Amine-Induced Coupling of Carbonyl and Nitrile Ligands in Tungsten(II) Complexes

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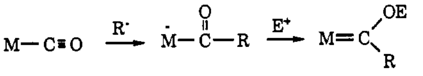
Reaction of $[Tp'(CO)_3W(N{\equiv}CMe)][BF_4]$ (**1**), an intermediate formed in situ from $Tp'W(CO)_3I$ and $AgBF_4$ in acetonitrile, with ammonia or *n*-butylamine generates neutral complexes of the type $Tp'(CO)_2W{-}C({=}O){-}N(R){-}C(Me){=}N(H)$ (R = H (**2**), *n*-butyl (**3**)). Protonation of these heteroatom metallacycle complexes occurs at the acyl oxygen atom to produce cationic metallacycle hydroxycarbene complexes, $[Tp'(CO)_2W{=}C(OH){-}N(R){-}C(Me){=}N(H)][BF_4]$ (R = H (**4**), *n*-butyl (**5**)). NMR spectra and a single crystal X-ray structure indicate that the five-membered ring is planar and effectively lies in the molecular mirror plane with the carbene carbon adjacent to the two terminal carbonyl ligands. Methylation of the metallacycle acyl complexes at the acyl oxygen produces analogous cationic metallacycle methoxycarbene complexes of the type $[Tp'(CO)_2W{=}C(OMe){-}N(R){-}C(Me){=}N(H)][CF_3SO_3]$ (R = H (**6**), *n*-butyl (**7**)). Reaction of the $[Tp'(CO)_3W(N{\equiv}CMe)][BF_4]$ intermediate with the bulky *tert*-butylamine nucleophile results in formation of an unusual amido complex, $Tp'(CO)_2W{-}N{-}C({=}CH_2){-}N(Bu^t){-}C({=}O)$ (**8**), with the original nitrile nitrogen now three-coordinate and bound to the metal and both carbons of the four-membered ring. Donation of the lone pair of electrons on the nitrogen of the amido ligand to the tungsten center is reflected by the low IR stretching frequencies of the carbonyl ligands and their downfield carbon resonance in the ^{13}C NMR. NMR spectra and an X-ray structure indicate that the planar four-membered ring of the amido ligand lies on the molecular mirror plane.

Introduction

Coordination of organic molecules such as carbon monoxide and nitriles to Lewis acidic transition metal centers can activate these ligands toward nucleophilic attack.[1] Reduction of a metal-bound carbonyl group by successive nucleophilic addition at carbon followed by electrophilic addition at the oxygen is a common route to Fischer carbene complexes (eq 1).[2] One example is provided by the tris(pyrazolyl)borate tungsten(II) system $[Tp'(CO)_2W(PhC{\equiv}CMe)]^+$ which can form acyl complexes by addition of nucleophiles to a carbonyl ligand. Formation of cationic Fischer carbenes of the type $[Tp'(CO)(PhC{\equiv}CMe)W{=}C(OE)R]^+$ can then result from electrophilic addition to the η^1-acyl complexes.[3]



$$M{-}C{\equiv}O \xrightarrow{R^-} M{-}\overset{\overset{O}{\|}}{\underset{\cdot}{C}}{-}R \xrightarrow{E^+} M{=}C\begin{smallmatrix}OE\\R\end{smallmatrix} \quad (1)$$

Metal-bound nitriles are activated toward nucleophilic attack at the α-carbon of the nitrile ligand.[4-8] We recently reported stepwise reduction of acetonitrile to chiral amino nitriles, and the chiral $Tp'(CO)(RC_2Me)W$ (R = Me, Ph) moiety provided excellent stereocontrol of the addition reactions (Scheme 1).[7] We have also reported reactions of these tungsten(II) nitriles with amines to generate the corresponding amidines (eq 2).[8] This one step addition of

$$[Tp'(CO)(PhC{\equiv}CR)W{\leftarrow}N{\equiv}CR']^+ + H_2NR'' \rightarrow [Tp'(CO)(PhC{\equiv}CR)W{\leftarrow}NH{=}CR'(NHR'')]^+ \quad (2)$$

the H-NHR reagent across the nitrile triple bond is

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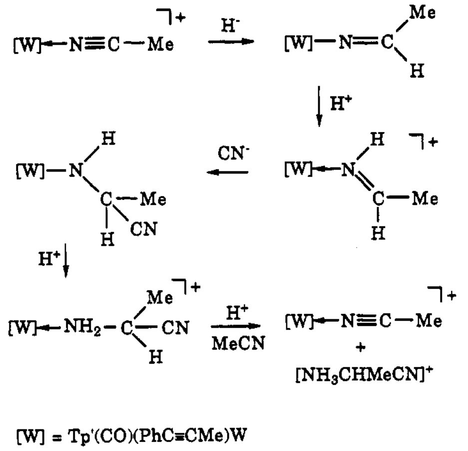
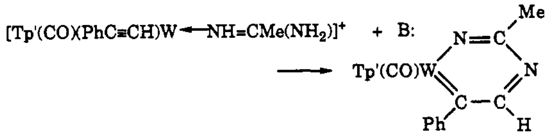
Scheme 1

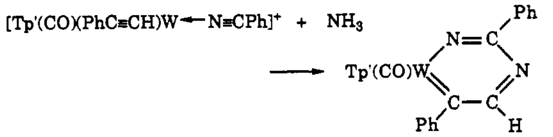


attractive and contrasts with the earlier stepwise nucleophile/electrophile sequence.

Aromatic metallacycles constitute an intriguing class of compounds.[9-11] The introduction of heteroatoms in addition to the metal into the ring system complicates the assessment of aromaticity, but the metallafuran ring has some properties which are compatible with an aromatic contribution.[12] Likewise sulfur incorporation can occur with retention of delocalization.[13] Regardless, the aromaticity of organometallic species appears to be relatively small as measured by the molecular hardness criterion.[14] Certain metallabenzenes possess strong aromaticity, and (η^6-metallabenzene)metal complexes have been reported in molybdabenzene[15a] and iridabenzene[15b] systems where the metallabenzene fragments bond to a Mo(CO)$_3$ moiety. We have previously reported formation of six-membered metallaheterocycles from base-induced coupling reactions in a terminal alkyne system (eqs 3 and 4).[8]



(3)



(4)

This paper presents a study of reactions of cationic nitrile complexes with amines in the [Tp′(CO)$_3$W(N≡CMe)]$^+$ system. The metallacyclic products we observe reflect activation of both nitrile and carbonyl ligands toward nucleophilic attack, and some of the metallacyclic products can be considered aromatic. We now report (1) formation of five-membered metallacycles from amine-induced coupling of the coordinated nitrile and carbonyl ligands; (2) formation of cationic five-membered pseudoaromatic metallacycles from addition of an electrophile to the neutral metallacycles; (3) a crystal structure of a cationic metallohydroxycarbene complex, [Tp′(CO)$_2$W=C(OH)—N(Bu^n)—C(Me)=N(H)][CF$_3$SO$_3$]; (4) formation of an unusual amido complex, Tp′(CO)$_2$W—N—C(=CH$_2$)—N-(Bu^t)—C(=O), from the reaction of [Tp′(CO)$_3$W(N≡CMe)][BF$_4$] with *tert*-butylamine as the nucleophile; and (5) a crystal structure of Tp′(CO)$_2$W—N—C(—CH$_2$)—N-(Bu^t)—C(=O).

Table 1. Crystallographic Data Collection Parameters

	5 (CH$_2$Cl$_2$)	8
molecular formula	WC$_{25}$H$_{38}$B$_2$F$_4$N$_8$O$_3$Cl$_2$	WC$_{24}$H$_{33}$BN$_8$O$_3$
fw	850.99	676.23
cryst dimens, mm	0.40 × 0.30 × 0.20	0.30 × 0.30 × 0.35
space group	$P2_1$	$P2_1/n$
cell param		
a, Å	10.31(1)	11.724(5)
b, Å	16.404(4)	14.061(6)
c, Å	10.989(4)	16.586(5)
β, deg	116.11(5)	97.76(3)
vol, Å^3	1669(2)	2709(2)
Z	2	4
density calcd, g/cm^3	1.694	1.658
Collection and Refinement Parameters		
radiation (wavelength, Å)	Mo Kα (0.709 30)	Mo Kα (0.709 30)
monochromator	graphite	graphite
linear abs coeff, cm^{-1}	37.6	43.9
scan type	θ/2θ	θ/2θ
2θ limit, deg	50	45
quadrant collected	±*h*, ±*k*, ±*l*	±*h*, ±*k*, ±*l*
total no. reflns	3035	3548
data with $I \geq 2.5\sigma(I)$	2413	2939
R, %	6.3	7.4
R_w, %	7.5	10.2
GOF	2.42	2.87
no. of params	405	335
largest param shift (shift/error ratio)	0.09	0.036

Experimental Section

General Methods. Manipulations involving air sensitive reagents were performed under a dry nitrogen atmosphere with standard Schlenk techniques. Solvents were purified as follows: methylene chloride was distilled from P$_2$O$_5$; Et$_2$O, THF, and hexanes were distilled from potassium benzophenone ketyl; acetonitrile was distilled from CaH$_2$; MeOH was dried over molecular sieves; other solvents were purged with N$_2$ prior to use. Reagents were used as obtained from commercial sources. Tp′(CO)$_3$WI was prepared according to literature methods.[16]

Infrared spectra were recorded on a Mattson Polaris FT IR spectrometer. NMR spectra were recorded on a Varian XL-400 (400-MHz) spectrometer. Elemental analyses were performed by Oneida Research Services Inc., Whitesboro, NY.

Syntheses. [Tp′(CO)$_3$W(N≡CMe)][BF$_4$] (1). This complex is prepared in situ for use as a reagent, and it has only been characterized by infrared spectroscopy. A stoichiometric amount of AgBF$_4$ (0.58 g, 2.9 mmol) was added to a dark red MeCN solution (30 mL) containing Tp′(CO)$_3$WI (2.0 g, 2.9 mmol; ν_{CO} =

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2020, 1921 (br) cm^{-1}) under a nitrogen atmosphere at 0 °C. After stirring for 25 min, the solution was yellow-orange with a gray precipitate. The resulting solution was filtered to another flask for use as a reagent. Efforts to isolate a tractable solid containing the Tp′(CO)$_3$W(N≡CMe)$^+$ cation have been unsuccessful. IR (MeCN): ν_{CO} = 2045, 1956 (b) cm^{-1}.

Tp′(CO)$_2$W—C(=O)—N(H)—C(Me)=N(H) (2). Ammonia gas was bubbled through a solution of 1 in 30 mL of acetonitrile (see above) at 0 °C, resulting in a color change to red and a shift in infrared CO stretching frequencies to lower wavenumbers (1938, 1835 cm^{-1}). After 10 min the excess ammonia was removed by evacuation, and then the acetonitrile solvent was removed. The solid residue was dissolved in CH$_2$Cl$_2$ and then chromatographed with MeOH/CH$_2$Cl$_2$ as the eluent. A yellow band was collected, and the solvents were removed. The oily residue was recrystallized from CH$_2$Cl$_2$/hexanes to yield yellow crystals of **2** (0.90 g, 44% based on Tp′(CO)$_3$WI). IR (KBr, cm^{-1}): ν_{BH} = 2546; ν_{CO} = 1938, 1834; $\nu_{N=CN}$ = 1619; $\nu_{C=N(Tp')}$ = 1543. ^{1}H NMR (CDCl$_3$, δ): 11.74 (b, C(=O)—N(*H*)—C(Me)), 7.13 (b, C(Me)=N(*H*)—W), 5.87, 5.82 (1:2, Tp′C*H*), 2.49, 2.45, 2.35, 1.96 (3:3:9:6, N(H)—C(*Me*)=N(H), Tp′CC*H*$_3$). ^{13}C NMR (CD$_2$Cl$_2$, δ): 239.5 ($^1J_{WC}$ = 153 Hz, 2*C*O), 225.1 ($^1J_{WC}$ = 30 Hz, W—*C*(=O)—N(H)), 158.6 (N(H)—*C*(Me)=N(H)), 152.7, 151.4, 145.0, 144.0 (1:2:1:2, Tp′*C*CH$_3$), 107.3, 106.7 (1:2, Tp′*C*H), 16.8 (N(H)—C(*Me*)=N(H)), 16.2, 14.6, 13.1, 12.5 (1:2:1:2, Tp′C*C*H$_3$). Anal. Calcd for **2**·CH$_2$Cl$_2$, WC$_{21}$H$_{29}$N$_8$O$_3$BCl$_2$: C, 35.67; H, 4.10; N, 15.85. Found: C, 35.86; H, 4.13; N, 15.87.

Tp′(CO)$_2$W—C(=O)—N(Bu^n)—C(Me)=N(H) (3). NH$_2$Bu^n (2 equiv) was dissolved in 10 mL of MeCN and added to a solution of 1 in 30 mL of acetonitrile (see above) at 0 °C, resulting in a color change to brown and a shift in infrared CO stretching frequencies to lower wavenumbers (1933, 1834 cm^{-1}). The solvent was removed, and the solid residue was chromatographed on alumina with CH$_2$Cl$_2$ as the eluent. A yellow band was collected and the solvent was removed. The oily residue was recrystallized from CH$_2$Cl$_2$/hexanes to yield yellow crystals of **3** (1.18 g, 56% based on Tp′(CO)$_3$WI). IR (KBr, cm^{-1}): ν_{BH} = 2528; ν_{CO} = 1931, 1828; $\nu_{N=CN}$ = 1601; $\nu_{C=N(Tp')}$ = 1542. ^{1}H NMR (CDCl$_3$, δ): 7.17 (b, 1H, C(Me)=N(*H*)—W), 5.85, 5.81 (1:2, Tp′C*H*), 3.79 (m, 2H, C*H*$_2$CH$_2$CH$_2$CH$_3$), 2.49, 2.41, 2.35, 1.90 (3:3:9:6, C(*Me*)=N(H), Tp′CC*H*$_3$), 1.61 (m, 2H, CH$_2$C*H*$_2$CH$_2$CH$_3$), 1.37 (m, 2H, CH$_2$CH$_2$C*H*$_2$CH$_3$), 0.93 (t, 3H, $^3J_{HH}$ = 7.0 Hz, CH$_2$CH$_2$CH$_2$C*H*$_3$). ^{13}C NMR (CD$_2$Cl$_2$, δ): 239.3 ($^1J_{WC}$ = 157 Hz, 2*C*O), 217.8 ($^1J_{WC}$ = 35 Hz, W—*C*(=O)—N(Bu^n)), 157.3 (*C*(Me)=N(H)), 152.6, 151.0, 144.9, 144.0 (1:2:1:2, Tp′*C*CH$_3$), 107.2, 106.6 (1:2, 3Tp′*C*H), 42.5 (*C*H$_2$CH$_2$CH$_2$CH$_3$), 31.9 (CH$_2$*C*H$_2$CH$_2$CH$_3$), 20.1 (CH$_2$CH$_2$*C*H$_2$CH$_3$), 18.5 (C(*Me*)=N(H)), 16.0, 14.4, 13.1, 12.4 (1:2:1:2, Tp′C*C*H$_3$), 13.8 (CH$_2$CH$_2$CH$_2$*C*H$_3$). Anal. Calcd for **3**·$^1/_2$CH$_2$Cl$_2$, WC$_{24.5}$H$_{36}$N$_8$O$_3$BCl: C, 40.83; H, 5.00; N, 15.56. Found: C, 41.34; H, 4.90; N, 16.00.

[Tp′(CO)$_2$W=C(OH)—N(H)—C(Me)=N(H)][BF$_4$] (4). A stoichiometric amount of HBF$_4$·Me$_2$O was added dropwise to a cold (−78 °C) solution of **2** (0.50 g, 0.80 mmol) in 20 mL of CH$_2$Cl$_2$, resulting in a shift in the CO stretching frequencies to higher wavenumbers (1989, 1890 cm^{-1}). The solution volume was reduced to 5 mL. Addition of 35 mL of Et$_2$O with stirring caused the product to precipitate from the solution as a yellow powder, which was isolated by filtration, washed with Et$_2$O (2 × 10 mL), and dried in vacuo (0.48 g, 77%). Recrystallization from CH$_2$Cl$_2$/Et$_2$O yields yellow crystals of 4. IR (KBr, cm^{-1}): ν_{BH} = 2556; ν_{CO} = 1986, 1882; $\nu_{N=CN}$ = 1618; $\nu_{C=N(Tp')}$ = 1545; ν_{BF} = 1071. ^{1}H NMR (CDCl$_3$, δ): 10.99 (b, C(OH)—N(*H*)—C(Me)), 8.47 (b, C(Me)=N(*H*)—W), 5.97, 5.91 (1:2, Tp′C*H*), 2.63, 2.43, 2.39, 2.38, 1.76 (3:3:6:3:6, N(H)—C(*Me*)=N(H), Tp′CC*H*$_3$); the OH proton was not located. ^{13}C NMR (CD$_2$Cl$_2$, δ): 242.6 ($^1J_{WC}$ = 53 Hz, W=*C*(OH)—N(H)), 227.6 ($^1J_{WC}$ = 139 Hz, 2*C*O), 157.6 (N(H)—*C*(Me)=N(H)), 153.7, 151.7, 146.9, 145.5 (1:2:1:2, Tp′*C*CH$_3$), 108.4, 107.7 (1:2, Tp′*C*H), 16.5, 16.0, 14.7, 13.2, 12.4 (N(H)—C(*Me*)=N(H), Tp′C*C*H$_3$). Anal. Calcd for **4**·Et$_2$O, WC$_{24}$H$_{38}$N$_8$O$_4$B$_2$F$_4$: C, 36.76; H, 4.85; N, 14.29. Found: C, 36.49; H, 4.78; N, 13.98.

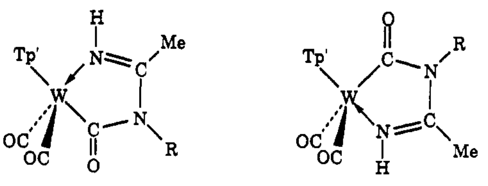
[Tp′(CO)$_2$W=C(OH)—N(Bu^n)—C(Me)=N(H)][BF$_4$] (5). This compound was prepared by acidification of **3** following the procedure described for **4** (yellow, 0.48 g, 73%). IR (KBr, cm^{-1}): ν_{BH} = 2551; ν_{CO} = 1984, 1891; $\nu_{N=CN}$ = 1607; $\nu_{C=N(Tp')}$ = 1546; ν_{BF} = 1067. ^{1}H NMR (CDCl$_3$, δ): 8.66 (b, 1H, C(Me)=N(*H*)—W), 5.93, 5.90 (1:2, Tp′C*H*), 4.05 (m, 2H, C*H*$_2$CH$_2$CH$_2$CH$_3$), 2.66, 2.51, 2.37, 2.36, 1.69 (3:3:6:3:6, N(Bu^n)—C(*Me*)=N(H), Tp′CC*H*$_3$), 1.67 (m, 2H, CH$_2$C*H*$_2$CH$_2$CH$_3$), 1.34 (m, 2H, CH$_2$CH$_2$C*H*$_2$CH$_3$), 0.90 (t, 3H, $^3J_{HH}$ = 7.2 Hz, CH$_2$CH$_2$CH$_2$C*H*$_3$); the OH proton was not located. ^{13}C NMR (CD$_2$Cl$_2$, δ): 238.2 ($^1J_{WC}$ = 53 Hz, W=*C*(OH)—N(Bu^n)), 228.8 ($^1J_{WC}$ = 140 Hz, 2*C*O), 158.9 (N(Bu^n)—*C*(Me)=N(H)), 154.2, 151.6, 146.8, 145.4 (1:2:1:2, Tp′*C*CH$_3$), 108.4, 107.8 (1:2, Tp′*C*H), 46.0 (*C*H$_2$CH$_2$CH$_2$CH$_3$), 31.6 (CH$_2$*C*H$_2$CH$_2$CH$_3$), 19.8 (CH$_2$CH$_2$*C*H$_2$CH$_3$), 18.3 (N(Bu^n)—C(*Me*)=N(H)), 16.4, 14.4, 13.2, 12.4 (1:2:1:2, Tp′C*C*H$_3$), 13.6 (CH$_2$CH$_2$CH$_2$*C*H$_3$). Anal. Calcd for **5**·CH$_2$Cl$_2$, WC$_{25}$H$_{38}$N$_8$O$_3$B$_2$F$_4$Cl$_2$: C, 35.28; H, 4.47; N, 13.17. Found: C, 35.18; H, 4.41; N, 13.18.

[Tp′(CO)$_2$W=C(OMe)—N(H)—C(Me)=N(H)][CF$_3$SO$_3$] (6). A stoichiometric amount of CF$_3$SO$_3$Me was added dropwise to a solution of **2** (0.50 g, 0.80 mmol) in 20 mL of CH$_2$Cl$_2$ at 0 °C, resulting in a shift in the CO stretching frequencies to higher wavenumbers (2000, 1903 cm^{-1}). The solution volume was reduced to 5 mL. Addition of 30 mL of Et$_2$O with stirring caused the product to precipitate from the solution. The flask was cooled in a freezer for 10 h to allow more product to precipitate. The yellow microcrystals which formed were isolated by filtration, washed with Et$_2$O (2 × 10 mL), and dried in vacuo (0.53 g, 77%). IR (KBr, cm^{-1}): ν_{BH} = 2557; ν_{CO} = 1993, 1896; $\nu_{N=CN}$ = 1624; $\nu_{C=N(Tp')}$ = 1545. ^{1}H NMR (CD$_2$Cl$_2$, δ): 12.08 (b, C(OMe)—N(*H*)—C(Me)), 8.82 (b, C(Me)=N(*H*)—W), 6.04, 5.96 (1:2, Tp′C*H*), 4.46 (W=C(O*Me*)), 2.79, 2.46, 2.42, 1.78 (3:3:9:6, N(H)—C(*Me*)=N(H), Tp′CC*H*$_3$). ^{13}C NMR (CD$_2$Cl$_2$, δ): 244.7 ($^1J_{WC}$ = 54 Hz, W = *C*(OMe)), 229.5 ($^1J_{WC}$ = 139 Hz, 2*C*O), 159.6 (N(H)—*C*(Me)=N(H)), 153.8, 152.1, 147.7, 146.2 (1:2:1:2, Tp′*C*CH$_3$), 120.9 (q, $^1J_{FC}$ = 318 Hz, *C*F$_3$SO$_3^-$), 108.6, 107.8 (1:2, Tp′*C*H), 61.9 (W=C(O*Me*)), 17.4, 16.2, 15.0, 13.3, 12.6 (1:1:2:1:2, N(H)—C(*Me*)=N(H), Tp′C*C*H$_3$). Anal. Calcd for **6**·Et$_2$O, WC$_{26}$H$_{40}$N$_8$O$_7$BF$_3$S: C, 36.29; H, 4.65; N, 13.03. Found: C, 35.63; H, 4.22; N, 13.21.

[Tp′(CO)$_2$W=C(OMe)—N(Bu^n)—C(Me)=N(H)][CF$_3$SO$_3$] (7). This compound was prepared by methylation of **3** following the procedure described for **6** (yellow, 0.59 g, 88%). IR (CH$_2$Cl$_2$, cm^{-1}): ν_{BH} = 2560; ν_{CO} = 1996, 1907; $\nu_{N=CN}$ = 1602; $\nu_{C=N(Tp')}$ = 1546. ^{1}H NMR (CDCl$_3$, δ): 9.65 (b, 1H, C(Me)=N(*H*)—W), 5.96, 5.90 (1:2, Tp′C*H*), 4.74 (s, 3H, W=C(O*Me*)), 4.02 (m, 2H, C*H*$_2$CH$_2$CH$_2$CH$_3$), 2.69, 2.46, 2.38, 2.37, 1.65 (3:3:3:6:6, N(Bu^n)—C(*Me*)=N(H), Tp′CC*H*$_3$), 1.62 (m, 2H, CH$_2$C*H*$_2$CH$_2$CH$_3$), 1.37 (m, 2H, CH$_2$CH$_2$C*H*$_2$CH$_3$), 0.96 (t, 3H, $^3J_{HH}$ = 7.4 Hz, CH$_2$CH$_2$CH$_2$C*H*$_3$). ^{13}C NMR (CD$_2$Cl$_2$, δ): 243.5 ($^1J_{WC}$ = 57 Hz, W=*C*(OMe)), 232.8 ($^1J_{WC}$ = 137 Hz, 2*C*O), 159.1 (N(Bu^n)—*C*(Me)=N(H)), 153.2, 151.5, 147.1, 145.7 (1:2:1:2, Tp′*C*CH$_3$), 120.5 (q, $^1J_{FC}$ = 319 Hz, *C*F$_3$SO$_3^-$), 108.9, 108.0 (1:2, Tp′*C*H), 62.0 (W=C(O*Me*)), 46.6 (*C*H$_2$CH$_2$CH$_2$CH$_3$), 31.8 (CH$_2$*C*H$_2$CH$_2$CH$_3$), 19.8 (CH$_2$CH$_2$*C*H$_2$CH$_3$), 17.9 (N(Bu^n)—C(*Me*)=N(H)), 16.3, 14.4, 13.2, 12.4 (1:2:1:2, Tp′C*C*H$_3$), 13.6 (CH$_2$CH$_2$CH$_2$*C*H$_3$). Anal. Calcd for **7**, WC$_{26}$H$_{38}$N$_8$O$_6$BSF$_3$: C, 37.07; H, 4.51; N, 13.31. Found: C, 36.92; H, 4.49; N, 13.29.

Tp′(CO)$_2$W—N—C(=CH$_2$)—N(Bu^t)—C(O) (8). NH$_2$Bu^t (2 equiv) was dissolved in 10 mL of MeCN, and the mixture was added to an orange solution of 1 in 30 mL of acetonitrile (see above) at 0 °C, resulting in a color change to brown and a shift in CO stretching frequencies to lower wavenumbers (1921, 1790 cm^{-1}). The solvent was removed, and the solid residue was chromatographed on alumina with toluene/CH$_2$Cl$_2$ as the eluent. An orange band was collected, and the solvents were removed. The oily residue was recrystallized from CH$_2$Cl$_2$/MeOH to yield orange crystals of 8 (0.49 g, 23% based on Tp′(CO)$_3$WI). IR (KBr, cm^{-1}): ν_{BH} = 2542; ν_{CO} = 1916, 1785; $\nu_{C=N(Tp')}$ = 1541. ^{1}H NMR (CDCl$_3$, δ): 6.07, 5.81 (1:2, Tp′C*H*), 4.42 (d, 1H, $^2J_{HH}$ = 4

Chart 1



A **B**

Hz, N—C(=C*H*H)—N(Bu^t)), 3.74 (d, 1H, $^2J_{HH}$ = 4 Hz, N—C(=CH*H*)—N(Bu^t)), 2.58, 2.40, 2.39, 1.71 (6:3:3:6, Tp′CC*H*$_3$), 1.38 (C(C*H*$_3$)$_3$). ^{13}C NMR (CD$_2$Cl$_2$, δ): 253.0 ($^1J_{WC}$ = 167 Hz, 2*C*O), 163.3 (N(Bu^t)—*C*(O)—N), 163.1 (t, $^2J_{HC}$ = 6 Hz, N—*C*(=CHH)—N(Bu^t)), 150.7, 148.0, 144.2 (3:1:2, Tp′*C*CH$_3$), 109.4, 106.2 (1:2, Tp*C*H), 70.1 (t, $^1J_{HC}$ = 163 Hz, N—C(=*C*HH)—N(Bu^t)), 54.1 (*C*(CH$_3$)$_3$), 27.8 (C(*C*H$_3$)$_3$), 17.2, 16.0, 12.9, 12.3 (1:2:1:2, Tp′C*C*H$_3$). Anal. Calcd for 8·$^1/_2$CH$_2$Cl$_2$, WC$_{24.5}$H$_{34}$N$_8$O$_3$BCl: C, 40.94; H, 4.73; N, 15.60. Found: C, 40.93; H, 4.71; N, 16.16.

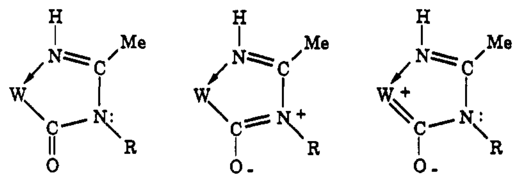
X-ray Diffraction Data Collection for [Tp′(CO)$_2$W=C(OH)—N(H)—C(Me)=N(H)][BF$_4$] (5) and Tp′(CO)$_2$W—N—C(=CH$_2$)—N(Bu^t)—C(O) (8). A yellow rectangular parallelepiped of 5 and an orange rectangular parallelepiped of 8 were mounted on glass wands and coated with epoxy. Diffraction data were collected on a Rigaku automated diffractometer. Twenty-five centered reflections found in the region 25.0° < 2θ < 31.0° for 5 and in the region 40.0° < 2θ < 45.0° for 8 and refined by least-squares calculations indicated a monoclinic cell for each crystal. The cell parameters for 5 and 8 are listed in Table 1.

Diffraction data for both crystals were collected under the conditions specified in Table 1. Only data with $I > 2.5\sigma(I)$ were used in structure solution and refinement.[17] Correction was made for absorption using ψ scans. The minimum and maximum transmission factors for 5 were 0.286 and 0.452; for 8 they were 0.259 and 0.388. The crystals were checked for orientation every 200 reflections and were recentered if necessary.

Solution and Refinement of the Structures. Space group $P2_1$ was confirmed for 5 and $P2_1/n$ for 8. In each case the position of the tungsten 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. Data for 5 was collected at -150 °C because one molecule of methylene chloride found in each unit cell evaporated easily at room temperature and caused collapse of the crystal. Data were collected at -140 °C for 8 because the crystal decayed significantly during data collection at room temperature and less so, but still noticeably, at -140 °C. This is reflected in the high final R factors. The residual electron density is all in the region of W(1).

The 45 non-hydrogen atoms for 5 and the 37 non-hydrogen atoms for 8 were refined anisotropically. Hydrogen atom positions were calculated by using a C–H distance of 0.96 Å and an isotropic thermal parameter calculated from the anisotropic values for the atoms to which they were connected. In the case of methyl groups the group was treated as a rigid body to determine the orientation. In the case of O(6) in 5, the hydrogen was located in the most likely position determined from a slant plane difference Fourier map. The final residuals for 5 for 405 variables refined against 2413 data with $I > 2.5\sigma(I)$ were R = 6.3% and R_w = 7.5%. The final difference Fourier map for 5 had no peak greater than 3.27 e/Å^3.[18] The final residuals[19] for 8 for 335 variables refined against 2877 data with $I > 2.5\sigma(I)$ were R = 7.4% and R_w = 10.2%.[20] The final difference Fourier map for 8 had no peak greater than 2.71 e/Å^3.[18]

Chart 2



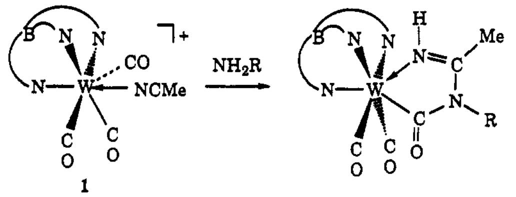
C **D** **E**

Chart 3

F **G**

Results and Discussion

Metallacyclic Acyl–Imine Complexes (2 and 3). Metallacyclic acyl–imine complexes 2 and 3 were synthesized by reaction of a cationic acetonitrile complex, [Tp′(CO)$_3$W(N≡CMe)]$^+$ (1), prepared in situ from reaction of Tp′(CO)$_3$WI with AgBF$_4$ in acetonitrile, with NH$_2$R (R = H, Bu^n) reagents (eq 5). New carbonyl stretching frequencies appeared at lower energies (1938, 1934 cm^{-1} for 2 and 1931, 1928 cm^{-1} for 3) when NH$_2$R′ was introduced into the acetonitrile solution of cation 1. Purification of the neutral product by chromatography on alumina followed by recrystallization from CH$_2$Cl$_2$/hexanes yielded yellow crystals. The net result, independent of mechanism, is that the original amine reagent transfers one proton to the original nitrile nitrogen and loses a second proton. The NR nitrene unit then serves to zip together the carbon atoms of the original nitrile and one carbonyl ligand to form the observed five-membered metallacycle product.



1

R = H (2), Bu^n (3)

(5)

Nucleophilic attack at the carbon of either a coordinated acetonitrile[7] or a carbonyl[3] ligand is well precedented in related systems. Nucleophilic reactions of amines with coordinated nitriles lead to addition of H–NHR across the coordinated nitrile triple bond to form amidine complexes in related monomeric complexes.[8] In particular, trans addition of H–NH$_2$ across the carbon–nitrogen triple bond has been observed. Amine-induced coupling of a nitrile ligand and a terminal alkyne ligand forms six-membered metallacycles.[8]

Two isomers are potentially possible on the basis of the orientation of the dissymmetric chelating ligand which is formed (Chart 1). The only isomer observed for both 2 and 3 has the carbonyl group of the metallacycle cis to the two terminal carbonyls. This geometric preference may

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(17) Programs used during solution and refinement were from the NRCVAX structure determination package. Gabe, E. J.; Le Page, Y.; Charland, J. P.; Lee, F. L.; White, P. S. *J. Appl. Chem.* **1989**, *22*, 384.

(18) The function minimized was $\sum w(|F_o| - |F_c|)^2$, where w is based on counter statistics.

(19) $R_{unweighted} = \sum(|F_o| - |F_c|)/\sum|F_o|$ and $R_{weighted} = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$.

(20) Scattering factors were taken from the following: Cromer, D. T.; Waber, J. T. In *International Tables for X-Ray Crystallography*; Ibers, J. A., Hamilton, J. C., Eds.; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2.

Table 2. Selected IR Data (cm^{-1}) for Complexes 2–7

	ν_{B-H}	ν_{CO}	ν_{NCN}
Tp(CO)$_2$W—C(=O)—N(R)—C(Me)=N(H)			
2 (R = H)	2546	1938, 1834	1619
3 (R = Bu^n)	2528	1931, 1828	1601
[Tp(Co)$_2$W=C(OE)—N(R)—C(Me)=N(H)][BF$_4$]			
4 (R = H, E = H)	2556	1986, 1882	1618
5 (R = Bu^n, E = H)	2551	1984, 1891	1607
6 (R = H, E = Me)	2557	1993, 1896	1624
7 (R = Bu^n, E = Me)	2560	1996, 1907	1602

Table 3. Selected NMR Data [ppm ($^1J_{W-C}$ in Hz)] for Complexes 2–7

	W—N*H*	CN*H*C	*C*O	W—*C*(=O)R or W—*C*(OE)R
Tp(CO)$_2$W—C(=O)—N(R)—C(Me)=N(H)				
2 (R = H)	7.13	11.74	239.5(153)	225.1(30)
3 (R = Bu^n)	7.17		239.3(157)	217.8(35)
[Tp(CO)$_2$W=C(OE)—N(R)—C(Me)=N(H)][BF$_4$]				
4 (R = H, E = H)	8.47	10.99	227.6(139)	242.6(53)
5 (R = Bu^n, E = H)	8.66		228.8(140)	238.2(53)
6 (R = H, E = Me)	8.82	12.08	229.5(139)	244.7(54)
7 (R = Bu^n, E = Me)	9.65		232.8(137)	243.5(57)

Table 4. Atomic Positional Parameters for [Tp′(CO)$_2$W=C(OH)—N(Bu^n)—C(Me)=N(H)][BF$_4$] (5)

	x	*y*	*z*	B_{iso}, Å^2
W(1)	0.68674(8)	0.56666	0.54583(6)	1.98(5)
C(1)	0.4865(23)	0.560(3)	0.4034(18)	2.3(11)
C(1)	0.3642(16)	0.5664(21)	0.3216(12)	3.5(11)
C(2)	0.7811(24)	0.5363(13)	0.4444(19)	2.2(10)
O(2)	0.8529(20)	0.5160(10)	0.3809(16)	3.7(9)
N(3)	0.7145(22)	0.4890(10)	0.7034(19)	2.8(10)
C(4)	0.6829(24)	0.4162(15)	0.7028(22)	2.8(11)
N(5)	0.6357(19)	0.3881(10)	0.5688(16)	2.0(8)
C(6)	0.6305(24)	0.4464(13)	0.4741(19)	2.1(10)
O(6)	0.5780(21)	0.4152(10)	0.3546(14)	3.6(9)
C(7)	0.596(3)	0.2990(12)	0.5303(22)	2.5(11)
C(8)	0.740(3)	0.2476(15)	0.5675(24)	3.2(12)
C(9)	0.811(3)	0.2681(17)	0.4780(23)	3.9(14)
C(10)	0.949(3)	0.2057(17)	0.523(3)	4.2(16)
C(11)	0.694(3)	0.3621(15)	0.8102(21)	3.8(15)
B(11)	0.828(3)	0.7404(17)	0.705(3)	3.0(13)
N(11)	0.6272(21)	0.6465(10)	0.6789(17)	2.4(9)
N(12)	0.7081(22)	0.7128(11)	0.7368(20)	3.0(10)
C(13)	0.660(3)	0.7477(14)	0.8240(22)	3.3(12)
C(14)	0.5391(24)	0.7020(13)	0.8101(22)	2.5(10)
C(15)	0.522(3)	0.6404(13)	0.7246(20)	2.4(10)
C(16)	0.722(3)	0.8218(17)	0.9058(24)	3.7(14)
C(17)	0.4131(22)	0.5759(24)	0.6790(20)	2.7(11)
N(21)	0.9071(20)	0.5981(10)	0.6978(16)	2.6(9)
N(22)	0.9459(18)	0.6752(11)	0.7470(16)	2.1(8)
C(23)	1.081(3)	0.6801(14)	0.819(3)	3.1(13)
C(24)	1.145(3)	0.6038(15)	0.8358(20)	3.3(11)
C(25)	1.029(3)	0.5531(13)	0.7567(21)	2.7(12)
C(26)	1.160(3)	0.7577(17)	0.888(3)	4.6(16)
C(27)	1.034(3)	0.4627(16)	0.7298(23)	4.1(15)
N(31)	0.6999(20)	0.6876(11)	0.4561(17)	2.3(8)
N(32)	0.7621(22)	0.7523(11)	0.5465(18)	2.5(9)
C(33)	0.752(3)	0.8183(12)	0.4727(22)	2.8(12)
C(34)	0.692(3)	0.8015(14)	0.3417(23)	3.1(12)
C(35)	0.655(3)	0.7197(11)	0.3288(18)	2.4(11)
C(36)	0.816(4)	0.8984(14)	0.544(3)	4.2(16)
C(37)	0.591(3)	0.6692(16)	0.2033(22)	3.9(14)
B(1)	0.545(4)	0.4514(18)	0.0236(23)	3.4(16)
F(1)	0.6330(19)	0.4990(11)	−0.0086(17)	5.2(10)
F(2)	0.588(3)	0.3761(12)	0.0620(23)	8.3(16)
F(3)	0.4104(20)	0.4457(13)	−0.0905(15)	6.1(11)
F(4)	0.5090(20)	0.4900(9)	0.1222(15)	5.0(10)

Table 5. Selected Bond Distances (Å) and Angles (deg) for [Tp′(CO)$_2$W=C(OH)—N(Bu^n)—C(Me)=N(H)][BF$_4$] (5)

W–C(1)	1.97(2)	C(1)–O(1)	1.19(3)
W–C(2)	1.84(2)	C(2)–O(2)	1.26(3)
W–N(3)	2.07(2)	N(3)–C(4)	1.24(3)
W–C(6)	2.11(2)	C(4)–N(5)	1.41(3)
W–N(11)	2.24(2)	N(5)–C(6)	1.40(3)
W–N(21)	2.21(2)	C(6)–O(6)	1.29(2)
C(1)–W–C(2)	98.8(9)	N(3)–W–N(31)	154.1(6)
C(1)–W–N(3)	110(1)	C(6)–W–N(11)	133.0(7)
C(1)–W–C(6)	69(1)	C(6)–W–N(21)	121.5(7)
C(1)–W–N(11)	93(1)	C(6)–W–N(31)	136.2(7)
C(1)–W–N(21)	169(1)	N(11)–W–N(21)	81.7(6)
C(1)–W–N(31)	87(1)	N(11)–W–N(31)	81.8(6)
C(2)–W–N(3)	115.2(8)	N(21)–W–N(31)	83.4(6)
C(2)–W–C(6)	69.6(9)	W–C(1)–O(1)	171(3)
C(2)–W–N(11)	157.3(8)	W–C(2)–O(2)	177(2)
C(2)–W–N(21)	83.1(8)	W–N(3)–C(4)	131(2)
C(2)–W–N(31)	79.8(8)	N(3)–C(4)–N(5)	107(2)
N(3)–W–C(6)	69.5(7)	C(4)–N(5)–C(6)	116(2)
N(3)–W–N(11)	77.9(6)	W–C(6)–N(5)	117(1)
N(3)–W–N(21)	78.1(7)	W–C(6)–O(6)	133(2)

be due to the fact that π-acid ligands often prefer to be cis to each other in order to optimize back-bonding from the filled metal dπ orbitals. Here both carbonyl ligands and the acyl carbon are potential π-acceptor ligands.

Infrared spectra of both **2** and **3** display a medium intensity absorption for ν_{BH} in the Tp′ ligand (2546 cm^{-1} for **2** and 2528 cm^{-1} for **3**) and strong ν_{CO} absorptions (1938, 1834 cm^{-1} for **2** and 1931, 1828 cm^{-1} for **3**); the relatively low frequencies are indicative of neutral complexes.[21] The carbonyl absorptions for **3** are slightly lower than those of **2**, consistent with the fact that a butyl group is a better electron donor than a hydrogen. We tentatively assign absorptions near 1600 cm^{-1} to the metallacyclic ring rather than to the C=O absorptions; similar infrared absorptions are observed in the protonated and methylated derivatives **4**–**7**, which lack the C=O moiety. Assuming the ring assignment is correct implies that the $\nu_{C=O}$ absorption of the acyl was not observed; it probably is located below 1545 cm^{-1} and is therefore difficult to identify among the absorptions for ν_{CN} of the Tp′ ligand. A major contribution from resonance form D or E with multiple carbon—nitrogen or metal—carbon bonding would lower the energy of the $\nu_{C=O}$ absorption (Chart 2).

Note that there are six electrons available for the π-system in these metallacycle rings. Typical aromatic metallacycles contain a planar skeleton and exhibit low field ^{1}H NMR chemical shifts. The requisite $4n + 2$ π-electrons may originate from a combination of a metal d orbital, a carbon p orbital, and a lone pair on a heteroatom. The metal can contribute one d orbital to overlap with carbon or heteroatom p orbitals in the π-system. Metallaheterocycles can contain heteroatoms such as nitrogen, oxygen, or sulfur in the π-system. A common five-membered metallaheterocycle is metallafuran (F)[12] and one example of a six-membered metallaheterocycle is metallathiopyrylium (G)[13] (Chart 3).

The presence of a mirror plane on the NMR time scale was indicated by the two equivalent pyrazolyl rings evident in both ^{1}H and ^{13}C NMR spectra. The proton on the nitrogen bound to tungsten appears near 7.15 ppm (WN*H*) for both **2** and **3** while the proton on the nitrogen β to the metal resonates at 11.74 ppm (CN*H*C) for **2** as a broad singlet. The equivalent terminal metal carbonyl carbons resonate downfield near 239 ppm with a large one-bond tungsten–carbon coupling of ~155 Hz. The carbonyl carbons of the five-membered metallocycles appear near

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[21] Feng, S. G.; Templeton, J. L. *Organometallics* **1992**, *11*, 2168.

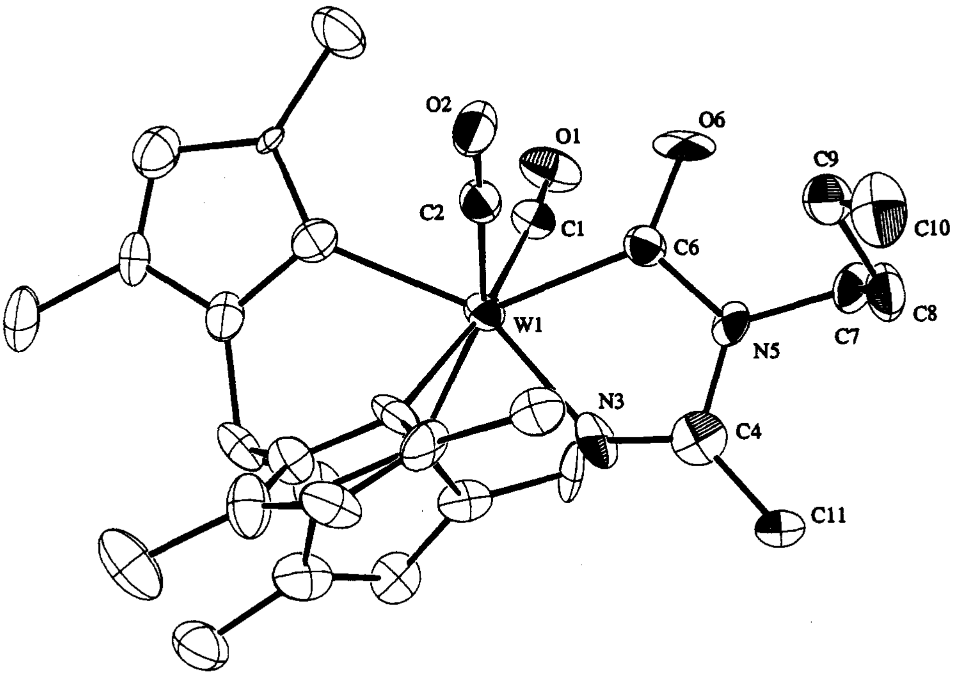
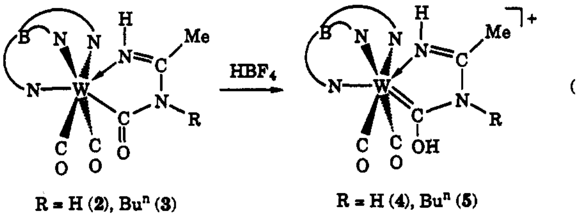


Figure 1. ORTEP drawing of $[\mathrm{Tp'(CO)_2}\overline{\mathrm{W{=}C(OH){-}N(R){-}C(Me){=}N}}\mathrm{(H)}][\mathrm{BF_4}]$ (**5**).

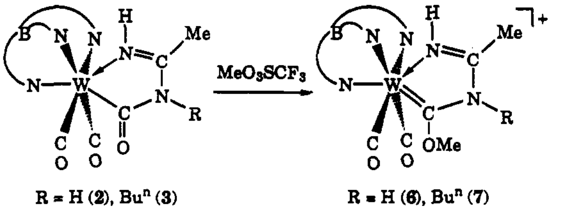
220 ppm with a relatively small one-bond tungsten–carbon coupling of ~35 Hz; these numerical values for the chemical shift and the coupling constant are smaller than those for η^1-acyl carbons in W–C(O)R units (290 ppm and 120 Hz).[3] Presumably, charge delocalization from the adjacent nitrogen makes the carbonyl carbon less electron deficient in the metallacycle than in the acyl, and thus the metal–carbon multiple bond character decreases (D in Chart 2). The β-carbons of the chelate ligand resonate near 158 ppm.

Reaction of **1** with aniline generates a small amount of the phenylamido complex $\mathrm{Tp'(CO)_2W(NHPh)}$.[22] Presumably, aniline is not as good a nucleophile for attack at the acetonitrile ligand. Instead, in some sequence, it replaces one carbonyl and the acetonitrile ligand and is deprotonated to give the amido product.

Cationic Metallacyclic Carbene–Imine Complexes. Complexes **4**–**7** were synthesized by protonation or methylation of the carbonyl oxygen of the appropriate neutral complex, **2** or **3**, at a low temperature (eqs 6 and 7).

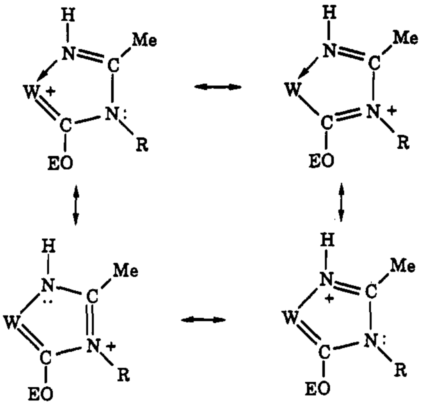


(6)



(7)

Chart 4



Crystalline products were isolated in good yield by adding ether to the concentrated methylene chloride solution followed by recrystallization of the solid from $\mathrm{CH_2Cl_2/Et_2O}$. Elaboration of metal carbonyl ligands by sequential nucleophilic addition at the carbon and electrophilic addition at oxygen is the classic route to Fischer carbenes.[2,3] The fact that the electrophiles here add to the acyl oxygen instead of the nitrogens of the metallacycle suggests that resonance structure D is an important valence bond representation of the molecule.

Infrared spectra of complexes **4**–**7** exhibit an absorption around 2555 $\mathrm{cm^{-1}}$ (ν_{BH}) which is 10–20 $\mathrm{cm^{-1}}$ higher than comparable values for the Tp' ligand B–H stretches in neutral complexes.[3,7,16,21] The terminal carbonyl ν_{CO} absorptions appear near 1985 and 1885 $\mathrm{cm^{-1}}$ for the hydroxycarbene derivatives **4** and **5** and near 1995 and 1900 $\mathrm{cm^{-1}}$ for the methoxycarbene complexes **6** and **7**.

A 2:1 symmetry pattern for the Tp' ligand was evident in both ^{1}H and ^{13}C NMR spectra, indicating retention of mirror symmetry in the cationic products. ^{1}H NMR assignments are straightforward. The metallacyclic ring proton (WN*H*) of the chelating ligand in complexes **4**–**7** resonates well downfield (8.45–9.65 ppm), substantially below the shift for this proton in the neutral metallacyclic

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[22] (a) Luan, L.; White, P. S.; Brookhart, M.; Templeton, J. L. *J. Am. Chem. Soc.* **1990**, *112*, 8190. (b) Luan, L.; Brookhart, M.; Templeton, J. L. *Organometallics* **1992**, *11*, 1433.

Diagram 1. Qualitative Bonding Scheme for the dπ–Ligand Interactions in [Tp′(CO)$_2$W(=C(OR)—N(R′)—C(Me)=N(H))]$^+$

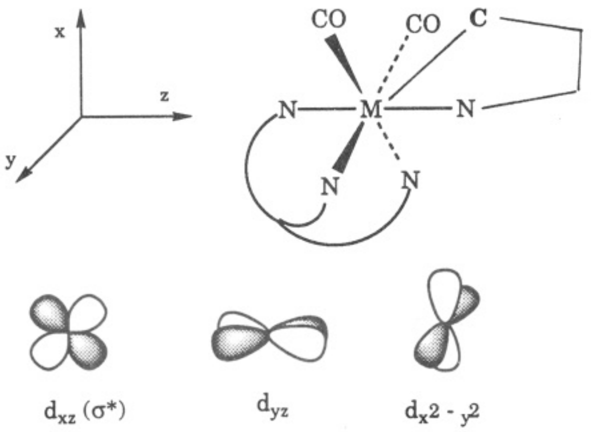

Table 6. Atomic Positional Parameters for Tp′(CO)$_2$W—N—C(=CH$_2$)—N(Bu^t)—C(=O) (8)

	x	*y*	*z*	B_{iso}, Å^2
W(1)	0.60170(5)	0.15851(4)	0.19079(3)	1.82(3)
C(1)	0.4529(13)	0.1943(11)	0.1505(8)	2.4(6)
O(1)	0.3594(9)	0.2353(8)	0.1218(6)	3.2(5)
C(2)	0.5748(14)	0.2748(10)	0.2468(9)	2.6(6)
O(2)	0.5498(11)	0.3459(8)	0.2793(7)	3.6(5)
N(3)	0.5406(10)	0.0742(9)	0.2728(7)	2.2(5)
C(4)	0.4416(13)	0.0702(10)	0.3115(8)	2.1(6)
O(5)	0.3633(9)	0.1263(8)	0.3134(6)	2.7(5)
N(6)	0.4659(10)	–0.0171(9)	0.3439(7)	2.5(5)
C(7)	0.3981(14)	–0.0949(12)	0.3722(9)	3.0(7)
C(8)	0.2955(15)	–0.0505(12)	0.4048(10)	3.4(7)
C(9)	0.4696(20)	–0.1465(19)	0.4402(19)	7.1(14)
C(10)	0.3579(21)	–0.1608(14)	–0.3031(15)	5.1(10)
C(11)	0.5680(12)	–0.0189(11)	0.3030(8)	2.0(6)
C(12)	0.6490(13)	–0.0823(10)	0.2930(9)	2.6(6)
B(1)	0.8157(14)	0.0836(13)	0.1006(10)	2.2(7)
N(21)	0.6809(9)	0.2259(8)	0.0963(6)	1.8(4)
N(22)	0.7647(10)	0.1746(8)	0.0601(7)	2.0(5)
C(23)	0.7836(12)	0.2164(11)	–0.0096(8)	2.1(6)
C(24)	0.7166(12)	0.3014(12)	–0.0202(9)	2.5(6)
C(25)	0.6550(13)	0.3030(11)	0.0485(9)	2.6(6)
C(26)	0.8637(14)	0.1795(12)	–0.0641(9)	2.9(7)
C(27)	0.5751(14)	0.3788(12)	0.0659(9)	2.7(7)
N(31)	0.7775(10)	0.1297(8)	0.2367(7)	2.1(5)
N(32)	0.8600(9)	0.1038(8)	0.1899(6)	1.8(5)
C(33)	0.9668(13)	0.0972(10)	0.2334(9)	2.4(6)
C(34)	0.9568(13)	0.1160(13)	0.3143(9)	3.0(7)
C(35)	0.8372(13)	0.1344(10)	0.3162(9)	2.3(6)
C(36)	1.0709(13)	0.0727(14)	0.1983(10)	3.3(8)
C(37)	0.7788(16)	0.1545(11)	0.3879(10)	2.9(7)
N(41)	0.6190(9)	0.0317(9)	0.1185(7)	2.2(5)
N(42)	0.7244(9)	0.0074(8)	0.0929(7)	2.1(5)
C(43)	0.7182(12)	–0.0790(9)	0.0574(8)	1.9(6)
C(44)	0.6053(14)	–0.1138(11)	0.0560(9)	2.5(6)
C(45)	0.5481(12)	–0.0429(11)	0.0942(8)	2.3(6)
C(46)	0.8176(13)	–0.1209(12)	0.0218(9)	2.7(6)
C(47)	0.4260(12)	–0.0456(11)	0.1105(9)	2.2(6)

precursors **2** and **3**. On the other hand, the proton bound to the nitrogen β to the tungsten (CN*H*C) appears near 11–12 ppm for **4** and **6**, which is close to the chemical shift observed for the analogous proton in **2** and **3**. The methoxy methyl protons in **6** and **7** appear near 4.5 ppm. The hydroxy proton was not located for **4** or **5**; it may be buried under the pyrazole methyl signals or it may simply be too broad to observe at room temperature. Seven coordinate complexes are often fluxional due to soft energy surfaces, but the presence of the tridentate and bidentate chelating ligands here restricts molecular motion. There is no indication of fluxional behavior in these NMR studies.

Table 7. Selected Bond Distances (Å) and Angles (deg) for Tp′(CO)$_2$W—N[—C(=CH$_2$)—N(Bu^t)—C(O)] (8)

W–C(1)	1.85(1)	N(3)–C(4)	1.40(2)
W–C(2)	1.93(2)	N(3)–C(11)	1.42(2)
W–N(3)	2.01(1)	C(2)–O(2)	1.19(2)
W–N(21)	2.15(1)	C(4)–O(5)	1.22(2)
W–N(31)	2.14(1)	C(4)–N(6)	1.36(2)
W–N(41)	2.17(1)	N(6)–C(11)	1.45(2)
C(1)–O(1)	1.27(2)	C(11)–C(12)	1.33(2)

C(1)–W–C(2)	74.7(6)	N(31)–W–N(41)	83.3(4)
C(1)–W–N(3)	90.0(6)	W–C(1)–O(1)	169(1)
C(1)–W–N(21)	95.5(6)	W–C(2)–O(2)	175(1)
C(1)–W–N(31)	175.1(6)	W–N(3)–C(4)	137(1)
C(1)–W–N(41)	100.2(5)	W–N(3)–C(11)	134.2(9)
C(2)–W–N(3)	94.5(5)	C(4)–N(3)–C(11)	88(1)
C(2)–W–N(21)	95.3(5)	N(3)–C(4)–O(5)	132(1)
C(2)–W–N(31)	101.7(5)	N(3)–C(4)–N(6)	94(1)
C(2)–W–N(41)	174.4(5)	O(5)–C(4)–N(6)	134(1)
N(3)–W–N(21)	169.8(4)	C(4)–N(6)–C(7)	135(1)
N(3)–W–N(31)	93.6(5)	C(4)–N(6)–C(11)	88(1)
N(3)–W–N(41)	87.6(4)	C(7)–N(6)–C(11)	131(1)
N(21)–W–N(31)	81.5(4)	N(3)–C(11)–N(6)	89(1)
N(21)–W–N(41)	83.0(4)	N3–C(11)–C(12)	135(1)
		N(6)–C(11)–C(12)	136(1)

The carbene-type carbons of the chelating ligand are located at 238–245 ppm (one-bond tungsten coupling of 53–57 Hz), which is well upfield from the carbene shift value for Tp′(CO)(PhC≡CMe)W=C(R)OMe]$^+$ (330 ppm with $^1J_{WC}$ = 135 Hz).[3] Again, this difference can be explained by recognizing the contribution of the adjacent nitrogen lone pair to the electron deficient carbon. The terminal carbonyl carbon in each complex resonates around 230 ppm with a one-bond tungsten coupling of 140 Hz. These values are smaller than those of carbonyl ligands in the neutral complexes **2** and **3** (240 ppm and 155 Hz), which reflects the fact that the cationic complexes **4**–**7** are more electron deficient than the neutral precursors **2** and **3**. The carbon between the two nitrogens of the chelating ligand resonates near 159 ppm. The methoxy methyl carbons in **6** and **7** appear near 62 ppm. The $SO_3CF_3^-$ anion appears at 121 ppm as a quartet (318 Hz).

Selected IR data for complexes **2**–**7** are shown in Table 2, and selected NMR data for these complexes are listed in Table 3. The trends mentioned earlier regarding the infrared stretches of the Tp′ ligand and of the metal carbonyl ligands are evident here. Likewise the systematic changes in ^{1}H and ^{13}C signals for the neutral and cationic complexes are obvious.

Crystal Structure of [Tp′(CO)$_2$W=C(OH)—N(Bu^n)—C(Me)=N(H)][BF$_4$] (5). The tungsten metal center can be considered as adopting a seven-coordinate 3:3:1 geometry. The Tp′ ligand occupies three facial coordination sites and the cis carbonyl ligands occupy two coordination sites. The chelating ligand then fills the remaining two coordination sites with the carbene carbon atom in the capping position. Atomic positional parameters are listed in Table 4, and selected intramolecular bond distances and angles appear in Table 5. An ORTEP drawing of the complex cation in [Tp′(CO)$_2$W=C(OH)—N(Bu^n)—C(Me)=N(H)][BF$_4$] is shown in Figure 1.

Bond distances and angles for the Tp′ and the carbonyl ligands conform to expectations based on related tungsten(II) structures.[16,23] The three tungsten–nitrogen bond distances to the Tp′ donor atoms cluster between 2.20 and

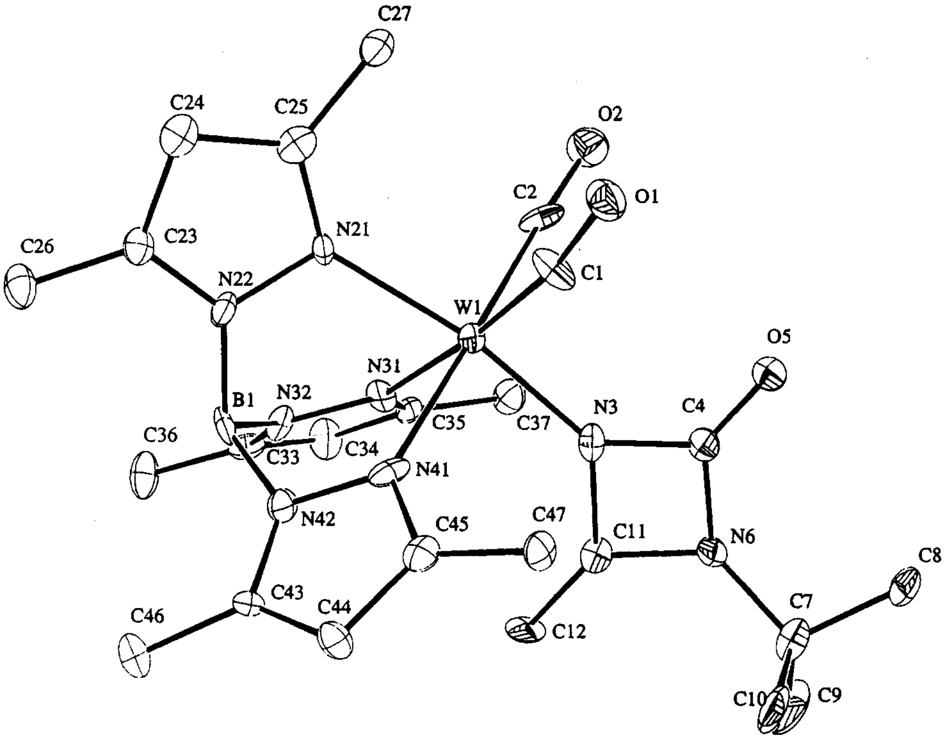

Figure 2. ORTEP drawing of $\mathrm{Tp'(CO)_2W\overline{—N—C({=}CH_2)—N(Bu^t)—C}({=}O)}$ (8).

2.25 Å (W-N(11) = 2.24(2) Å, W-N(21) = 2.21(2) Å, W-N(31) = 2.25(2) Å). As is often observed for metal carbonyls,[23,24] the carbonyl carbon atoms lie in soft positions along the W-CO axis (W-C(1) = 1.97(2) Å and W-C(2) = 1.84(2) Å). The sum of the W-C and C-O distances for both carbonyl ligands is more nearly constant (3.16 and 3.11 Å). The angle between the two metal carbonyl ligands is 98.8(9)°. The plane which contains the metallacycle bisects the two carbonyl ligands, a result which is compatible with the C_s symmetry reflected by solution NMR. The carbene unit of the metallacycle is cis to the carbonyl ligands. It is common for π-acid ligands to occupy adjacent coordination sites.

The chelating ligand deserves close inspection. The carbene W=C distance of 2.11(2) Å is close to distances characterizing low oxidation state Fischer carbenes ($\mathrm{Ph_2C{=}W(CO)_5}$, 2.14 Å)[25] but it is longer than distances in high oxidation state Schrock alkylidenes ($\mathrm{Bu^tCH{=}W(dmpe)(CBu^t)(CH_2Bu^t)}$, 1.94 Å).[26] The W—N bond distance of 2.07(2) Å is short for a simple W—N single bond. Bond distances around the ring for N(3)—C(4), C(4)—N(5), and N(5)—C(6) are intermediate between C—N single and double bonds at 1.24(3), 1.41(3), and 1.40(3) Å, respectively, suggesting some charge delocalization involving the two nitrogens (Chart 4). Note that three of the four resonance structures have double bonds from W to C(6) or from N(3) to C(4) while only one resonance form has a double bond between C(4) and N(5) or N(5) and C(6). The aromatic description is simply one potentially useful model, and it will surely be of limited utility. The angles around the N(5) nitrogen are 116(2)° [C(4)—N(5)—C(6)], 122(2)° [C(4)—N(5)—C(7)], and 122(2)° [C(6)—N(5)—C(7)], which add up to 360°, reflecting sp^2 hybridization at the nitrogen. The sum of the ring angles [69.5(7)° (N(3)—W—C(6)), 131(2)° (W—N(3)—C(4)), 107(2)° (N(3)—C(4)—N(5)), 116(2)° (C(4)—N(5)—C(6)), and 117(1)° (W—C(6)—N(5)] is close to 540°, as expected for a planar five-membered metallacycle.

The planar geometry of the five-membered metallacycle is reminiscent of the cyclopentadienide anion, and one can postulate that six π-electrons are present to support an aromatic description of the bonding. The low ^{1}H and ^{13}C chemical shifts are compatible with substantial ring current.

A qualitative view of the bonding is to build from an octahedral molecular orbital model. If one constructs an octahedral σ framework for the three Tp′ nitrogens, the two carbonyl ligands, and the metallacycle nitrogen, the three standard $d\pi$ orbitals of the metal remain. These then serve as the σ-acceptor orbital for the metallacycle carbon bond and house the four electrons of the d^4 tungsten center if the carbene is considered as a neutral two-electron σ donor unit (Diagram 1). In the coordinate system shown, where the d_{xy} lobes are directed along M-L axes (rather than $d_{x^2-y^2}$, as is more common), one lobe of the d_{xz} orbital is positioned for σ bonding to the capping carbon donor of the capped octahedral description. The d^4 electrons reside in $d_{x^2-y^2}$ and d_{yz}. Both of these metal $d\pi$ orbitals are stabilized by back-bonding to the two π-acid carbonyl ligands. The $d_{x^2-y^2}$ orbital lies between the two cis carbonyls and becomes the lowest energy molecular orbital combination in a three-center two-electron bond involving two CO π^* orbitals and $d_{x^2-y^2}$. The chelate orientation dictates that the vacant p orbital of the carbene carbon is oriented to overlap and stabilize the filled d_{yz} orbital. In addition overlap of both CO π^* orbitals orthogonal to the OC-M-CO plane with d_{yz} is increased as the OC-M-CO angle opens to the observed obtuse angle.

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(23) Feng, S. G.; White, P. S.; Templeton, J. L. *J. Am. Chem. Soc.* **1992**, *114*, 2951.

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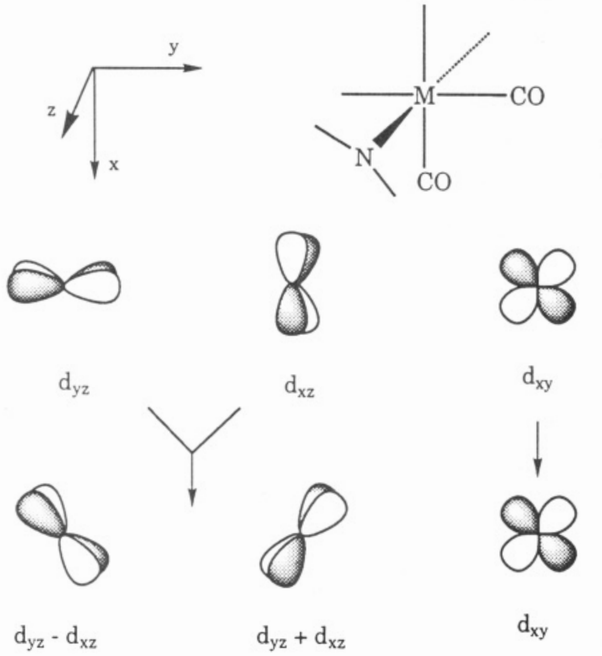
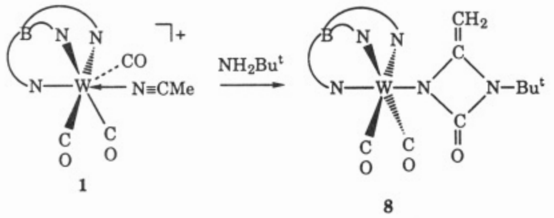
Diagram 2. Qualitative Bonding Scheme for the $d\pi$–Ligand Interactions in $\mathrm{Tp'(CO)_2W{-}\overline{M[{-}C({=}CH_2){-}N(Bu^t){-}C}(O)]}$



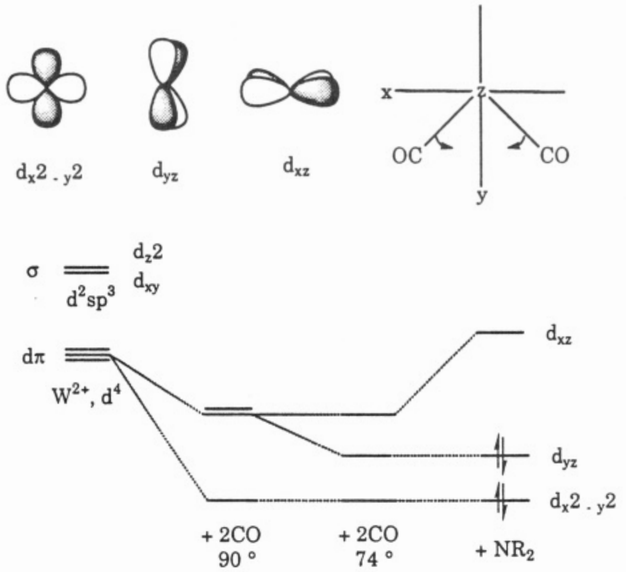
A Neutral Amido Complex (8). This unusual amido compound was prepared by treating the tricarbonyl acetonitrile cation 1 with NH_2Bu^t (eq 8). Purification by chromatography on alumina followed by recrystallization from CH_2Cl_2/MeOH produced brown crystals in 23% yield.



(8)

We have no data relevant to the mechanism of formation of 8. One can imagine initial formation of a metallacycle analogous to 2 or 3 followed by some reaction sequence leading to net H_2 loss and coupling of the metal bound atoms of the chelating ligand to form the observed products. Net loss of H_2 is only a formalism here; we have not detected hydrogen. Reaction of an amidine terminal alkyne complex, $[\mathrm{Tp'(CO)W(PhC{\equiv}CH)[N(H){=}C(Me)(NH_2)]}]^+$, with base has produced an unusual six-membered metallacycle, $\mathrm{Tp'(CO)\overline{W({=}C(Ph){-}C(H){=}N{-}C(Me){=}N})}$, which also involved a formal net loss of hydrogen (eq 3).[8] Another reaction corresponding to formal hydrogen elimination results from the reaction of $\mathrm{Tp'W(CO)_3I}$ with NH_2CH_2R which generates both amido and metalloimine complexes: $\mathrm{W{-}N(H)CH_2R}$ and $\mathrm{W{-}N{=}C(H)R}$.[27] The mechanism of these reactions is not clear, but a series of deprotonation and electron transfer reactions equivalent to loss of hydrogen seems probable.

Diagram 3. Qualitative Bonding Scheme for the $d\pi$–Ligand Interactions in $\mathrm{Tp'(CO)_2W{-}\overline{N[{-}C({=}CH_2){-}N(But){-}C}(O)]}$



The infrared spectrum of 8 displays a medium intensity absorption at 2542 cm^{-1} for ν_{BH} in the Tp′ ligand. The ν_{CO} absorptions at 1916 and 1785 cm^{-1} are consistent with an electron rich metal center. Amido complexes of the type $\mathrm{Tp'(CO)_2W(NHR)}$[22] and $\mathrm{Tp'(CO)_2W[N(R)CH{=}CHPh]}$[28] also reflect strong electron donation from the lone pair on the nitrogen as evidenced by low infrared carbonyl stretching frequencies.

NMR data support the formulation of 8 as an amido complex. A 2:1 pattern for the Tp′ ligand is observed in both ^{1}H and ^{13}C NMR spectra, consistent with an orientation of the amido ligand in the mirror plane that bisects the two carbonyl ligands. The two inequivalent geminal protons on the amido ligand appear at 4.42 and 3.17 ppm, respectively, as doublets ($^2J_{HH}$ = 4 Hz). The ^{13}C NMR spectrum reveals the metal-bound carbonyl carbons at 253 ppm ($^1J_{WC}$ = 167 Hz), and this low field chemical shift and large one-bond tungsten–carbon coupling are also compatible with the amido ligand acting as a π-donor ligand. The carbonyl carbon of the amido ligand ring is located at 163.3 ppm and the vinyl carbons appear at higher field as triplets at 163.1 ppm ($^2J_{HC}$ = 6 Hz) and at 70.1 ppm ($^1J_{HC}$ = 163 Hz).

Crystal Structure of $\mathrm{Tp'(CO)_2W{-}\overline{N[{-}C({=}CH_2){-}N(Bu^t){-}C}(O)]}$ (8). The coordination sphere of this tungsten center is similar to related six-coordinate tungsten(II) dicarbonyl complexes. The Tp′ ligand occupies three facial coordination sites with the two carbonyls and the amido ligand in the remaining coordination sites. Atomic positional parameters are listed in Table 6, and selected intramolecular bond distances and angles appear in Table 7. An ORTEP drawing of $\mathrm{Tp'(CO)_2W{-}\overline{N[{-}C({=}CH_2){-}N(Bu^t){-}C}(O)]}$ is shown with the atomic numbering in Figure 2.

The prominent geometrical features of 8 are compatible with those of related W(II) carbonyl amido complexes.[28,29] The carbonyl carbons lie in soft positions along the W–CO axis (W–C(1) = 1.85(1) Å and W–C(2) = 1.93(2) Å). The sum of the W–C and C–O distances for both carbonyl

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[27] Luan, L.; Brookhart, M.; Templeton, J. L. Unpublished results.

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ligands is nearly constant (3.12 Å). The W–C–O angles are 169(1) and 175(1)°. The amido W–N distance of 2.01(1) Å is appropriate for a formal double bond and compares well with values in related W–NR_2 complexes (~2.00 Å).[28,29] The Tp′ W–N distance trans to the amido nitrogen is 2.15(1) Å, which is close to those trans to the carbonyls here (2.14(1) and 2.17(1) Å), suggesting that the amido ligand is also a strong trans influence ligand. The amido heterocycle lies in the molecular mirror plane and bisects the two pyrazole rings and the two carbonyl ligands. The angles around the amido N(3) nitrogen are 137(1)° [W–N(3)–C(4)], 134.2(9)° [W–N(3)–C(11)], and 88(1)° [C(4)–N(3)–C(11)], which sum to near 360°, reflecting sp^2 hybridization at the nitrogen. Furthermore, C(4) and C(11) are also sp^2 hybridized, and the four-membered ring is nearly planar. The angles around the N(6) nitrogen are 135(1)° [C(4)–N(6)–C(7)], 131(1)° [C(7)–N(6)–C(11)], and 88(1)° [C(4)–N(6)–C(11)], which add to 354°, so the lone pair electrons on the nitrogen N(6) can be delocalized in the π-system. The angle between the two metal carbonyls is 74.7(6)°. This acute angle reflects preferential stabilization of the two filled $d\pi$ orbitals by back-bonding to the two π-acid carbonyl ligands, as described below.

The coordinate system chosen puts the amido nitrogen on the *z* axis and the two carbonyl ligands on the *x* and *y* axes, respectively (Diagram 2). The orientation of the NRR′ unit between the cis carbonyls will allow donation from the nitrogen lone pair into the lone vacant $d\pi$ orbital of the tungsten center, here a $d_{yz} + d_{xz}$ combination. The linearly ligating carbonyl ligands will effectively mix CO π^* orbitals with d_{xy} to lower the energy of this metal based orbital. Two electrons of this d^4 configuration then fill the d_{xy} orbital, and the d_{xz} and d_{yz} orbitals will combine to generate one filled $d\pi$ orbital ($d_{yz} - d_{xz}$) and one vacant $d\pi$ orbital ($d_{yz} + d_{xz}$) in order to optimize $d\pi$ back-donation to the two carbonyl ligands and to provide the acceptor orbital for nitrogen lone pair donation.

A simpler way to visualize the bonding is to rotate the coordinate system by 45° along the *z* axis so that the *y* axis will bisect the two carbonyl ligands (Diagram 3). In this case the $d_{x^2-y^2}$ orbital will be stabilized more than d_{xz} and d_{yz} because of effective orbital overlap between $d_{x^2-y^2}$ and both CO π^* orbitals in the *xy* plane. Closure of the carbonyl angle from 90° to the observed 75° will stabilize d_{yz} by increasing the overlap of the out-of-plane CO π^* orbitals with d_{yz}. This breaks the degeneracy of d_{xz} and d_{yz}, and so the second pair of metal d electrons will occupy the d_{yz} orbital. Simply considered, d_{yz} is the HOMO stabilized by CO back-bonding and d_{xz} is the LUMO as the π^* component of the W–N double bond in this system.

Summary

Cationic metal carbonyl nitrile complexes are electrophilic at the nitrile carbon and at the carbonyl carbon sites. Consistent with these reactivity patterns, the net result of primary amine addition to $[Tp'(CO)_3W(N{\equiv}CMe)]^+$ is bond formation between the amine nitrogen and both a carbonyl carbon and an acetonitrile carbon. Coupling of nitrile and carbonyl ligands with an NR link to form five-membered metallacycle imine–acyl complexes in this system may occur via metal amidine intermediates which then couple the amidine ligand with a terminal carbonyl through nucleophilic attack at the carbonyl carbon. The metallacycle imine–carbene complexes have six π-electrons available (from a filled metal $d\pi$ orbital, one nitrogen lone pair, and one C=N π pair) and can be considered aromatic. Formation of an unusual amido carbonyl compound with H_2NBu^t as a reagent involves a formal oxidation equivalent to net loss of H_2. The mechanism is not clear and actual hydrogen elimination is unlikely. The acute OC—M—CO angle observed in the dicarbonyl complex here containing the single-faced π-base amido ligand is the result of preferential stabilization of two filled metal $d\pi$ orbitals by back-bonding to the two π-acid carbonyl ligands with π-donation from the single-faced amido unit destabilizing the lone vacant metal $d\pi$ orbital.

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Supplementary Material Available: A labeled diagram of 5 and tables of anisotropic temperature factors and complete bond distances and angles for 5 and 8 (9 pages). Ordering information is given on any current masthead page.

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