0.4708(7)	−0.0362(13)	11.9(10)
C(55)	0.3455(11)	0.4985(6)	0.0652(9)	8.7(7)

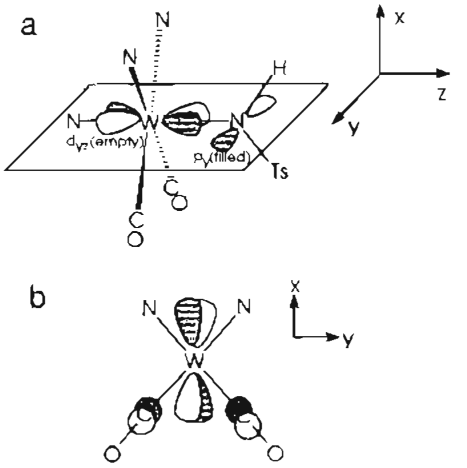


Figure 2. Qualitative orbital representation of two of the metal dπ interactions with the amido and carbonyl ligands.

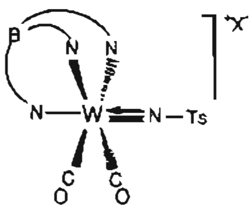
2a). In this way the metal d_{yz} and the nitrogen p_y orbitals overlap efficiently. The acute angle between the carbonyl groups (C(1)−W(1)−C(2), 74.1(3)°) is also a consequence of orbital overlap maximization. The interaction of the CO π^* orbitals with the filled d_{xz} orbital increases as the angle between the two CO ligands decreases (Figure 2b).

$[Tp'(CO)_2W(NTs)]X$ Complexes (X = OTf, 2a; X = I_3, 2b). Compounds of the type $Tp'(CO)_2W(N(H)R)$ are known to react with oxidants to yield cationic imido species $[Tp'(CO)_2W(NR)]^+$. Complex **1** displays similar behavior. When **1** is stirred with silver triflate (AgOTf; Tf = O_2SCF_3) or iodine for several hours (eq 3) in CH_2Cl_2 the characteristic 1945, 1828 cm^{-1} IR pattern for the starting material disappears as two new absorptions appear at 2100 and 2035 cm^{-1}, corresponding to $[Tp'(CO)_2W(NTs)]X$ (X = OTf, **2a**; X = I_3, **2b**). Both complexes **2a** (blue) and **2b** (red) can be isolated as crystalline materials, and they are stable in the solid state at room temperature for several days when stored under nitrogen. No decomposition has been observed when the solids are stored at 0 °C for several weeks.

$$\underset{\mathbf{1}}{Tp'(CO)_2W(N(H)Ts)} \xrightarrow{\text{AgOTf or } I_2} [Tp'(CO)_2W(NTs)][X] \quad (3)$$

$$X = OTf,\ \mathbf{2a}$$
$$X = I_3,\ \mathbf{2b}$$

NMR data for complexes **2a**,**2b** display a 2:1 pattern of lines for all the Tp′ resonances in the ^1H NMR spectra as well as in the $^{13}C\{^1H\}$ NMR spectra (see Experimental Section). The presence of a molecular mirror plane is also consistent with a single resonance at 210.5 ppm for both carbonyl ligands in the $^{13}C\{^1H\}$ NMR spectrum (CD_2Cl_2, J_{W-C} = 150 Hz). No ^1H resonances appear in the low-field region, consistent with removal of the NH proton from **1**. The CF_3 group of the triflate counteranion[13] gives rise to a quartet in the $^{13}C\{^1H\}$ NMR spectrum of **2a** with δ 121.3 ppm, J_{C-F} = 320 Hz. All these data indicate that the structure shown below is appropriate for complexes **2a**,**b** in solution.



2a and 2b

We have performed X-ray studies with a single crystal of $[Tp'(CO)_2W(NTs)]I_3$, **2b**. Figure 3 shows an ORTEP view of this complex. Data collection parameters are displayed in Table 1, and selected bond distances and angles and atomic coordinates appear in Tables 4 and 5, respectively. The ligands are

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[13] Caldarelli, J. L.; Templeton, J. L. *J. Am. Chem. Soc* **1993**, *114*, 10097.

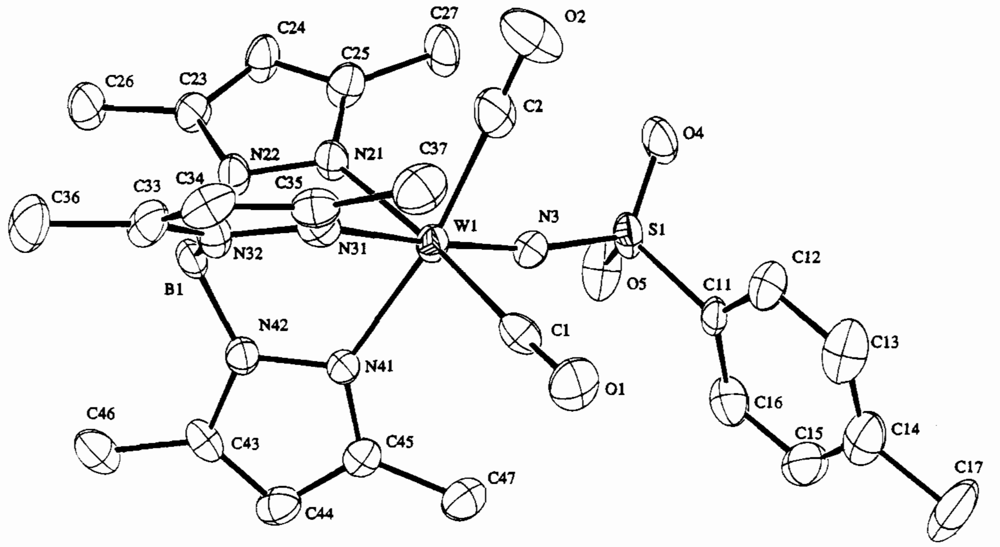


Figure 3. ORTEP view of the molecules of [Tp'(CO)$_2$W(NTs)][I$_3$] (**2b**). The probability level of the ellipsoids is 50%.

Table 4. Selected Bond Distances (Å) and Angles (deg) for [Tp'(CO)$_2$W(NTs)]I$_3$, **2b**

W(1)−C(1)	2.091(13)	W(1)−C(2)	2.053(15)
W(1)−N(3)	1.772(11)	W(1)−N(21)	2.173(10)
W(1)−N(31)	2.169(11)	W(1)−N(41)	2.133(10)
S(1)−N(3)	1.663(11)	C(1)−O(1)	1.123(16)
C(2)−O(2)	1.139(18)		
C(1)−W(1)−N(3)	87.6(5)	C(1)−W(1)−C(2)	89.6(5)
C(1)−W(1)−N(31)	87.1(4)	C(1)−W(1)−N(21)	173.0(4)
C(2)−W(1)−N(3)	88.6(6)	C(1)−W(1)−N(41)	92.7(4)
C(2)−W(1)−N(31)	84.0(5)	C(2)−W(1)−N(21)	91.6(5)
N(3)−W(1)−N(21)	99.3(4)	C(2)−W(1)−N(41)	167.8(5)
N(3)−W(1)−N(41)	103.5(4)	N(3)−W(1)−N(31)	170.9(4)
N(21)−W(1)−N(41)	84.6(4)	N(21)−W(1)−N(31)	86.2(4)
N(3)−S(1)−O(4)	106.7(6)	N(31)−W(1)−N(41)	84.1(4)
N(3)−S(1)−C(11)	103.8(6)	N(3)−S(1)−O(5)	105.3(6)
W(1)−C(2)−O(2)	178.2(14)	W(1)−C(1)−O(1)	177.1(11)
W(1)−N(3)−S(1)	167.6(7)		

Table 5. Selected Atomic Parameters *x*, *y*, *z* and B_{iso} Values (Å^2) for [Tp'(CO)$_2$W(NTs)]I$_3$

	x	*y*	*z*	B_{iso}
W(1)	0.03858(3)	0.33139(3)	0.124132(22)	3.240(23)
I(1)	0.32710(10)	0.73496(8)	0.11798(5)	7.95(8)
I(2)	0.43456(8)	0.60758(8)	0.16106(4)	6.48(6)
I(3)	0.52386(9)	0.48144(10)	0.21594(5)	8.69(9)
S(1)	0.21870(23)	0.23619(20)	0.07709(15)	4.24(18)
C(1)	−0.0288(7)	0.2242(8)	0.1158(5)	3.6(6)
O(1)	−0.0618(6)	0.1652(6)	0.1108(4)	5.7(5)
C(2)	0.0889(10)	0.2918(8)	0.1904(6)	5.2(8)
O(2)	0.1190(8)	0.2703(7)	0.2268(4)	7.9(7)
N(3)	0.1291(7)	0.2863(6)	0.0936(4)	3.7(5)
O(4)	0.2701(7)	0.2264(6)	0.1207(4)	6.8(6)
O(5)	0.2526(7)	0.2768(6)	0.0349(4)	6.5(6)
C(11)	0.1772(8)	0.1430(7)	0.0584(5)	3.2(6)
C(12)	0.1584(10)	0.0893(8)	0.0951(6)	4.9(8)
C(13)	0.1299(10)	0.0153(9)	0.0797(6)	6.0(9)
C(14)	0.1231(10)	−0.0053(9)	0.0312(7)	5.8(9)
C(15)	0.1410(11)	0.0497(10)	−0.0048(7)	6.5(9)
C(16)	0.1680(11)	0.1264(9)	0.0094(6)	5.3(8)
C(17)	0.0947(13)	−0.0880(10)	0.0154(10)	10.0(14)
B(1)	−0.0589(9)	0.5022(9)	0.1220(6)	3.6(7)
N(21)	0.0934(6)	0.4488(6)	0.1358(4)	4.0(6)
N(22)	0.0400(7)	0.5141(6)	0.1353(4)	3.8(5)
C(23)	0.0869(9)	0.5773(7)	0.1475(6)	4.1(7)
C(24)	0.1720(9)	0.5532(8)	0.1554(6)	4.9(8)
C(25)	0.1747(9)	0.4740(8)	0.1498(6)	4.5(7)
C(26)	0.0470(10)	0.6582(8)	0.1529(7)	5.6(8)
C(27)	0.2519(10)	0.4192(9)	0.1531(7)	6.4(9)
N(31)	−0.0712(7)	0.3705(6)	0.1695(4)	3.8(5)
N(32)	−0.1017(7)	0.4485(6)	0.1620(4)	3.6(5)
C(33)	−0.1703(9)	0.4612(9)	0.1928(5)	4.4(7)
C(34)	−0.1851(9)	0.3941(8)	0.2198(5)	4.2(7)
C(35)	−0.1238(9)	0.3398(8)	0.2052(5)	3.9(7)
C(36)	−0.2141(10)	0.5397(9)	0.1961(6)	5.7(8)
C(37)	−0.1148(11)	0.2559(9)	0.2262(5)	5.2(8)
N(41)	−0.0326(7)	0.3861(6)	0.0651(4)	3.4(5)
N(42)	−0.0658(7)	0.4628(6)	0.0710(4)	3.4(5)
C(43)	−0.1087(8)	0.4838(7)	0.0294(5)	3.4(6)
C(44)	−0.1007(9)	0.4239(9)	−0.0049(5)	4.5(7)
C(45)	−0.0550(8)	0.3646(8)	0.0197(5)	3.3(6)
C(46)	−0.1513(10)	0.5651(9)	0.0241(6)	5.2(8)
C(47)	−0.0320(10)	0.2845(8)	−0.0015(5)	5.0(8)

distributed around the metal center in an octahedral environment. The 1.772(11) Å W−N distance is significantly shorter than that found for **1** as the result of the increase in the metal−nitrogen bond order.[1] (A 1.75 Å value was reported for the analog [Tp'(CO)$_2$W(NPh)][PF$_6$].[10a]) The W−N−Ts linkage is close to linear (167.6(2)°) as expected for a change in nitrogen hybridization from sp^2 to sp. The angle between both carbonyl groups is 89.6(5)°, near the ideal 90° for octahedral complexes.

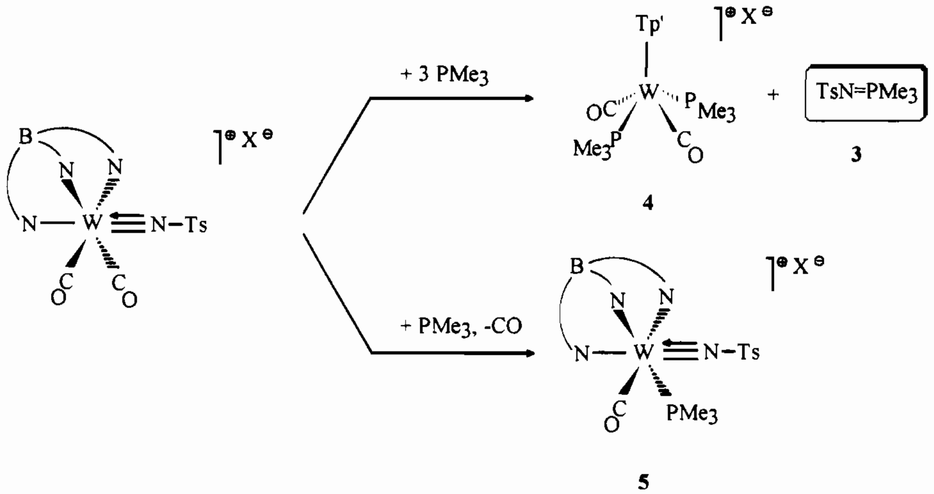
Reactivity of [Tp'(CO)$_2$W(NTs)]X (2) with Nucleophiles. Compounds **2a,b** show unusually high ν(CO) frequencies (2100 and 2035 cm^{-1}) in their IR spectra, an indication of an electron-poor metal center. This fact, along with the presence of the electron-withdrawing tosyl group attached to the nitrogen, should increase the electrophilicity of the complex and perhaps favor nitrene group transfer. Evidence for net addition of nucleophiles at nitrogen is the reaction of **2** with a hydride source. Complexes [Tp'(CO)$_2$W(NTs)]X react readily with LiBH$_4$ to regenerate the amido species Tp'(CO)$_2$W(N(H)Ts), **1** (eq 4).

$$\underset{\mathbf{2}}{[\mathrm{Tp'(CO)_2W(NTs)}][\mathrm{X}]} \xrightarrow{\mathrm{LiBH_4}} \underset{\mathbf{1}}{\mathrm{Tp'(CO)_2W(N(H)Ts)}} + \mathrm{LiX} + \mathrm{BH_3} \quad (4)$$

Similar behavior has been reported for [Tp'(CO)$_2$W(NPh)][PF$_6$]. Mechanistic studies with the phenylnitrene complex demonstrated that these transformations occur through formyl intermediates such as Tp'(CO)(CHO)W(NPh).[10c] Note that no reaction was observed when complexes **2** were treated with electron-rich olefins such as *p*-methoxystyrene or ethyl vinyl ether.

An instantaneous transformation occurs when an excess of PMe$_3$ (4 equiv) is added to a solution of compound **2a** or **2b**. NMR studies of the reaction mixture have led to the detection

Scheme 1



of three different species: the phosphinimine TsN=PMe$_3$ (**3**) and two organometallic compounds, [Tp′(CO)$_2$W(PMe$_3$)$_2$]X (X = OTf, **4a**; X = I$_3$, **4b**) and [Tp′(CO)(PMe$_3$)W(NTs)]X, (X = OTf, **5a**; X = I$_3$, **5b**). These three products form in a 1:1:2.5 ratio. The existence of the phosphinimine was established by comparison of its ^{1}H NMR spectrum with that of an authentic sample (see Experimental Section). The tungsten species **4** and **5** were also characterized using NMR spectroscopy. Both [Tp′(CO)$_2$W(PMe$_3$)$_2$]X (**4**) complexes display similar ν(CO) absorptions at 1936 and 1842 cm^{-1} (CH$_2$Cl$_2$). Both CO groups are equivalent in the ^{13}C NMR spectrum, appearing as a triplet due to C–P coupling (δ 220.5 ppm, $J_{\text{C-P}} = 4.5$ Hz). The proton signals of the PMe$_3$ methyl groups appear as a pseudotriplet (δ 1.15 ppm, $J_{\text{PH}_{\text{app}}} = 10$ Hz) whereas the Tp′ ligand generates a 2:1 pattern of lines in both ^{1}H and ^{13}C NMR spectra. These data suggest a trans–trans distribution of carbonyl and phosphine ligands for complexes **4**.

The second organometallic species presents a unique ν(CO) absorption (1996 cm^{-1} in CH$_2$Cl$_2$). The ^{1}H NMR spectrum shows distinct resonances for each pyrazole ring of the Tp′ ligand indicating a chiral metal center. A doublet is observed for PMe$_3$ (1.59 ppm, 9 H, $^2J_{\text{PH}} = 10$ Hz) and the aromatic protons of the tosyl group resonate in the 7.9–7.4 range. These data support the formulation of complex **5** as [Tp′(CO)(PMe$_3$)W(NTs)]X (X = OTf, **5a**; X = I$_3$, **5b**). In contrast to complexes **4a,b**, where the chemical properties seem to be identical, there is a significant difference between **5a,b**. The triflate derivative is relatively stable for days, while the complex with triodide as the counterion, [Tp′(CO)(PMe$_3$)W(NTs)]I$_3$ (**5b**), is only observed in the reaction mixture. This species decomposes during the workup to yield a neutral imido complex, Tp′(CO)(I)W(NTs) (**6**). This monocarbonyl compound has been also prepared from Tp′(CO)$_2$WI and TsN$_3$ in refluxing THF (eq 5).

$$\mathrm{Tp'(CO)_2WI + TsN_3 \longrightarrow \underset{\mathbf{6}}{Tp'(CO)IW(NTs)} + CO + N_2} \qquad (5)$$

The reaction of complex **2** with trimethylphosphine is extremely rapid, even at −80 °C, so no intermediates have been observed. However, some hypotheses can be set forth on the basis of the available data. The formation of products **3**–**5** (Scheme 1) can be explained in terms of two separate transformations. The dicarbonyl [Tp′(CO)$_2$W(PMe$_3$)$_2$]$^+$ products could result from nitrene transfer to PMe$_3$ followed by trapping of the [Tp′(CO)$_2$W]$^+$ organometallic fragment by two molecules of trimethylphosphine. On the other hand, the monocarbonyl species [Tp′(CO)(PMe$_3$)W(NTs)]$^+$ is a result of simple substitution of one CO ligand in **2** by PMe$_3$. The high ν(CO) frequencies (2100 and 2035 cm^{-1}) in **2** support facile CO substitution by phosphine. Decomposition of [Tp′(CO)(PMe$_3$)W(NTs)]I$_3$ presumably reflects the nucleophilicity of the triiodide counteranion. Evidently loss of PMe$_3$ and tungsten–iodide bond formation is favorable in this system.

Conclusions

The new amido species Tp′(CO)$_2$W(N(H)Ts) (**1**) has been prepared from the tungsten hydride Tp′(CO)$_3$WH and tosyl azide. The nitrene complexes derived from **1** by oxidation, [Tp′(CO)$_2$W(NTs)][X] (**2**), are electrophilic at nitrogen, and reaction with PMe$_3$ yields phosphinimine TsN=PMe$_3$, **3**. These results may constitute a point of departure for developing a system capable of nitrene transfer to other substrates.

Experimental Section

General Methods. Microanalyses were carried out by Atlantic Microlab, Atlanta, GA. Infrared spectra were recorded on a Mattson Polaris FT IR spectrometer. Proton NMR spectra were recorded on a Varian 250 MHz spectrometer, and C -13 NMR spectra were recorded on a 400 MHz instrument. All preparations and manipulations were carried out under an oxygen-free nitrogen atmosphere following conventional Schlenk techniques. Solvents were rigorously dried and degassed before use. The complexes Tp′(CO)$_3$WH[11] and Tp′(CO)$_2$WI[10b] and tosyl azide[14] were prepared according to literature methods.

Synthesis of Tp′(CO)$_2$W(N(H)Ts), 1. Complex Tp′(CO)$_3$WH (2.5 g, 4.4 mmol) was suspended in THF (150 mL), and the suspension was heated until the solid dissolved. Excess tosyl azide was added via syringe (2.2 mL, 3 equiv), and the mixture was heated for 10 h. Volatiles were removed under vacuum, and the residue was washed with hexane (4 × 50 mL) to give 1.9 g of Tp′(CO)$_2$W(N(H)Ts) as a yellow-brown solid (75% yield). Compound **1** was crystallized by cooling a THF solution to −20 °C or by slow diffusion of hexane into a THF solution at room temperature. In both cases yellow crystals of **1** were collected after a few hours. IR (THF): 1944, 1828 cm^{-1} (ν(CO)). IR (Nujol mull): 3132 (ν(N–H)), 2567 (ν(B–H)), 1938, 1815 cm^{-1} (ν(CO)). ^{1}H NMR (CD$_2$Cl$_2$): 14.39 (N–*H*), 7.86 (d, 2H, C$_6$H$_4$), 7.29 (d, 2H, C$_6$H$_4$), 6.15 (1 H, C–*H*–Tp′), 5.82 (2 H, C–*H*–Tp′), 2.58 (6 H, 2 *Me*–Tp′), 2.42 (3 H, 1 *Me*–

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(14) Regitz, M.; Hocker, J.; Liedhegener, A. In *Organic Syntheses, Coll. Vol. V*; Wiley & Sons: New York, 1973; pp 179–180.

Tp′), 2.41(3 H, 1 *Me*−Tp′), 2.40 (3 H, C_6H_4*Me*), 1.51 (6 H, 2 *Me*−Tp′). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): 248.4 (2 C, *C*O, J_{W-C} = 168 Hz), 152.9 (1 C, *ipso*-C_6H_4), 165.9 (1), 150.1 (1), 145.9 (2) 143.4 (2) (6 C, 6 *C*−Me Tp′), 138.8 (1 C, *p*-C_4H_6), 129.9, 127.7 (4 C, 2 *o*- and 2 *m*-C_6H_4), 110.3 (1 *C*−H Tp′), 106.9 (2 *C*−H Tp′), 21.6 (1 C, *Me*−C_6H_4), 17.4 (1), 17.0 (2) 13.1 (1), 12.3 (2) (6 C, 6 *Me*-Tp′). Anal. Calcd for **1** (with a molecule of THF): C, 44.06; H, 5.02; N,12.84. Found: C, 43.40; H, 4.97; N, 12.68.

Synthesis of [Tp′(CO)₂W(NTs)][X] (X = OSO_2CF_3, 2a; X = I_3^-, 2b). Method a. Silver triflate (0.48 g, 2 mmol) was added to a yellow stirred solution of **1** (0.5 g, 0.75 mmol) in CH_2Cl_2 (30 mL). The mixture turned blue in a few minutes. After the mixture was stirred for 3 h, the solvent was removed under vacuum, the residue was extracted with CH_2Cl_2 (10 mL), and the resulting suspension was centrifuged. The blue solution was placed in a Schlenk tube, and hexane was added as a second layer. Blue crystals of **2a** were collected after several hours. Yield: 0.35 g, 55%.

Method b. Excess iodine (0.4 g, 3.1 mmol) was added to a stirred solution of complex **1** (0.9 g, 1.2 mmol) in CH_2Cl_2 (40 mL). After 1 h of stirring the reaction was complete as assessed by IR monitoring. Volatiles were removed under reduced pressure, and the residue was washed with Et_2O (4 × 50 mL) to eliminate excess iodine. Complex **2b** was obtained as a dark orange powder in 60% yield (0.75 g). Single crystals suitable for X-ray studies can be obtained by slow diffusion of hexane into CH_2Cl_2 solutions of **2b**.

[Tp′(CO)₂W(NTs)][OTf] (2a). IR (CH_2Cl_2): 2100, 2035 cm^{-1} (ν(CO)). IR (Nujol mull): 2563 (ν(B−H)), 2106, 2040 cm^{-1} (ν(CO)). ^1H NMR (CD_2Cl_2): 7.94 (d, 2H, C_6*H_4*), 7.55 (d, 2H, C_6*H_4*), 6.24 (2 H, 2 C−*H*−Tp′), 6.07 (1 H, C−*H*−Tp′), 2.54 (3 H, C_6H_4*Me*), 2.50 (6 H, 2 *Me*−Tp′), 2.42(3 H, 1 *Me*−Tp′), 2.37 (3 H, 1 *Me*−Tp′), 2.33 (6 H, 2 *Me*−Tp′). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): 210.5 (2C, 2 *C*O, J_{W-C} = 150 Hz), 151.6 (1 C, *i*-C_6H_4), 154.7 (1), 153.7 (2) 149.7 (1) 149.2 (2) (6 C, 6 *C*−Me Tp′), 131.6 (1 C, *p*-C_6H_4), 131.6, 129.2 (4 C, 2 *o*- and 2 *m*- C_6H_4), 110.4 (1 C, *C*−H Tp′), 109.4 (2 C, *C*−H Tp′), 22.1 (1 C, *Me*−C_6H_4), 16.6 (1), 15.9 (2) 13.6 (1), 12.5 (2) (6 C, 6 *Me*−Tp′). Anal. Calcd for **2a**: C, 35.78; H, 3.48; N, 11.68; S, 7.64. Found: C, 34.92; H, 3.46; N, 11.37; S, 7.58.

[Tp′(CO)₂W(NTs)][I₃](2b). IR (CH_2Cl_2): 2100, 2033 cm^{-1} (ν(CO)). IR (Nujol mull): 2573 (ν(B−H)), 2096, 2033 cm^{-1} (ν(CO)). ^1H NMR (CD_2Cl_2): 7.92 (d, 2H, C_6H_4), 7.54 (d, 2H, C_6H_4), 6.23 (2 H, C−*H*−Tp′), 6.03 (1 H, C−*H*−Tp′), 2.53 (3 H, C_6H_4*Me*) 2.50 (6 H, 2 *Me*−Tp′), 2.41 (3 H, 1 *Me*−Tp′), 2.37 (3 H, 1 *Me*−Tp′), 2.31 (6 H, 2 *Me*−Tp′). The ^{13}C NMR spectrum is essentially identical to that obtained for the triflate analog, **2a**. Anal. Calcd for **2b**: C, 26.52; H, 2.69; N, 9.02; I, 35.03. Found: C, 26.46; H, 2.66; N, 9.03; I, 35.13.

Reactions of Complexes [Tp′(CO)₂W(NTs)][X] (2) with PMe₃. Method a. Trimethylphosphine (1.5 mmol, 1.5 mL of a 1 M solution in CH_2Cl_2) was added to a blue solution of [Tp′(CO)₂W(NTs)][OTf] (0.3 g, 0.36 mmol) in CH_2Cl_2 (30 mL). The initial blue color changed to red immediately. After the mixture was stirred for 15 min, the volatiles were removed under vacuum. ^1H NMR studies carried out to examine the residue revealed three species: TsN=PMe₃ (**3**), [Tp′(CO)₂W(PMe₃)₂][OTf] (**4a**), and [Tp′(CO)(PMe₃)W(NTs)][OTf] (**5a**) in a 2:2:5 ratio, respectively. This ratio was identical to that obtained when the reaction was performed at −80 °C. The residue was washed with Et_2O (2 × 20 mL). The filtrate contains the phosphinimine **3** whereas complexes **4a** and **5a** remain in the solid left after filtration. These two species can be separated by fractional crystallization from THF−hexane mixtures.

Method b. A similar reaction took place when **2b** was used as the starting material. A mixture of TsN=PMe₃ (**3**), [Tp′(CO)₂W(PMe₃)₂][I₃], (**4b**), and [Tp′(CO)(PMe₃)W(NTs)][I₃] (**5b**) was obtained in the same 2:2:5 ratio as assessed from NMR data. Again, the phosphinimine **3** was separated by washing with Et_2O. However, complex **5b** decomposed during the workup to give a new monocarbonyl species of composition Tp′(CO)IW(NTs) (**6**). Complex **6** has also been prepared by an alternative route (see below).

Spectroscopic Data for Complexes [Tp′(CO)₂W(PMe₃)₂][X] (4a,b). IR (CH_2Cl_2): 1936, 1840 cm^{-1} (ν(CO)). IR (Nujol mull): 2570 (ν(B−H)), 1930, 1830 (ν(CO)), 1250 cm^{-1} (ν(OTf)). ^1H NMR (CD_2Cl_2): 6.20 (1 H, C−*H*−Tp′), 5.94 (2 H, C−*H*−Tp′), 2.56 (3 H, 1 *Me*−Tp′), 2.37 (6 H, 2 *Me*−Tp′), 2.34 (6 H, 2 *Me*−Tp′), 2.23 (3 H, 1 *Me*−Tp′), 1.15 (doublet with central intensity, 18 H, 2 P*Me₃*, $J_{PH_{app}}$ = 10 Hz).$^{13}C\{^1H\}$ NMR (CD_2Cl_2): 220.6 (t, 2C, *C*O, J_{P-C} = 4.5 Hz), 109.6 (2 C, *C*−H Tp′), 109.4 (1 *C*−H Tp′), 19.8(1), 17.8 (2) 13.6 (2), 13.1 (1) (6 C, 6 *Me*−Tp′), 17.0 (pseudotriplet, 6 C, 2 P*Me₃*, $J_{P-C_{app}}$ = 16 Hz).

Spectroscopic Data for Complexes [Tp′(CO)(PMe₃)W(NTs)][X] (5a,b). IR (CH_2Cl_2): 1996 cm^{-1} (ν(CO)). ^1H NMR (CD_2Cl_2): 7.83 (d, 2H, C_6H_4), 7.45 (d, 2H, C_6H_4), 6.32, 6.02, 5.94 (3 H, 3 C−*H*−Tp′), 2.56, 2.47, 2.43, 2.39, 2.36, 2.34, 1.95 (21 H, 7 Me, 6 *Me*−Tp′ and 1 *Me*−Ts), 1.15 (d, 9 H, P*Me₃*, J_{PH} = 10 Hz).

Preparation of an Authentic Sample of TsN=PMe₃ (3). Following a procedure similar to that reported for TsN=PMe₂Ph,[7] 0.3 mL (3 mmol) of PMe₃ was stirred together with 1 equiv of TsN₃ (0.5 mL) in THF (30 mL) for 30 min. The colorless solution was taken to dryness to give a white solid of TsN=PMe₃, **3**. ^1H NMR (CD_2Cl_2): 7.68 (m, 2 H, C_6*H_4*), 7.21 (m, 2 H, C_6*H_4*), 2.36 (3 H, *Me*−Ts), 1.63 (d, 9 H, N=P*Me₃*, J_{PH} = 14 Hz).

Synthesis of Tp′(CO)IW(NTs) (6). After 1.0 g (1.5 mmol) of Tp′(CO)₂WI was dissolved in dry THF (50 mL), tosyl azide (0.5 mL, 3 mmol) was added to the solution and the mixture was heated at reflux temperature for 2 h. The IR spectrum of the resulting green solution shows a single absorption (1975 cm^{-1}) in the carbonyl region. The mixture was taken to dryness, and the residue was dissolved in 20 mL of THF. Green crystals (0.80 g) of Tp′(CO)IW(NTs) were collected in 75% yield upon slow diffusion of hexane into the THF solution. IR (CH_2Cl_2): 1975 cm^{-1} (ν(CO)). IR (Nujol mull): 2561 (ν(B−H)), 1957 cm^{-1} (ν(CO)). ^1H NMR (CD_2Cl_2): 7.79 (d, 2 H, C_6*H_4*), 7.36 (d, 2 H, C_6*H_4*), 6.16, 6.07, 5.69 (3 H, 3 C−*H*−Tp′), 2.58, 2.55, 2.50, 2.47, 2.43, 2.39, 2.25 (21 H, 6 *Me*−Tp′ and C_6H_4*Me*). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): 271.4 (2C, *C*O, J_{W-C} = 166 Hz), 155.3, 154.8, 154.4, 147.4, 147.3, 146.3, 145.6 (6 *C*−Me Tp′ and 1 C *i*-C_6H_4), 134.3 (1 C, *p*-C_6H_4), 129.9, 129.0 (4 C, 2 *o*- and 2 *m*-C_6H_4), 109.2, 108.2, 108.0 (3 C, 3 *C*−H Tp′), 21.8 (1 C, *Me*−C_6H_4), 18.1, 17.8, 17.1, 13.0, 12.5 (2) (6 C, *Me*−Tp′). Anal. Calcd for **6**: C, 34.30; H, 3.60; N,12.18. Found: C, 34.37; H, 3.58; N, 12.25

X-ray Data Collection and Structure Solution and Refinement[15] for Complexes 1 and 2b. (a) Tp′(CO)₂W(N(H)-Ts)·THF. A yellow brick of dimensions 0.25 × 0.25 × 0.30 mm was selected, mounted on a glass wand, and coated with epoxy. Diffraction data were collected on a Rigaku diffractometer. Sixty-four centered reflections found in the range 15° < θ < 20° and refined by least-squares calculations indicated a monoclinic cell. The cell parameters are listed in Table 1.

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(15) (a) Full system reference: Gabe, E. J.; LePage, Y.; Charland, J.-P.; Lee, F. L.; White, P. S. *J. Appl. Crystallogr.* **1989**, *22*, 384. (b) Scattering factors from: *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.

Diffraction data were collected at 20 °C in the (−14,0,0) to (14,24,15) *h,k,l* range. A graphite monochromator was used. The data were corrected for Lorentz−polarization effects during the final stages of data reduction. Solution of the structure was straightforward from application of the heavy-atom method. All calculations were performed using the NRCVAX[15a] program. Space group $P2_1/n$ was confirmed, and the position of the tungsten atom was deduced from the three-dimensional Patterson function. The positions of the remaining non-hydrogen atoms were determined through subsequent Fourier and difference Fourier calculations. Final refinement resulted in residuals of $R = 3.8\%$ and $R_w = 4.6\%$.

(b) [Tp′(CO)$_2$W(NTs)][I$_3$]. The procedure was essentially identical to that described above. The crystal dimensions were 0.22 × 0.22 × 0.15 mm. Seventy-four reflections in the $15° < \theta < 20°$ range were used to determine the orthorhombic cell. The *h,k,l* range was (0,0,0) to (16,18,28). The space group was found to be *Pcab*. Final refinement resulted in residual $R = 4.4\%$ and $R_w = 5.2\%$.

Acknowledgment. We are grateful to the National Institutes of Health (Grant GM28938) and the Department of Energy (Grant DE-FG05−85ER13430) for financial support. P.J.P. also thanks the Ministerio de Educación y Ciencia (Spain) for a research studentship.

Supplementary Material Available: Tables SI-SVII, listing bond distances and angles, complete atomic coordinates, thermal parameters, and crystal and refinement data for complexes **1** and **2b** (10 pages). Ordering information is given on any current masthead page