Stepwise Oxidation of Benzylamine Coordinated to the $[Tp'W(CO)(PhC_2Me)]^+$ Moiety

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Abstract: Coordination of benzylamine to the $[Tp'W(CO)(PhC_2Me)]^+$ moiety activates the amine for stepwise oxidation by sequential hydride/proton removal steps. Each metal complex along the stepwise reaction path (amine, amido, imine, azavinylidene, and nitrile) has been isolated and characterized. The structure of the imine complex $[Tp'W(CO)(PhC_2Me)(NH{=}CHPh)][BF_4]$ (**4**) has been confirmed by an X-ray diffraction study. Complex **4** crystallizes in the space group $P2_1/c$ ($Z = 4$, $a = 13.790(3)$ Å, $b = 13.225(3)$ Å, $c = 19.150(4)$ Å, $\beta = 108.769(1)°$, $R = 3.5\%$, $R_w = 4.4\%$), and key geometric features include a W−N dative bond length of 2.135(6) Å to the imine nitrogen and a W−N−C angle of 129.7(5)°.

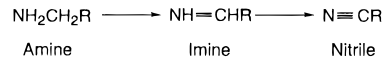
Introduction

Oxidation of amines to imines or nitriles is common, but isolation of intermediates along the oxidation route remains elusive. This paper reports a detailed study of the stepwise oxidation of benzylamine coordinated to tungsten. Isolation of intermediates along the reaction pathway from amine to nitrile proved more difficult than in the companion study of stepwise nitrile reduction.

Numerous procedures exist for stoichiometric[1] and catalytic[2−8] oxidation of amines to imines or nitriles (Scheme 1), although isolation of imines is complicated by their susceptibility to hydrolysis[9] or further oxidation to nitriles. Coordination of amines to transition metals activates the amine toward dehydrogenation and often allows isolation at the imine stage.

Oxidation of benzylamine bound to ruthenium(II) with Ce(IV) forms benzonitrile.[10] Bound imine groups were postulated as intermediates, but these imine complexes were not isolated. Oxidation of benzylamine coordinated to pentaamine Ru(II) to benzonitrile passes through a deep red intermediate proposed to be the imine complex $[(NH_3)_5Ru^{III}(NH{=}CHPh)]^{3+}$.[11] Dehydrogenation of isopropylamine in $[Ru(tpy)(bpy)(NH_2CHMe_2)]^{2+}$ (tpy = 2,2′:6′,2″-terpyridine) occurs via a two-electron oxidation to yield the imine complex $[Ru(tpy)(bpy)(NH{=}CMe_2)]^{2+}$.[12] A second two-electron oxidation yields the azavinylidene complex $[Ru(tpy)(bpy)(NCMe_2)]^{3+}$. Amine to imine conversions are also known for chelating nitrogen ligands, in both ruthenium(II)[13−17] and osmium(II)[18] systems.

Scheme 1. Amine Dehydrogenation



Imines coordinated to transition metals are often vulnerable to nucleophilic attack, to form functionalized amines.[19−21] Gladysz has synthesized a wide variety of imine complexes of the type $[\eta^5\text{-}(C_5H_5)Re(NO)(PPh_3)(N(R){=}C(R')(R''))]^+$,[19a] and imines coordinated to a chiral metal fragment can add nucleophiles stereoselectively.

Reduction of acetonitrile coordinated to chiral $[Tp'W(CO)(RC_2R')]^+$ (R = R′ = Me; R = Me, R′ = Ph; Tp′ = hydridotris(3,5-dimethylpyrazolyl)borate) (Scheme 2) templates has been accomplished.[21] Sequential nucleophilic and electrophilic additions result in conversion of the nitrile ligand to the corresponding amine. If a series of hydride/proton additions are utilized, acetonitrile is converted to ethylamine. However, if nucleophilic addition at the imine stage is accomplished with cyanide, a chiral center is created at the amido carbon with high diastereoselectivity (Scheme 3). Reaction of the amine complex with acid in acetonitrile results in replacement of the amine ligand by acetonitrile, thus reforming

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(1) (a) Stevens, T. E. *J. Org. Chem.* **1961**, *26*, 2531. (b) Stojiljkovic, A.; Andrejevic, V.; Mihailovi, M. L. *Tetrahedron* **1967**, *23*, 721. (c) Keirs, D.; Overton, K. *J. Chem. Soc., Chem. Commun.* **1987**, 1660. (d) Cornejo, J. J.; Larson, K. D.; Mendenhall, G. D. *J. Org. Chem.* **1985**, *50*, 5382. (e) Larsen, J.; Jorgensen, K. A. *J. Chem. Soc., Perkins Trans.*, **1992**, 1213. (f) Marino, J. P.; Larsen, R. D. *J. Am. Chem. Soc.* **1981**, *103*, 4642.

(2) March, J. *Advanced Organic Chemistry: Reactions, Mechanisms and Structures*; Wiley-Interscience: New York, 1992; pp 1172−1173.

(3) Capdevielle, P.; Lavigne, A.; Maumy, M. *Synthesis* **1989**, 453.

(4) Capdevielle, P.; Lavigne, A.; Maumy, M. *Tetrahedron* **1990**, *46 (8)*, 2835.

(5) Yamazaki, S.; Yamazaki, Y. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 301.

(6) Xu, B.; Yamaguchi, T.; Tanabe, K. *Chem. Lett.* **1988**, 281.

(7) Müller, P.; Gilavert, D. M. *Tetrahedron* **1988**, *44 (23)*, 7171.

(8) (a) Murahashi, S.; Naota, T.; Taki, H. *J. Chem. Soc., Chem. Commun.* **1985**, 613. (b) Murahashi, S. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2443.

(9) Carey, F. A.; Sundberg, R. J. *Advanced Organic Chemistry, Part A: Structure and Mechanisms*; Plenum Press: New York, 1990.

(10) Keene, F. R.; Salmon, D. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1976**, *98 (7)*, 1884.

(11) Diamond, S. E.; Tom, G. M.; Taube, H. *J. Am. Chem. Soc.* **1975**, *97 (10)*, 2661.

(12) Adcock, P. A.; Keene, F. R. *J. Am. Chem. Soc.* **1981**, *103*, 6494.

(13) Lane, B. C.; Lester, J. E.; Basolo, F. *Chem. Commun.* **1971**, 1618.

(14) Goedken, V. L. *J. Chem. Soc., Chem. Commun.* **1972**, 207.

(15) Alvarez, V. E.; Allen, R. J.; Matsubara, T.; Ford, P. C. *J. Am. Chem. Soc.* **1974**, *96 (25)*, 7686.

(16) Goedken, V. L.; Busch, D. H. *J. Am. Chem. Soc.* **1972**, *94 (21)*, 7355.

(17) (a) Dabrowiak, J. C.; Lovechio, F. V.; Goedken, V. L.; Busch, D. H. *J. Am. Chem. Soc.* **1972**, *94 (15)*, 5502. (b) Brown, G. M.; Weaver, T. R.; Keene, F. R.; Meyer, T. J. *Inorg. Chem.* **1976**, *15 (1)*, 190.

(18) Keene, F. R.; Lay, P. A.; Sneddon, G. E.; Whebell, G. W. *Aust. J. Chem.* **1993**, *46*, 1763.

(19) (a) Knight, D. A.; Dewey, M. A.; Stark, G. A.; Bennett, B. K.; Arif, A. M.; Gladysz, J. A. *Organometallics* **1993**, *12*, 4523. (b) Cantrell, W. R., Jr.; Richter-Addo, G. B.; Gladysz, J. A. *J. Organomet. Chem.* **1994**, *472*, 195. (c) Richter-Addo, G. B.; Knight, D. A.; Dewey, M. A.; Arif, A. M.; Gladysz, J. A. *J. Am. Chem. Soc.* **1993**, *115*, 11863.

(20) (a) Faller, J. W.; Ma, Y.; Smart, C. J.; Diverdi, M. J. *J. Organomet. Chem.* **1991**, *420*, 237. (b) Buchwald, S. L.; Watson, B. T.; Wannamaker, M. W.; Dewan, J. C. *J. Am. Chem. Soc.* **1989**, *111*, 4486. (c) Hoberg, H.; Götz, V.; Krüger, C.; Tsay, Y. H. *J. Organomet. Chem.* **1979**, *169*, 209. (d) Durfee, L. D.; Hill, J. E.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1990**, *9*, 75. (e) Martin, G. C.; Boncella, J. M.; Wucherer, E. J. *Organometallics* **1991**, *10*, 2804.

(21) Feng, S. G.; Templeton, J. L. *Organometallics* **1992**, *11*, 1295.

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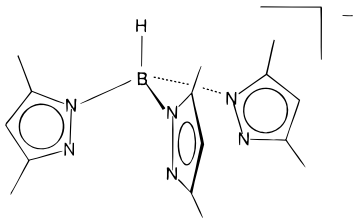
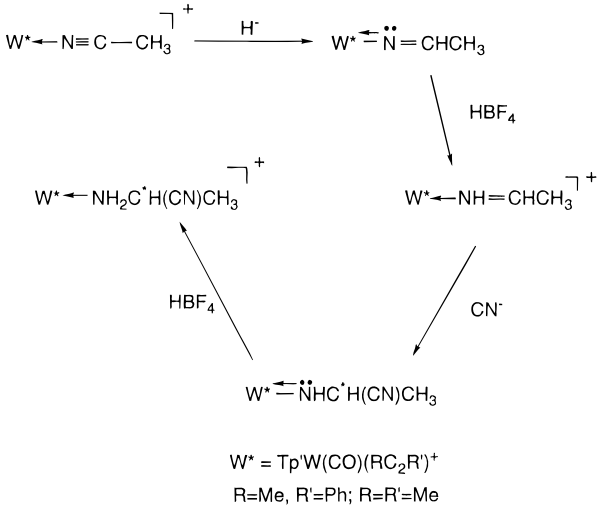
Scheme 2

Tp' = (Hydridotris-(3,5-dimethylpyrazolyl)borate)



Scheme 3



W* = Tp'W(CO)(RC$_2$R')$^+$
R=Me, R'=Ph; R=R'=Me

the original nitrile complex (eq 1).

$$W^*{\leftarrow}NH_2CH_2CH_3]^+ + HBF_4 \xrightarrow{CH_3CN} [NH_3CH_2CH_3][BF_4] + W^*{\leftarrow}N{\equiv}CCH_3]^+ \quad (1)$$

W* = Tp′W(CO)(RC$_2$R′)$^+$;
R = Me, R′ = Ph, R = R′ = Me

Resolution of a chiral tungsten amido complex has been accomplished, opening the possibility for enantioselective reduction of nitriles.[22]

In a complementary study of oxidation reactions accessible to coordinated nitrogen donor ligands, we now report coordination of benzylamine to the [Tp′W(CO)(PhC$_2$Me)]$^+$ fragment and subsequent stepwise oxidation. Isolation of key intermediates, mechanistic considerations for amido to imine conversion, and a crystal structure of the imine complex [Tp′W(CO)(PhC$_2$Me)(NH=CHPh)][BF$_4$] are the thrusts of this work.

Experimental Section

Chemicals, Reagents, and Manipulations. All reactions were performed under a dry nitrogen atmosphere with standard Schlenk manipulations. Solvents were purified as follows: methylene chloride was distilled from P_2O_5; THF and hexane were distilled from sodium metal and benzophenone. These solvents and additional solvents were purged with nitrogen prior to use. The complex [Tp′W(CO)$_2$(PhC$_2$Me)][OTf] was prepared according to literature methods.[22] All other reagents were used as obtained from commercial sources.

Equipment and Analysis. Infrared spectra were taken on a Mattson Polaris FT-IR spectrometer. One-dimensional NMR spectra were recorded on a Varian XL-400 (400 MHz) spectrometer or a Bruker WM250 instrument. Two-dimensional spectra and variable-temperature NMR spectra were recorded on a Bruker AMX-300 (300 MHz). Cyclic voltammetry was performed on a Bioanalytical Systems CV-27 instrument. Samples were dissolved in dry CH_2Cl_2 (under a N_2 atmosphere) containing 0.10 M [Et$_4$N][PF$_6$] as the supporting electrolyte. The electrode array consisted of a Ag reference electrode and platinum disk (working) and wire (auxiliary) electrodes. Elemental analyses were performed by Atlantic Microlab, Inc., Norcross, GA, or Galbraith Laboratories, Inc., Knoxville, TN.

Synthesis: Tp′(CO)(PhC$_2$Me)W(NHCH$_2$Ph) (1). In a representative synthesis, 1.86 g (2.30 mmol) of [Tp′W(CO)$_2$(PhC$_2$Me)][OTf] was refluxed in THF for 2 h. Disappearance of CO absorptions at 2048 and 1971 cm^{-1} in the IR (in THF) accompanied by the appearance of a CO stretching absorption at 1923 cm^{-1} indicated the formation of Tp′W(CO)(PhC$_2$Me)(OTf).[26] A color change from green to deep blue accompanied the formation of Tp′W(CO)(PhC$_2$Me)(OTf). Heating was continued while 0.555 mL (5.06 mmol) of benzylamine were added. After 4 h of refluxing, the solution color changed from blue to reddish-orange. The solution was cooled to room temperature before the solvent was evaporated under vacuum. The resulting orange solid was washed with methanol before it was chromatographed on alumina with methylene chloride as eluent. An orange band which came off the column was collected. Although the band appeared to be blue on the column, it turned orange upon elution. The solvent was evaporated, and the orange solid was recrystallized from methylene chloride/methanol. Orange crystals were isolated (0.94 g, 55% yield). IR (KBr): ν_{CO} = 1840 cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$, δ): 7.19 (m), 7.08 (m), 6.88 (m), 6.31 (m) (10 H, 2 C$_6$*H*$_5$); 6.89 (1 H, dd, $^3J_{HH}$ = 10.8 Hz, 5.0 Hz, N*H*CH$_2$Ph); 5.91, 5.77, 5.60 (3H, Tp′C*H*); 5.36 (1H, dd, $^2J_{HH}$ = 13.6 Hz, $^3J_{HH}$ = 10.8 Hz, NHC*H*(H)Ph), 5.22 (1 H, dd, $^2J_{HH}$ = 13.6 Hz, $^3J_{HH}$ = 5.0 Hz, NHCH(*H*)Ph), 3.10 (3 H, PhC$_2$C*H*$_3$); 2.88, 2.52, 2.40, 2.36, 1.62, 1.35 (18 H, Tp′CC*H*$_3$). ^{13}C NMR (CD$_2$Cl$_2$, δ): 237.8 ($^1J_{WC}$ = 167 Hz, *C*O); 170.5 (Ph*C*CMe); 168.2 (PhC*C*Me); 153.5, 151.5, 150.8, 145.4, 144.6, 144.5 (Tp′*C*CH$_3$); 144.5, 137.9, 128.4, 128.3, 128.1, 127.6, 126.4, 126.3 (Ph); 108.3, 107.3, 106.4 (d, $^1J_{CH}$ = 172 Hz, Tp′*C*H); 70.0 (t, $^1J_{CH}$ = 133 Hz, NH*C*H$_2$Ph), 18.4 (q, $^1J_{CH}$ = 128 Hz, PhC$_2$*C*H$_3$); 16.0, 15.7, 14.3, 12.9, 12.8 (2 peaks) (q, $^1J_{CH}$ = 127 Hz, Tp′C*C*H$_3$). Anal. Calcd for Tp′W(CO)(PhC$_2$Me)(NHCH$_2$Ph), WC$_{32}$H$_{38}$N$_7$OB: C, 52.55; H, 5.24; N, 13.41. Found: C, 52.36; H, 5.17; N, 13.37.

[Tp′(CO)(PhC$_2$Me)W(NH$_2$CH$_2$Ph)][BF$_4$] (2): To a cold (−78 °C) methylene chloride solution containing 0.145 g of **1** (0.20 mmol) were added 0.024 mL (0.20 mmol) of HBF$_4$·Me$_2$O. In about 3 min the solution turned from orange to olive green and then to deep blue. The solution was allowed to warm to room temperature, then it was stirred for 30 min. The solvent was evaporated to form a blue oil, and the oil was washed with hexanes, leaving a blue powder. Recrystallization from CH_2Cl_2/hexanes yielded deep blue crystals (0.130 g, 80% yield). IR (KBr): ν_{CO} = 1907 cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$, δ): 7.35 (m), 7.14 (m), 6.78 (m) (10 H, 2 C$_6$*H*$_5$); 6.10, 5.97, 5.79 (3 H, Tp′C*H*); 4.26, 3.27 (2 H, m, N*H*$_2$CH$_2$Ph); 4.05, 3.14 (2 H, m, NH$_2$C*H*$_2$Ph); 3.80 (3 H, PhC$_2$*C*H$_3$); 2.75, 2.58, 2.52, 2.44, 1.56, 1.32 (18 H, Tp′C-*C*H$_3$). ^{13}C NMR (CD$_2$Cl$_2$, δ): 230.3 ($^1J_{WC}$ = 149 Hz, *C*O); 215.2 (PhCCMe); 213.7 (PhC*C*Me); 153.1, 152.0, 151.0, 148.1, 148.0, 146.5 (Tp′*C*-CH$_3$): 137.7, 136.3 (ipso Ph*C*′s); 130.8, 129.9, 129.7, 129.5, 129.3, 128.1 (d, $^1J_{CH}$ = 158 Hz, Ph); 109.4, 109.3, 108.0 (d, $^1J_{CH}$ = 174 Hz, Tp′*C*H),

(22) Caldarelli, J. L.; White, P. S.; Templeton, J. L. *J. Am. Chem. Soc.* **1992**, *114*, 10097.

(23) Use of the BAr′$_4^-$ counterion to stabilize cationic complexes for chromatography on alumina has been previously observed by Dr. Julio Pérez in our laboratory.

(24) (a) Brookhart, M.; Grant, B.; Volpe, A. F., Jr. *Organometallics* **1992**, *11*, 3920. (b) Strauss, S. H. *Chem. Rev.* **1993**, *93*, 927.

(25) (a) Werner, L.; Knaup, W.; Dziallas, M. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 248. (b) Bercaw, J. E.; Davies, D. L.; Wolczanski, P. T. *Organometallics* **1986**, *5*, 443. (c) Bochmann, M.; Wilson, L. M.; Hursthouse, M. B.; Motevalli, M. *Organometallics* **1988**, *7*, 1148. (d) Simpson, S. J.; Andersen, R. A. *J. Am. Chem. Soc.* **1981**, *103*, 4063. (e) Jordan, R. F.; Bajgur, C. S.; Dasher, W. E. *Organometallics* **1987**, *6*, 1041. (f) Borkowsky, S. L.; Jordan, R. F.; Hinch, G. D. *Organometallics* **1991**, *10*, 1268. (g) Alelyunas, Y. W.; Jordan, R. F.; Echols, S. F.; Borkowsky, S. L.; Bradley, P. K. *Organometallics* **1991**, *10*, 1406.

(26) Powell, K. R.; Perez, P. J.; Luan, L.; Feng, S. G.; White, P. S.; Brookhart, M.; Templeton, J. L. *Organometallics* **1994**, *13*, 1851.

(27) Templeton, J. L. *Adv. Organomet. Chem.* **1989**, *29*, 1.

(28) Francisco, L. W.; Templeton, J. L. Unpublished work.

(29) March, J. *Advanced Organic Chemistry: Reactions, Mechanisms and Structures*; Wiley-Interscience: New York, 1992; p 21.

(30) Paz-Sandoval, M. A.; Domínguez-Durán, M. E.; Pazos-Mayen, C.; Ariza-Castolo, A.; Rosales-Hoz, M. J.; Contreras, R. *J. Organomet. Chem.* **1995**, *492 (1)*, 1.

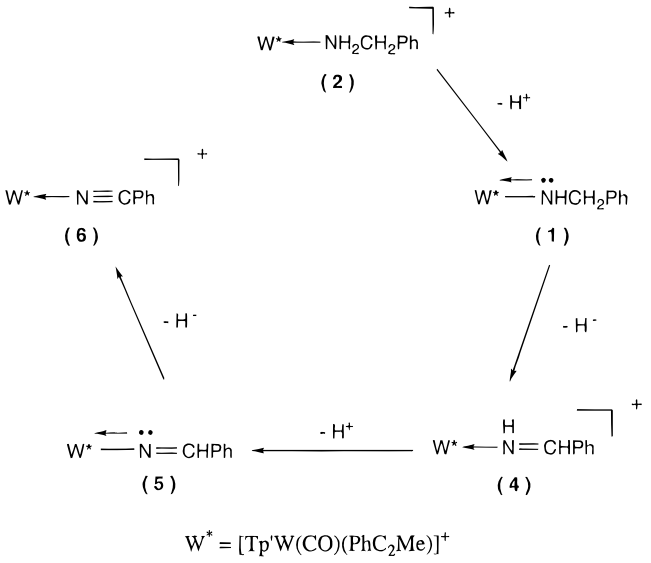
55.2 (t, $^1J_{CH}$ = 142 Hz, NH_2CH_2Ph); 23.2 (q, $^1J_{CH}$ = 129 Hz, PhCCCH_3); 16.0, 15.9, 14.3, 13.0, 12.9, 12.8 (q, $^1J_{CH}$ = 128 Hz, Tp′C-CH_3). Anal. Calcd for [Tp′(CO)(PhC_2Me)W(NH_2CH_2Ph)][BF_4]·CH_2Cl_2, $WB_2C_{33}H_{41}N_7OF_4Cl_2$: C, 43.84; H, 4.57; N, 10.84. Found: C, 43.16; H, 4.59; N, 10.69.

[Tp′(CO)(PhC_2Me)W(NH=CHPh)][BAr'_4] (3). To a cold (−78 °C) methylene chloride solution of **1** (0.275 g, 0.375 mmol) was added 0.073 g (0.375 mmol) of $AgBF_4$. The solution color changed from orange to reddish-brown to dark green over 10 min. During this time, a transient CO stretch was observed at 1890 cm^{-1}. After 1 h of stirring, the solution was green. The solution was filtered into a separate flask, leaving behind a gray precipitate (presumably Ag(s)). The solvent was evaporated leaving a green oil. The green oil was washed with hexanes, yielding a green powder. A CH_2Cl_2/Et_2O (1:1) solution of 0.40 g (0.45 mmol) of $NaBAr'_4$ ([BAr'_4] = tetrakis[3,5-bis(trifluoromethyl)phenyl]-borate) was added to a methylene chloride solution of the green powder. The solution was stirred for 2 h and filtered, leaving behind a tan precipitate. The solvent was evaporated from the filtrate. The green product was dissolved in cold (−78 °C) CH_2Cl_2 and filtered. This process was repeated. The green solid was eluted on an acidic alumina column twice using a 1:1 mixture of CH_2Cl_2/hexanes. Recrystallization from CH_2Cl_2/hexanes yielded green air stable crystals (0.236 g, 45% yield). IR (KBr): ν_{CO} = 1940 cm^{-1}. ^{1}H NMR (CD_2Cl_2, δ): 9.90 (1H, d, $^3J_{HH}$ = 21.5 Hz, N*H*=CHPh); 7.72 (broad s), 7.56 (broad s), 7.52 (m), 7.32 (m), 6.79 (m), (22H, 2 C_6H_5 and *H*'s from BAr'_4^-); 7.17 (1H, d, $^3J_{HH}$ = 21.5 Hz, NH=C*H*Ph); 6.04, 5.93, 5.81 (3H, Tp′C*H*); 3.91 (3H, PhC_2CH_3); 2.60, 2.54, 2.46, 2.41, 1.35, 1.14 (18 H, Tp′CCH_3). ^{13}C NMR (in CD_2Cl_2, δ): 227.5 (*C*O); 215.2 (Ph*C*CMe); 212.0 (Ph*C*CMe); 172.9 (d, $^1J_{CH}$ = 174 Hz, NH=*C*HPh); 162.2 (q, $^1J_{BC}$ = 48 Hz, *ipso*-Ar′$_4$); 153.8, 152.4, 151.2, 148.1, 146.7 (1:1:1:2:1, Tp′*C*CH_3); 135.9, 135.5, 131.3, 130.2, 130.1, 129.4, 128.5 (1:1:1:1:2:1:1, NH=CH(C_6H_5), MeC_2(C_6H_5)); 135.2 (broad, $^1J_{CH}$ = 156 Hz, *o*-Ar′$_4$); 129.3 (d, $^2J_{CF}$ = 36 Hz, *m*-Ar′$_4$); 125.0 (q, $^1J_{CF}$ = 264 Hz, Ar′$_4$*C*F_3); 117.9 (d, $^1J_{CH}$ = 162 Hz, *p*-Ar′$_4$); 109.6, 109.5, 108.3 (d, $^1J_{CH}$ = 174 Hz, Tp′*C*H); 23.7 (q, $^1J_{CH}$ = 125 Hz, PhC_2CH_3); 16.0, 15.7, 14.4, 13.0, 12.9, 12.8 (q, Tp′CCH_3). Anal. Calcd for [Tp′(CO)(PhC_2Me)W(NH=CHPh)][BAr'_4], $WB_2C_{64}H_{49}N_7OF_{24}$: C, 48.24; H, 3.10; N, 6.15. Found: C, 48.17; H, 3.14; N, 6.20.

[Tp′(CO)(PhC_2Me)W(NH=CHPh)][BF_4] (4). A syringe was used to slowly add 0.017 mL (0.137 mmol) of HBF_4·Me_2O to a cold (−78 °C) methylene chloride solution of Tp′(CO)(PhC_2Me)W(N=CHPh) (**5**) (*vide infra*) (0.100 g, 0.14 mmol). The color of the solution slowly changed from orange to green. The solvent was evaporated, leaving a dark green solid. The green solid was recrystallized from methylene chloride/hexanes, yielding dark green crystals (0.102 g, 91% yield). IR (KBr): ν_{CO} = 1921 cm^{-1}. ^{1}H NMR (CD_2Cl_2, δ): 11.10 (1 H, d, $^3J_{HH}$ = 20.8 Hz, N*H*CHPh); 7.45 (m), 7.29 (m), 6.86 (m) (10 H, 2 C_6H_5); 6.77 (1 H, d, $^3J_{HH}$ = 20.8 Hz, NHC*H*Ph); 6.07, 5.87, 5.81 (3 H, Tp′C*H*); 3.98 (3 H, PhC_2CH_3); 2.61, 2.55, 2.50, 2.44, 1.38, 1.15 (18 H, Tp′CH_3). ^{13}C NMR (CD_2Cl_2, δ): 227.8 ($^1J_{WC}$ = 148 Hz, *C*O); 215.6 (Ph*C*CMe); 215.5 (Ph*C*CMe); 170.6 (d, $^1J_{CH}$ = 176 Hz, NH=*C*HPh); 153.8, 153.1, 151.0, 147.6, 147.5, 146.0 (Tp′*C*CH_3); 137.1, 134.1, 132.2, 130.2, 129.9, 129.6, 129.2, 129.0 (phenyl *C*'s); 109.2, 108.0 (2:1, each a d, $^1J_{CH}$ = 174 Hz, Tp′*C*H); 23.5 (q, $^1J_{CH}$ = 130 Hz, PhC_2CH_3); 16.1, 15.7, 14.3, 13.1, 13.0, 12.9 (Tp′C*C*H_3). Anal. Calcd for [Tp′(CO)(PhC_2-Me)W(NH=CHPh)][BF_4], $WB_2C_{32}H_{37}N_7F_4O$: C, 47.04; H, 4.56; N, 12.00. Found: C, 46.53; H, 4.59; N, 11.90.

Tp′(CO)(PhC_2Me)W(N=CHPh) (5). Method A. Iodine, 0.080 g (0.32 mmol, 1.2 equiv), and an excess of KH were added to a cold (0 °C) THF solution of 0.188 g (0.26 mmol) of **1**. The solution immediately turned from orange to green. The solution slowly turned brownish-orange, then orange. The solution was warmed to room temperature, and the solvent was removed under vacuum. The dark orange solid was chromatographed on an alumina column with methylene chloride as eluent. The green band, which turned orange as it came off the column, was collected, and the solvent was evaporated yielding an orange solid. The orange solid was recrystallized from methylene chloride/hexanes (0.085 g, 45% yield). IR (KBr): ν_{CO} = 1882 cm^{-1}. ^{1}H NMR (CD_2Cl_2, δ): 7.24 (m), 7.10 (m), 6.99 (m), 6.81 (m), 6.51 (m) (10 H, 2 C_6H_5); 6.83 (1 H, N=C*H*Ph); 5.99, 5.69, 5.66 (3 H, Tp′CH_3); 3.30 (3 H, PhC_2CH_3); 2.78, 2.51, 2.43, 2.41, 1.70, 1.30 (18 H, Tp′C-CH_3). ^{13}C NMR (CD_2Cl_2, δ): 228.4 ($^1J_{WC}$ = 156 Hz, *C*O); 157.8 (Ph*C*CMe); 157.6 (Ph*C*CMe); 152.8, 152.7, 151.2, 145.0, 144.5, 144.4 (Tp′*C*-CH_3); 147.3 (d, $^1J_{CH}$ = 170 Hz, $^2J_{WC}$ = 26 Hz, N=*C*HPh); 138.6, 137.6, 128.7, 128.3, 128.2, 126.7, 126.6, 125.5 (Ph); 107.6, 107.2, 106.8 (d, $^1J_{CH}$ = 172 Hz, Tp′*C*H); 18.2 (PhC_2CH_3); 15.9, 15.5, 14.7, 13.0, 12.9, 12.8 (Tp′C-*C*H_3). Anal. Calcd for Tp′(CO)-(PhCCMe)W(N=CHPh), $WBC_{32}H_{36}N_7O$: C, 52.70; H, 4.98; N, 13.44. Found: C, 52.64; H, 4.94: N, 13.33.

Scheme 4. Reaction Sequence for Stepwise Oxidation of Benzylamine



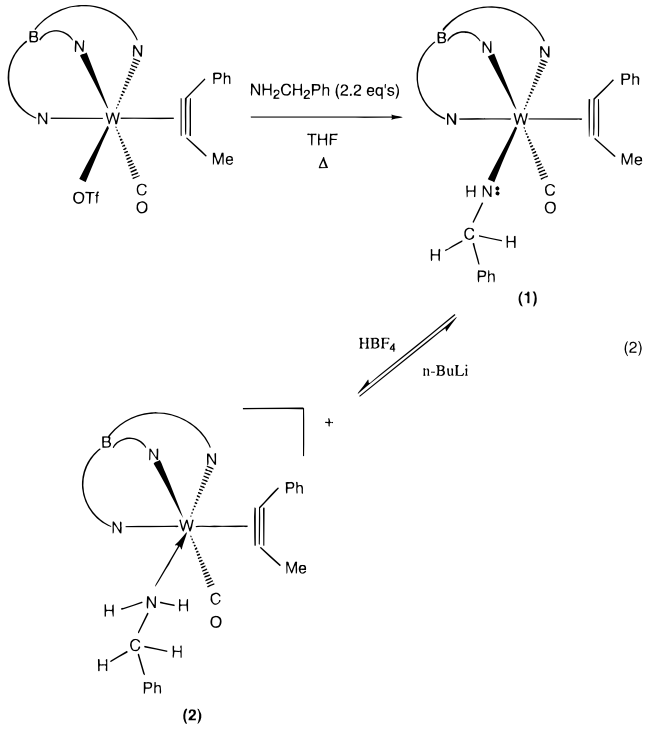
Method B. One equivalent of *n*-BuLi was syringed into a cold THF solution (−78 °C) of 0.037 g (0.045 mmol) of **4**. An immediate change in solution color from green to orange occurred. The solution was warmed to room temperature, and the solvent was evaporated. Recrystallization from CH_2Cl_2/MeOH yielded orange crystals (0.029 g, 88% yield).

[Tp′(CO)(PhC_2Me)W(NCPh)][BF_4] (6). To a cold (−78 °C) CH_2Cl_2 solution containing 0.082 g of **7** (0.112 mmol) was added 0.022 g (0.112 mmol) of $AgBF_4$. The solution color quickly changed from orange to blood red, followed by a slow conversion to blue. A gray precipitate was observed in the reaction flask (presumably Ag(s)). The solution was filtered and the solvent was removed under vacuum. The aqua-blue solid was washed with hexane and recrystallized from CH_2Cl_2/hexanes. Aqua-blue crystals were isolated (0.041 g, 45% yield). IR (KBr): ν_{CO} = 1928 cm^{-1}; ν_{CN} = 2233 cm^{-1}. ^{1}H NMR (CD_2Cl_2, δ): 7.78 (m), 7.61 (m), 7.36 (m), 6.86 (m) (10 H, 2 C_6H_5); 6.06, 5.95, 5.85 (3 H, Tp′C*H*); 3.87 (3 H, PhC_2CH_3); 2.74, 2.60, 2.58, 2.44, 1.55, 1.33 (18 H, Tp′C-CH_3). ^{13}C NMR (CD_2Cl_2, δ): 224.5 ($^1J_{WC}$ = 149 Hz, *C*O); 214.9 (Ph*C*CMe); 212.4 (Ph*C*CMe); 154.2, 153.2, 150.8, 148.1, 147.9, 146.1 (Tp′*C*-CH_3); 153.0 (N*C*Ph); 136.9, 136.3, 133.3, 131.3, 130.5, 130.1, 129.4 (2 peaks) (phenyl *C*'s); 108.9, 108.8, 108.3 (Tp′*C*H); 23.9 (PhC_2CH_3); 16.2, 16.0, 14.5, 13.0 (2 peaks), 12.8 (Tp′C-*C*H_3). Anal. Calcd for [Tp′(CO)(PhCCMe)W(NCPh)][BF_4]$-{}^1/_2CH_2Cl_2$, $WB_2C_{33.5}H_{38}N_7OF_4Cl_1$: C, 46.10; H, 4.29; N, 11.58. Found: C, 46.21; H, 4.16; N, 11.93.

Results and Discussion

Although our entry point to nitrogen donor ligand chemistry is the amido complex, reversible protonation to form the cationic amine complex provides a convenient conceptual point of departure for describing the stepwise oxidation of amine to nitrile. The reaction sequence accessible from coordinated benzylamine is summarized in Scheme 4.

Neutral Amido Complex. The amido complex Tp′W(CO)-(PhC_2Me)($NHCH_2Ph$) (**1**) was initially synthesized by reflux of a THF solution of Tp′W(CO)(PhC_2Me)(OTf) and excess NH_2-CH_2Ph (eq 2). The amido complex can also be formed by deprotonation of the cationic amine complex (**2**) with *n*-BuLi (eq 2). In both reactions formation of the amido complex is



(2)

accompanied by a color change from blue to orange. Repeated washing with methanol followed by recrystallization from CH_2Cl_2/methanol yields analytically pure orange crystals. Selected infrared and NMR data for **1** are presented in Tables 1 and 2.

The methylene protons are diastereotopic and a doublet of doubles pattern results for each as well as for the amido proton. The methylene carbon resonates as a triplet at 70.0 ppm in the ^{13}C NMR spectrum. Lone pair donation from nitrogen into the empty metal d_{xy} orbital competes with donation from the alkyne $\pi_\perp$ orbital (*vide infra*). The alkyne therefore adopts a three-electron donor role, as indicated by alkyne carbon resonances at 168 and 170 ppm.

A geometry with the NHR fragment in the same plane as the tungsten−carbonyl axis will result from nitrogen lone pair donation to the d_{xy} orbital. Two isomers are possible due to restricted rotation about the tungsten−nitrogen bond (Figure 1). One isomer places the benzyl fragment "syn" to the Tp′ ligand, while the other isomer results in the benzyl fragment "anti" to the Tp′ moiety. Two isomers due to restricted rotation about the tungsten−nitrogen bond have indeed been observed in the neutral complexes Tp′W(CO)(NHCH(R)CH_3)(R′C_2Me) (R = CN, H; R′ = Ph, Me).[21] However, only one isomer is apparent for complex **1**. Observation of only a single isomer in the NMR of **1** could be due to either (1) rapid rotation about the tungsten−nitrogen bond at room temperature or (2) one of the two rotational conformers being significantly thermodynamically favored such that the other isomer cannot be detected. Low-temperature NMR (−80 °C) did not reveal either a dynamic process or a second isomer, and given that a sizable barrier to rotation of the amido ligand is expected, it seems likely that only one isomer is present at detectable levels.

In these complexes, the metal d_{xz} and d_{yz} orbitals will overlap with the CO π^* orbitals (Figure 2). This lowers the energy of the d_{xz} and d_{yz} orbitals and breaks the degeneracy of the t_{2g} set. The four electrons of the W(II) d^4 metal center occupy these orbitals. Alignment of the alkyne parallel to the W−CO axis optimizes alkyne−metal bonding interactions. The filled d_{xz} orbital undergoes back-bonding not only with CO but also with the alkyne $\pi_{||}^*$ orbital. The alkyne can also interact with the metal $d\pi$ manifold through $\pi_\perp$ electron donation into the empty

Table 1. IR Data for Complexes **1**−**6**

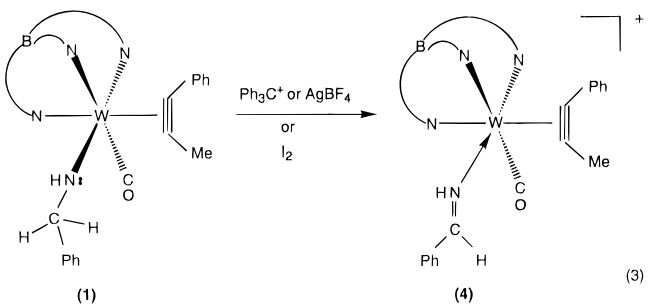
complex	ν_{CO} (cm^{-1})	other
(**1**) Tp′(CO)(PhC_2Me)W($NHCH_2Ph$)	1840	
(**2**) [Tp′(CO)(PhC_2Me)W(NH_2CH_2Ph)][BF_4]	1907	
(**3**) [Tp′(CO)(PhC_2Me)W(NH═CHPh)][BAr'_4]	1940	
(**4**) Tp′(CO)(PhC_2Me)W(NH═CHPh)][BF_4]	1921	
(**5**) Tp′(CO)(PhC_2Me)W(N═CHPh)	1882	
(**6**) [Tp′(CP)(PhC_2Me)W(NCPh)][BF_4]	1928	ν_{CN} = 2233 cm^{-1}

d_{xy} orbital. If the nitrogen has a lone pair available, it will align itself so that these electrons can also donate into the metal d_{xy} orbital. In this situation, a competition exists between the alkyne $\pi_\perp$ electrons and the lone pair on nitrogen for the empty d_{xy} orbital. Under these competitive circumstances, the alkyne can roughly be considered a "three-electron donor". If the nitrogen does not have a lone pair available, $\pi_\perp$ and d_{xy} form a simple 2-center 2-electron π bond, and the alkyne is formally a four-electron donor.

Cationic Amine Complex. Protonation of the amido complex Tp′W(CO)(PhC_2Me)($NHCH_2Ph$) (**1**) with HBF_4·Me_2O at −78 °C yields the cationic amine complex (**2**) (eq 2). Formation of the amine complex is indicated by a color change from orange to blue and a change in CO stretching frequency from 1851 to 1915 cm^{-1} in CH_2Cl_2. Recrystallization from CH_2Cl_2/hexanes yields deep-blue, air-stable crystals. Selected infrared and NMR data are presented in Tables 1 and 2.

Due to the presence of the chiral metal center, the hydrogen atoms of the NH_2CH_2Ph moiety are diastereotopic and yield four multiplets in the ^1H NMR spectrum. Each multiplet has approximate "triplet" character. A preferred confirmation with the phenyl anti to W can be envisioned (Scheme 5). In this confirmation, each hydrogen atom would be expected to have two larger coupling constants (>8 Hz) due to vicinal "trans" (dihedral angle ≈ 180°) and geminal coupling and one small coupling constant (<5 Hz) due to vicinal "cis" (dihedral angle ≈ 60°) coupling. If the two larger coupling constants are of similar magnitude, a pattern resembling a crude triplet would result. Two of the multiplets are particularly broad. A HETCOR (Heteronuclear Correlated) spectrum definitively assigned the methylene and amine proton peaks and corroborated the assumption that the amine proton signals are broadened by the quadrupolar nitrogen nucleus ($I = 1$). The carbonyl carbon resonates at 230.3 ppm with $^1J_{WC}$ = 149 Hz in the ^{13}C spectrum. The methylene carbon yielded a triplet at 55.2 ppm with $^1J_{CH}$ = 142 Hz, a coupling constant within the range expected for an sp^3 carbon. The alkyne carbons resonate at 215.2 and 213.7 ppm, compatible with a four-electron donor alkyne description.

Cationic Imine Complex. Hydride removal from the methylene unit of neutral amido complex **1** with various reagents ($AgBF_4$, I_2, or [Ph_3C][PF_6]) in cold CH_2Cl_2 yields the cationic imine complexes with different counterions (**4**) (eq 3). A change



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in CO stretching frequency from 1851 to 1930 cm^{-1} (when

Table 2. Selected NMR Data for Complexes **1**−**3, 5,** and **6**

	^{1}H NMR, ppm		^{13}C NMR, ppm		
complex Tp′(CO)(PhC$_2$Me)W(NH$_m$CH$_n$Ph)	N*H*$_{(m)}$	C*H*$_{(n)}$	NH$_{(m)}$*C*H$_{(n)}$Ph	Ph*C*$_2$Me	*C*O
(**1**) Tp′(CO)(PhC$_2$Me)W(NHCH$_2$Ph)	6.89	5.36 (d of d)	70.0 (t)	170.5 (≡*C*Ph)	237.8
$m = 1$; $n = 2$	(d of d)	$J_{HH} = 13.6, 10.8$	$^1J_{CH} = 133$	168.2 (≡*C*Me)	$^1J_{WC} = 167$
	$^3J_{HH} = 10.8, 5.0$	5.22 (d of d)			
		$J_{HH} = 13.6, 5.0$			
(**2**) [Tp′(CO)(PhC$_2$Me)W(NH$_2$CH$_2$Ph)][BF$_4$]	4.26, 3.27 (m)	4.05, 3.14 (m)	55.2 (t)	215.2 (≡*C*Ph)	230.3
$m = 2$; $n = 2$			$^1J_{CH} = 142$	213.7 (≡*C*Me)	$^1J_{WC} = 149$
(**3**) [Tp′(CO)(PhC$_2$Me)W(NH═CHPh)][BAr′$_4$]	9.90 (d)	7.17 (d)	172.9 (d)	215.2 (≡*C*Ph)	227.5
$m = 1$; $n = 1$	$^3J_{HH} = 21.5$	$^3J_{HH} = 21.5$	$^1J_{CH} = 174$	212.0 (≡*C*Me)	
(**5**) Tp′(CO)(PhC$_2$Me)W(N═CHPh)		6.83	147.3 (d)	157.8 (≡*C*Ph)	228.4
$m = 0$; $n = 1$			$^1J_{CH} = 170$	157.6 (≡*C*Me)	$^1J_{WC} = 156$
			$^2J_{WC} = 26$		
(**6**) [Tp′(CO)(PhC$_2$Me)W(NCPh)][BF$_4$]			153.0	214.9 (≡*C*Ph)	224.5
$m = 0$; $n = 0$				212.4 (≡*C*Me)	$^1J_{WC} = 149$

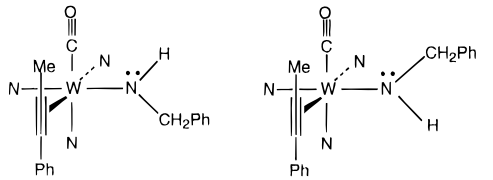


Figure 1. Two isomers due to restricted rotation about the W−N bond for complex **1**.

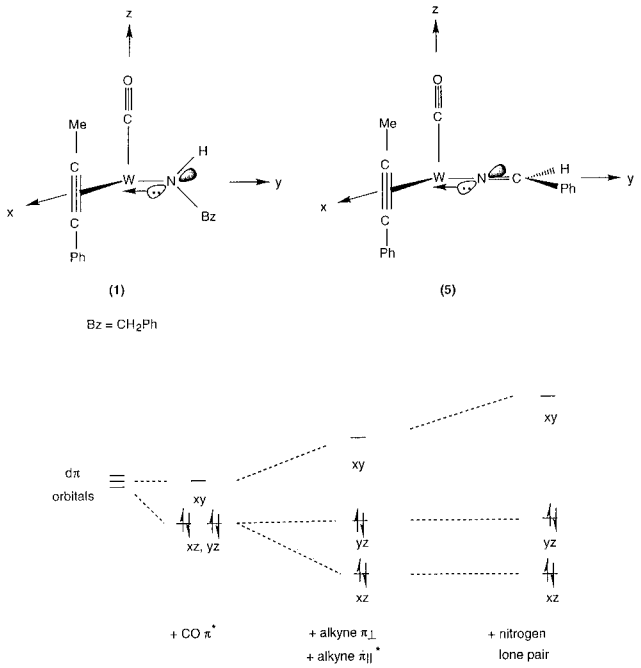
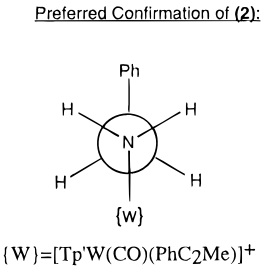


Figure 2. Qualitative molecular orbital scheme for dπ-ligand interactions.

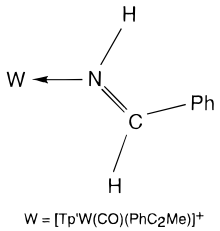
$AgBF_4$ is used) and a change in solution color from orange to green accompany formation of the imine product. Selected infrared and NMR data are presented in Tables 1 and 2.

Upon reaction of amido complex **1** with $AgBF_4$, formation of amine complex **2** accompanies formation of imine complex **4**. Efforts to separate these two complexes by standard techniques (i.e., recrystallization, solvent extraction) failed. Counterion metathesis (BAr'_4^- for BF_4^-) was achieved by reaction of **4** and **2** with $NaBAr'_4$;[23] the use of the BAr'_4 counterion to stabilize cationic complexes is well-known.[24] Exchange of BAr'_4 for BF_4^- resulted in a surprising increase in CO stretching frequency from 1921 to 1940 cm^{-1}. The complex [Tp′W(CO)(PhC$_2$Me)(NH═CHPh)][BAr′$_4$] (**3**) was

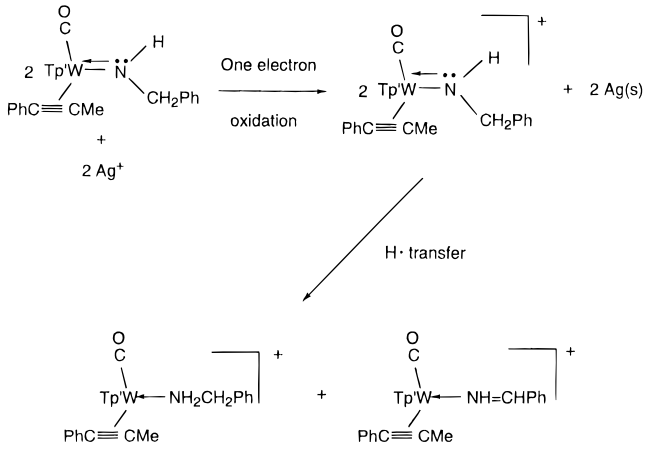
Scheme 5



Scheme 6. *E* Isomer for Complex **4**



Scheme 7



separated from the amine complex [Tp′W(CO)(PhC$_2$Me)(NH$_2$CH$_2$Ph)][BAr′$_4$] by chromatography on an acidic alumina column.

Formation of the imine complex results in the return of the alkyne to a four-electron donor role, as indicated by resonances at 215.2 and 212.0 ppm for the alkyne carbons in ^{13}C NMR. Only one isomer is observed by NMR. A vicinal coupling constant of 21.5 Hz across the C═N bond points to formation of the E isomer (Scheme 6). The imine carbon resonates as a doublet at 172.9 ppm with $^1J_{CH} = 174$ Hz, consistent with an sp^2 hybridized carbon center.

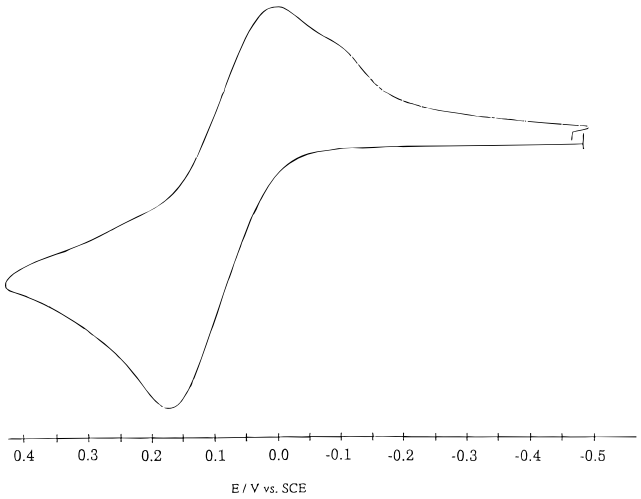


Figure 3. Cyclic voltammogram of **1** in CH_2Cl_2 containing 0.1 M $[Bu^nN][PF_6]$.

Table 3. Reversibility of Oxidation of the Amido Complex (**1**)

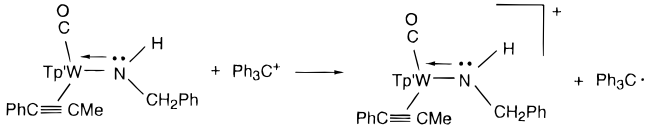
scan rate, mV/s	i_c/i_a
475	0.85
100	0.51
25	0.47

Each of the reactions to form imine products also results in formation of the amine complex $[Tp'(CO)(PhC_2Me)W(NH_2CH_2Ph)][X]$. Studies of the mechanism of these reactions to explain formation of both imine and amine complexes were not definitive, but they provide a basis for cautious speculation.

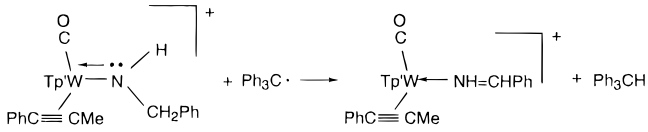
(A) Oxidation with $AgBF_4$: Observation of a gray precipitate upon treatment of **1** with $AgBF_4$ indicates that a one-electron reduction of Ag^+ to Ag(s) is occurring. Possibly an initial oxidation at the metal center takes place, as has been previously reported in oxidation of amines bound to metal fragments.[31−34] Reduction of silver cation couples with the observation of an intermediate species possessing an IR CO absorption at 1890 cm^{-1} to suggest that a reasonable initial step is a one-electron oxidation of **1**. If formation of the radical cation $[Tp'(CO)(PhC_2Me)W(NHCH_2Ph)]^{\bullet+}$ were followed by $H^\bullet$ transfer between two of these radical species, the result would be formation of the corresponding imine and amine complexes (Scheme 7).

The cyclic voltammogram of amido complex **1** shows a quasireversible oxidation ($E_{1/2}$ = 0.11 V vs SCE, ΔE_p = 0.18 V at 475 mV/s) (Figure 3). The reversibility of the oxidation is dependent on scan rate (Table 3). As the scan rate is decreased, the reversibility correspondingly decreases, and the i_c/i_a ratio decreases. This dependence on scan rate would be expected if the oxidized complex undergoes a chemical reaction on the electrochemical time scale.

(B) Oxidation with $[Ph_3C][PF_6]$: Treatment of **1** with $[Ph_3C][PF_6]$ results in formation of imine and amine complexes in a 7:3 ratio. A possible explanation for this result is an initial oxidation of **1** by Ph_3C^+ similar to that shown in eq 4. Oxidation of the metal complex by Ph_3C^+ to form $Ph_3C^\bullet$ is reminiscent of the proposed mechanism of hydride removal from $Cp_2W(CH_3)_2$ with Ph_3C^+.[35] At this point, the disproportionation reaction depicted in Scheme 7 could occur, resulting in formation of imine and amine complexes, or, $Ph_3C^\bullet$ could abstract $H^\bullet$ from $[Tp'(CO)(PhC_2Me)W(NHCH_2Ph)]^{\bullet+}$ to yield imine complex **4** with PF_6^- as the counterion (eq 5). If these competitive pathways occurred on approximately the same time scale, an imine:amine ratio >1 would be expected.



(4)



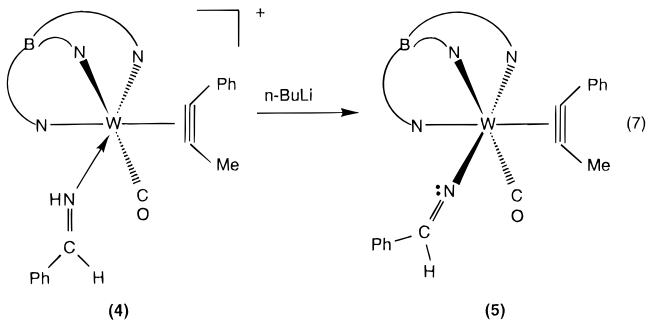
(5)

If an excess of $Ph_3C^\bullet$ existed in solution, predominant formation of imine complex would be expected. A reaction was performed in which a solution of **1** was dripped into a solution of 6 equiv of $[Ph_3C][PF_6]$ and 5 equiv of Cp_2Fe. Reduction of $[Ph_3C][PF_6]$ by one electron from Cp_2Fe should form an excess of $Ph_3C^\bullet$ in solution (eq 6). When this reaction was performed, a blue solid was isolated that exhibited electrochemical features consistent with $[Cp_2Fe][PF_6]$. In addition, a green solid was isolated that, by NMR, showed formation of the imine complex without formation of the amine complex.

$$6[Ph_3C][PF_6] + 5Cp_2Fe \longrightarrow 5[Cp_2Fe][PF_6] + 5Ph_3C\cdot + [Ph_3C][PF_6] \quad (6)$$

(C) Oxidation with I_2: Treatment of complex **1** with 1.5 equiv of I_2 results in formation of the corresponding imine and amine complexes in approximately a 1:1 ratio. A possible explanation for this reaction is formation of HI by net hydride abstraction with I^+ regardless of the mechanistic details (Scheme 8). HI could then protonate remaining **1** in solution yielding the cationic amine complex.

Neutral Azavinylidene Complex. Addition of n-BuLi to a cold (−78 °C) THF solution of the cationic imine complex $[Tp'(CO)(PhC_2Me)W(NH{=}CHPh)][BF_4]$ (**4**) results in deprotonation of the imine at nitrogen as neutral azavinylidene complex **5** forms (eq 7). A 40-cm^{-1} drop in CO stretching



(4) (5) (7)

frequency is consistent with transformation of a cationic complex to a neutral complex. A solution color change from green to orange accompanies formation of the neutral complex. Purification by chromatography on alumina followed by recrystallization from CH_2Cl_2/hexanes (or MeOH) results in isolation of orange air-stable crystals. Selected infrared and NMR data are presented in Tables 1 and 2.

Isomers could result for complex **5** due to restricted alkyne rotation or hindered rotation about the tungsten−nitrogen bond

(31) Ridd, M. J.; Keene, F. R. *J. Am. Chem. Soc.* **1981**, *103*, 5733.
(32) Hipp, C. J.; Lindroy, L. F.; Busch, D. H. *Inorg. Chem.* **1972**, *11 (9)*, 1988.
(33) Maruthamuthu, P.; Patterson, L. K.; Ferraudi, G. *Inorg. Chem.* **1978**, *17 (11)*, 3157.
(34) Jacobi, M.; Meyersteín, D.; Lilie, J. *Inorg. Chem.* **1979**, *18 (2)*, 429.
(35) Hayes, J. C.; Cooper, N. J. *J. Am. Chem. Soc.* **1982**, *104*, 5570.

Scheme 8

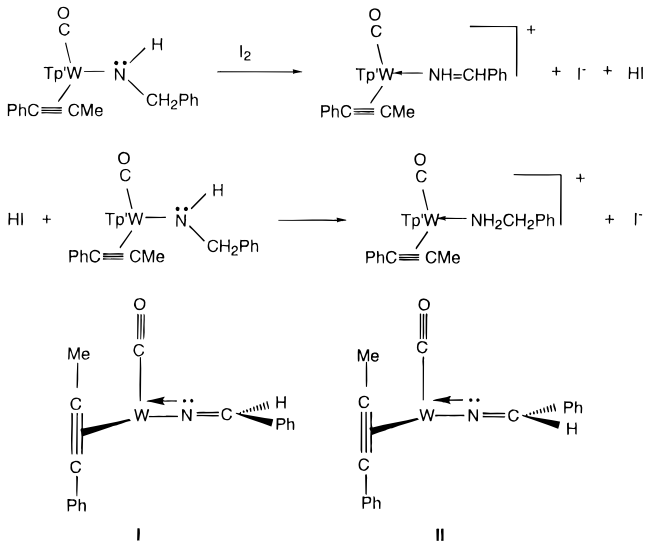
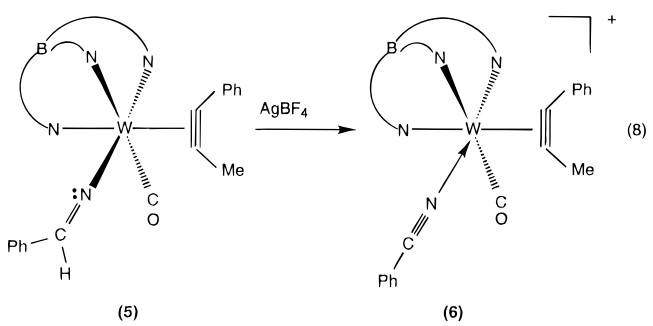


Figure 4. Two azavinylidene isomers due to restricted rotation about the W−N bond.

(Figure 4). For Tp′W(CO)(RC_2R')(N═$CHCH_3$) (R = R′ = Me; R = Me, R′ = Ph) complexes two isomers resulted from restricted rotation around the tungsten nitrogen bond.[21] In contrast, only one isomer is observed in the room temperature NMR of complex **5**. As with amido complex **1**, low-temperature NMR (−80 °C) did not result in the observation of a second isomer. The azavinylidene hydrogen (N═C*H*Ph) is obscured in the phenyl region when CD_2Cl_2 is used as solvent. Use of deuterated benzene (C_6D_6) as solvent allows the recondite azavinylidene hydrogen to be observed as a singlet at 4.25 ppm. The alkyne adopts a three-electron donor role as the alkyne carbons resonate at 157.8 and 157.6 ppm. The azavinylidene carbon yields a ^{13}C peak at 147.2 ppm ($^2J_{WC}$ = 26 Hz), and the carbonyl carbon resonates at 228.4 ppm ($^1J_{WC}$ = 156 Hz).

Donation to the metal from the lone pair on the nitrogen would form an sp-hybridized nitrogen atom. We assume that sufficient donation takes place to produce a nearly linear azavinylidene moiety, as has been previously observed with azavinylidenes.[25] Observation of tungsten−azavinylidene carbon coupling of 26 Hz supports the assumption that the azavinylidene backbone will approach linearity.[26] Donation from the nitrogen lone pair into the empty metal d_{xy} orbital would place the plane of the N═CHPh moiety perpendicular to the W−CO axis.

Cationic Nitrile Complex. Addition of 1 equiv of $AgBF_4$ to a cold (−78 °C) CH_2Cl_2 solution of the neutral azavinylidene complex Tp′W(CO)(PhC_2Me)(N═CHPh) (**5**) results in formation of the cationic nitrile complex [Tp′(CO)(PhC_2Me)W(NCPh)][BF_4] (**6**) (eq 8). A slow solution color change from



orange to blue accompanies formation of the cationic nitrile complex. Also, formation of the cationic product results in an increase in CO stretching frequency from 1896 to 1940 cm^{-1}. The nitrile CN stretch is observed at 2233 cm^{-1}. Recrystallization from CH_2Cl_2/hexanes gives aqua-blue crystals. Selected infrared and NMR data are presented in Tables 1 and 2.

Assignment of the ^1H NMR is unambiguous. ^{13}C NMR shows the nitrile carbon at 153.0 ppm. The alkyne carbons resonate at 214.9 and 212.4 ppm (four-electron donor) while the carbonyl carbon is observed at 224.5 ppm ($^1J_{WC}$ = 149 Hz).

Crystal Structure of [Tp′W(CO)(PhC_2Me)(NH═CHPh)][BF_4]. A single crystal X-ray diffraction study of [Tp′W(CO)(PhC_2Me)(NH═CHPh)][BF_4] (**4**) was carried out. Figure 5 shows an ORTEP diagram of **4**. Crystallographic data and collection parameters are given in Table 4. Table 5 presents selected bond distances and angles. The alkyne fragment lies parallel to the metal carbonyl axis, a feature typical of group VI d^4 alkyne complexes.[27] The W−N bond distance of 2.135(6) Å lies at the short end of dative tungsten−nitrogen single bond distances.[19a,22,28] The N═C bond distance of 1.285(10) Å is typical for a carbon−nitrogen double bond.[29] This value

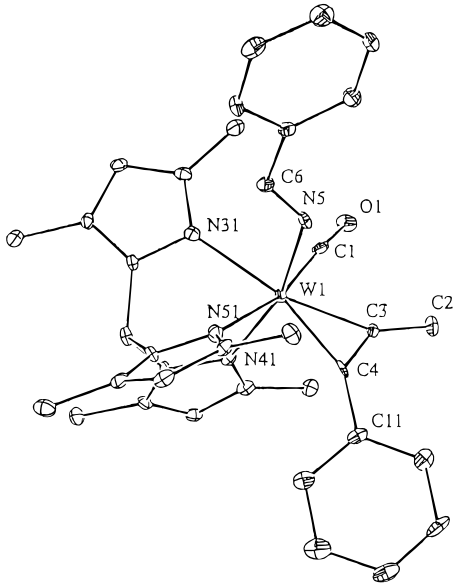


Figure 5. ORTEP of [Tp′W(CO)(PhC_2Me)(NH═CHPh)][BF_4] (**4**).

Table 4. Crystallographic Data for [Tp′W(CO)(PhC_2Me)(NH═CHPh)][BF_4] (**4**)

formula	$WC_{32}H_{37}B_2N_7OF_4$
mol wt	817.15
cryst syst	monoclinic
space group	$P2_1/c$
a, Å	13.790(3)
b, Å	13.225(3)
c, Å	19.150(4)
β, deg	108.769(1)
V, Å^3	3306.8(13)
Z	4
D_{calc}, g cm^{-3}	1.641
F(000)	1620.24
cryst dimens, mm	0.35 × 0.35 × 0.30
temp, °C	20
radiation,	Mo Kα (0.71073)
2*θ* range, deg	2*θ* < 46
μ, mm^{-1}	3.63
scan mode	*ω*
total no. of data	4591
total no. of unique data	4578
no. of obs data ($I > 2.5\sigma(I)$)	3653
R_f	0.035
R_w	0.044
GoF	1.54

Table 5. Selected Bond Distances and Bond Angles for [Tp′W(CO)(PhC_2Me)(NH═CHPh)][BF_4] (**4**)

Bond Distances (Å)			
W(1)−C(1)	1.953(8)	C(1)−O(1)	1.169(10)
W(1)−C(3)	2.050(7)	C(3)−C(4)	1.308(10)
W(1)−C(4)	1.998(7)	C(2)−C(3)	1.471(10)
W(1)−N(5)	2.135(6)	C(4)−C(11)	1.480(10)
W(1)−N(31)	2.252(6)	C(6)−C(21)	1.458(11)
W(1)−N(41)	2.159(6)		
W(1)−N(51)	2.217(6)		

Bond Angles (deg)			
C(1)−W(1)−C(3)	69.8(3)	N(5)−W(1)−N(31)	84.03(22)
C(1)−W(1)−C(4)	107.2(3)	N(5)−W(1)−N(41)	162.81(22)
C(1)−W(1)−N(5)	91.7(3)	N(5)−W(1)−N(51)	82.88(22)
C(1)−W(1)−N(31)	86.1(3)	N(31)−W(1)−N(41)	80.58(21)
C(1)−W(1)−N(41)	94.8(3)	N(31)−W(1)−N(51)	81.03(21)
C(1)−W(1)−N(51)	166.5(3)	N(41)−W(1)−N(51)	87.18(21)
C(3)−W(1)−C(4)	37.7(3)	W(1)−C(1)−O(1)	175.8(6)
C(3)−W(1)−N(5)	98.77(25)	W(1)−C(3)−C(2)	150.3(6)
C(3)−W(1)−N(31)	155.8(37)	W(1)−C(3)−C(4)	69.0(4)
C(3)−W(1)−N(41)	98.41(24)	C(2)−C(3)−C(4)	140.6(7)
C(3)−W(1)−N(51)	123.2(3)	W(1)−C(4)−C(3)	73.3(4)
C(4)−W(1)−N(5)	102.4(3)	W(1)−C(4)−C(11)	150.6(5)
C(4)−W(1)−N(31)	164.86(24)	C(3)−C(4)−C(11)	135.2(7)
C(4)−W(1)−N(41)	90.81(25)	W(1)−N(5)−C(6)	129.7(5)
C(4)−W(1)−N(51)	86.16(25)	N(5)−C(6)−C(21)	126.7(7)

is similar to the N═C bond length of 1.275(5) Å reported by Gladysz for the complex [(η^5-C_5H_5)Re(NO)(PPh_3)(N(Me)═C(H)(Ph))][OTf]. The W(1)−N(5)−C(6) bond angle of 129.7° is surprisingly large for an sp^2-hybridized N atom. The N(5)−C(6)−C(21) angle of 126.7° is also unexpectedly high for bond angles about a carbon−nitrogen double bond. It should be noted that reported M−N−C bond angles in imine complexes vary considerably.[19a,28,30] A large W(1)−N(5)−C(6) bond angle may result from steric crowding around the metal as the bulky Tp′ ligand increases the bond angle to relieve steric strain with the phenyl ring on the imine ligand.

Summary

A stepwise reduction of acetonitrile in [Tp′(CO)(RC_2R')W($NCCH_3$)]$^+$ (R = R′ = Me; R = Me, R′ = Ph) has previously been accomplished.[21] The reverse reaction, stepwise oxidation of an amine, proved more challenging to realize. The oxidation was accomplished by the sequential proton and net hydride abstractions.

The flexibility of the alkyne $\pi_\perp$ electrons allows the alkyne to fluctuate between serving as a three-electron and four-electron donor. This feature helps to stabilize metal complexes formed along the reaction path. In the complexes in which the nitrogen lone pair has been protonated (**2, 3,** and **6**), the alkyne adopts a four-electron donor role (Table 6). At the amido (**1**) and azavinylidene (**5**) stages, the ability of the alkyne to assume a three-electron donor role allows for electron donation from the nitrogen lone pair with π character, thus stabilizing the amido and azavinylidene moieties. Oxidation of the benzylamine ligand results in an overall removal of electron density, as is evidenced by the increase in CO stretching frequency (Table 1). Isolation of intermediates in the amine oxidation process provides a systematic understanding of this net four-electron oxidation.

Table 6. ^{13}C NMR Data for **1**, **2**, **3**, **5**, and **6**

complex	alkyne ^{13}C NMR (δ)
[Tp′(CO)(PhC_2Me)W(NH_2CH_2Ph)][BF_4] (**2**)	215.2, 213.7
[Tp′(CO)(PhC_2Me)W($NHCH_2Ph$)] (**1**)	170.5, 168.2
[Tp′(CO)(PhC_2Me)W(NH═CHPh)][BAr'_4] (**3**)	215.2, 212.0
[Tp′(CO)(PhC_2Me)W(N═CHPh)] (**5**)	157.8, 157.6
[Tp′(CO)(PhC_2Me)W(N≡CPh)][BF_4] (**6**)	214.9, 212.4

Acknowledgment. We thank the National Science Foundation (Grant No. CHE9208207) for generous support of this research.

Supporting Information Available: Figures showing the structures and tables of anisotropic temperature factors, complete bond distances and angles, and atomic positional parameter for **4** and experimental procedures for the preparation of cationic imine complexes via reaction of amido **1** with $AgBF_4$, [Ph_3C][PF_6], or I_2 (9 pages total). See any current masthead page for ordering and Internet access instructions.

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