Electrophilic Addition to Cyanide Ligands in Tungsten(II) Four-Electron-Donor Alkyne Complexes

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Extended reflux of Tp′(CO)(I)W(RC≡CR′) (Tp′ = hydridotris(3,5-dimethylpyrazolyl)borate) complexes in ethyl acetate in the presence of silver cyanide produces Tp′(CO)(CN)W(RC≡CR′) complexes in moderate to high yields. A single-crystal X-ray structure of Tp′(CO)(CN)W(PhC≡CMe) shows that the alkyne is aligned parallel to the M−CO axis. Electrophilic attack at the nitrogen of the cyanide ligand with methyl triflate or triflic acid yields cationic isocyanide complexes, whereas attack with HBF_4 results in neutral BF_3 adduct complexes. Coordination of the Tp′(CO)(PhC≡CMe)W^+ fragment to the cyanide nitrogen of Tp′(CO)(CN)W(HC≡CBu^n) to form a CN-bridged dinuclear complex has been achieved. Variable-temperature ^{1}H NMR measurements reflect acetylene rotation barriers in the Tp′(CO)(L)W(HC≡CH)$^{n+}$ series (L = CO, CNH, CNMe {$n = 1$}; CN^-, $CNBF_3^-$ {$n = 0$}) and, thus, quantify π-effects for the cyanide and isocyanide ligands with respect to steric considerations. Extended Hückel molecular orbital calculations were carried out on a series of model complexes, $[H_3(CO)(L)W(HC{\equiv}CH)]^{n-}$ (L = CO, CNH {$n = 1$}; CN^-, H^- {$n = 2$}) to augment the experimental data.

Introduction

Group VI transition-metal complexes with four-electron-donor (4e$^-$) alkyne ligands possess a rich and varied chemistry.[1] Nucleophilic addition to cationic 4e$^-$-donor alkyne complexes is known to produce η^2-vinyl, η^3-allyl, and carbyne complexes.[2−4] The propargyl site of 4e$^-$-donor alkynes in neutral Tp′(CO)(I)W(RC≡CR′) complexes can be regioselectively deprotonated and alkylated to form new alkyne derivatives.[5] The production of cycloalkynes from intramolecular alkylation has recently been realized using this route.[6] Additionally, the alkyne may function as an active spectator in promoting reactivity at other ligands through variable electron donation (4e$^-$ ↔ 3e$^-$ ↔ 2e$^-$).[7,8] A nearly universal feature of these 4e$^-$-donor alkyne systems is the presence of one or more carbonyl (CO) ligands which function in a complimentary manner to the alkyne. Cyanide (CN^-) ligands, isoelectronic and isolobal with CO, are stronger σ donors and weaker π acceptors than CO.[9] This report describes a foray into the formation and reactivity of the Tp′(CO)(CN)W(RC≡CR′) system.

Alkylation of electron-rich cyanide complexes to form isocyanide complexes is well-known.[10−14] Gladysz has recently used transition-metal electrophiles to expand the field of cyanide-bridged bimetallics to include complexes with chiral fragments at each end of the cyanide linkage.[15] Protonation of monocyanide complexes to yield stable complexes with a hydrogen isocyanide ligand is less common.[16−23] Free isohydrocyanic acid (CNH) is unstable and readily isomerizes into hydrogen cyanide (HCN).[24] Fehlhammer and co-workers have contributed significantly to the chemistry of hydrogen isocyanide complexes.[24−27]

Electrophilic additions to coordinated cyanide ligands attracted our attention because conversion of neutral cyanide alkyne complexes into cationic isocyanide alkyne complexes would provide a route to chiral analogues of

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Table 1. Selected IR and ^{1}H NMR Data for Tp′(CO)(CNX)W(RC≡CR′) Complexes

				IR		^{1}H NMR CD_2Cl_2, δ (ppm)		
				KBr (cm^{-1})	CH_2Cl_2 (cm^{-1})			
	X[a]	R	R′	ν_{CN}, ν_{CO}	ν_{CN}, ν_{CO}	H_{anti}	H_{syn}	$\Delta G^{\ddagger}_{rot}$[b]
1a		H	H	2114, 1910	2114, 1934	12.78	13.71	15.9
1b[c]	BF_3	H	H	2192, 1971	2195, 1956	13.13	13.99	13.5
1c[c]	Me	H	H	2225, 1974	2217, 1970	13.30	14.24	12.9
1d[c]	H	H	H	2134, 1945	2137, 1956	13.03	13.95	13.3
2a		H	Bu	2112, 1910	2115, 1917	12.72		
2b	BF_3	H	Bu	2188, 1948	2192, 1945	13.01		
2c	Me	H	Bu	2211, 1945	2213, 1957	13.19		
3a		Ph	H	2110, 1928	2110, 1932		13.68	
3b	BF_3	Ph	H	2185, 1958	2189, 1957		13.90	
3c	Me	Ph	H	2210, 1950	2210, 1967		14.10	
3a′		H	Ph			12.87		
3b′	BF_3	H	Ph			13.30		
3c′	Me	H	Ph			13.50		
4a		Ph	Me	2109, 1918	2109, 1922			
4b	BF_3	Ph	Me	2178, 1939	2186, 1942			
4c	Me	Ph	Me	2207, 1943	2205, 1955			

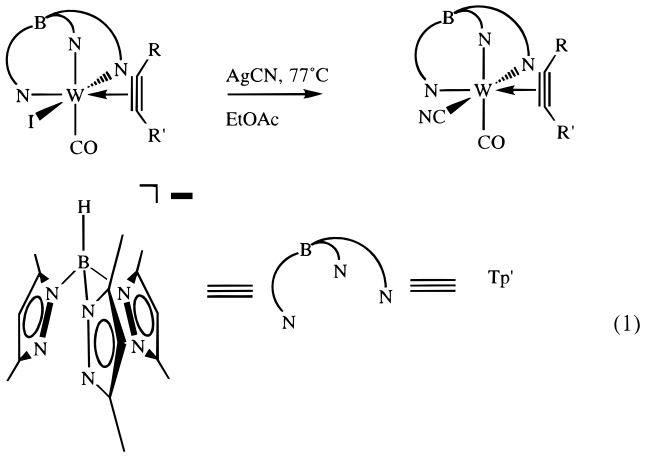
[a] For X = H, Me, the counterion is $O_3SCF_3^-$. [b] Value in kcal/mol. [c] Low-temperature ^{1}H NMR data; see Experimental Section.

the synthetically useful Tp′(CO)$_2$W(RC≡CR′)$^+$ family of complexes. The orientational preferences of alkynes are primarily determined by the π-characteristics of the ancillary ligand set.[1,28−31] We hypothesized that the difference in π-acidity between carbonyl and isocyanide ligands would be enough to align the alkyne preferentially along a ligand axis while still maintaining the desirable electronic properties of Tp′(CO)$_2$W(RC≡CR′)$^+$ complexes. Would isocyanide ligands compete effectively for back-bonding electrons in a cationic complex with two strong π-acids already present? Isocyanide ligands are known to act as effective π-acids in neutral[32] and anionic[33−35] complexes. Fenske and co-workers have stressed that although isocyanide ligands can compete for back-bonding electrons in cationic complexes,[36,37] the total molecular environment[38] plays a dominant role in the extent of isocyanide participation in the π-manifold of the complex.

We report here the synthesis of Tp′(CO)(CN)W(RC≡CR′) complexes and their reactions with simple electrophiles to produce both neutral and cationic isocyanide alkyne complexes. The availability of a complete series of acetylene complexes of the form Tp′(CO)(L)W(HC≡CH)$^{n+}$ (L = CO, CNH, CNMe {n = 1}; CN^-, $CNBF_3^-$ {n = 0}) has allowed us to directly assess the role of the isocyanide ligands in the metal−ligand π-framework by using acetylene rotational barriers as a probe. Extended Hückel molecular orbital (EHMO) calculations have been performed on representative models to amplify the experimental data.

Results and Discussion

Synthesis and Characterization of the Monocarbonyl Cyanide Alkyne Complexes. Extended reflux of Tp′(CO)(I)W(RC≡CR′) complexes with AgCN in ethyl acetate (EtOAc) produced the corresponding cyanide complexes, Tp′(CO)(CN)W(RC≡CR′) (**1a**−**4a**) (eq 1). The cyanation is relatively slow; reaction times



(1)

1a: R = R′ = H
2a: R = H, R′ = Bu^n
3a: R = Ph, R′ = H
3a′: R = H, R′ = Ph
4a: R = Ph; R′ = Me

in excess of 48 h were necessary to produce adequate yields (45%) of the acetylene complex (**1a**). A similar yield for the 1-hexyne complex (**2a**) resulted after 24 h. In contrast, the aryl−alkyne complexes (**3a**, **3a′**, **4a**) were produced in better than 80% yield after 24 h.

In the solid state, the cyanide ligands of **1a**−**4a** showed weak, sharp absorptions near 2110 cm^{-1} for stretching of the C≡N triple bond. Similar values have been reported for neutral monocyanide complexes.[19,39,40] The carbonyl ligand vibrations of **1a**−**4a** are more

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Chart 1. Nomenclature for Alkyne Termini

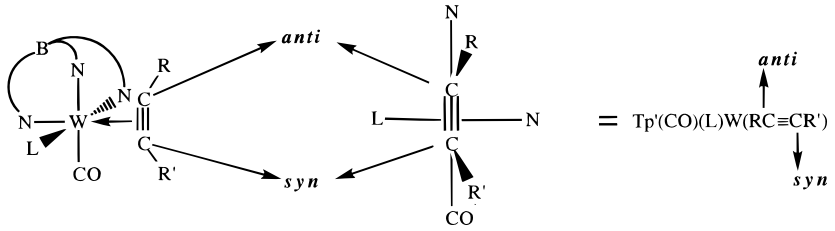
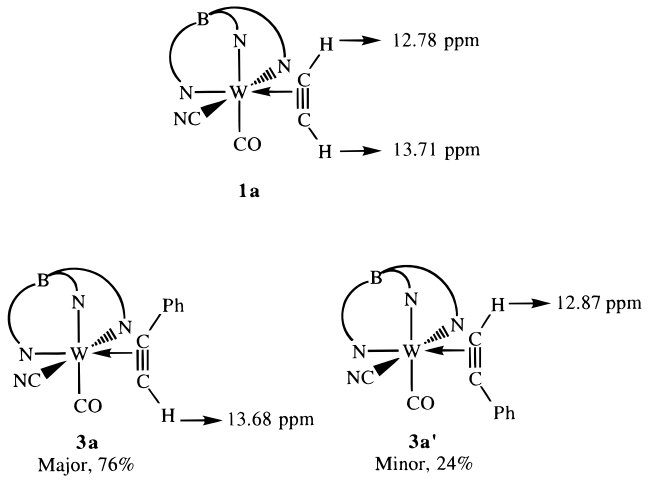


Chart 2. Representative Chemical Shifts for Terminal Alkyne Protons



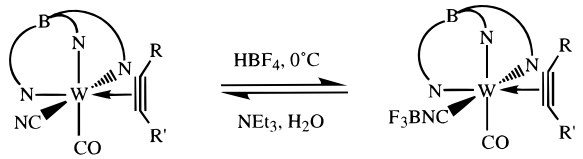
responsive to the nature of the alkyne; ν_{CO} values for the aryl alkynes are 10−20 cm^{-1} higher in the solid state than their alkyl counterparts. These values along with selected ^1H NMR data are presented in Table 1.

In the ^1H NMR spectra of **1a**−**4a**, chiral metal environments were indicated by the resonances seen for the pyrazole ligands; unique singlets were noted for both the pyrazole protons and the pyrazole methyl groups. The alkyne termini can be differentiated by their relative proximity to the CO ligand. The alkyne terminus closer to the CO ligand is termed the syn site; the other is the anti site (Chart 1).[6] In general, anti protons are shielded relative to syn protons. For example, in **1a**, H_{anti} resonated at 12.78 ppm whereas H_{syn} was located at 13.71 ppm. Additional confirmation was provided by the phenylacetylene complex, which exists as a 3:1 (**3a**:**3a′**) mixture of rotamers. The predominant rotamer in solution (**3a**) has the phenyl ring in the anti site, as evinced by a signal for H_{syn} at 13.68 ppm. The terminal proton in the opposite rotamer (**3a′**) was located at 12.87 (Chart 2). The preferential location of ligand aryl substituents near the aromatic pyrazole rings is a well-documented feature of tris(pyrazolyl)borate W(II) and Mo(II) complexes.[4,41−43]

Signals for terminal carbonyl ligands in the ^{13}C NMR spectra for **1a**−**4a** were located near 230 ppm with $^1J_{WC}$ values of 135−140 Hz. Table 2 provides selected ^{13}C NMR data. Signals for the alkyne carbons for **1a**−**4a** were located at 203−220 ppm, in the four-electron-donor range.[1] In contrast to the ^1H NMR spectra, no clear distinction between anti and syn sites could be made on the basis of ^{13}C chemical shifts for the alkyne carbons. However, the sites could be differentiated on the basis of $^1J_{WC}$ values: anti carbons experience coupling to the tungsten on the order of 50 Hz, whereas the syn alkyne carbons showed reduced coupling values of 11−16 Hz. The carbons of the cyanide ligands display reasonably sharp signals around 150 ppm with $^1J_{WC}$ values (138−140 Hz) similar to those of the carbonyl ligands.

X-ray Crystal Structure of Tp′(CO)(CN)W(PhC≡CMe). Royal blue, single crystals of **4a** were grown by layering hexanes over a saturated CH_2Cl_2 solution. The overall geometry of **4a** is roughly octahedral if the alkyne is considered to occupy one coordination site. As shown in Figure 1, the alkyne is aligned nearly parallel to the W−CO axis, as expected from molecular orbital considerations (vide infra). This is a common feature of Tp′(CO)(L)W(alkyne) complexes[5,8,42,44] as well as other d^4 group VI transition-metal complexes containing an alkyne and one cis carbonyl ligand.[1] Selected bond distances and bond angles for **4a** are given in Table 3. The preference for locating aryl substituents proximal to pyrazole rings has been mentioned earlier. The tungsten−pyrazole bond trans to the cyanide (W−N(21) = 2.192 Å) is slightly shorter than the W−N bonds trans to the carbonyl and the alkyne (W−(N31) = 2.219 Å and W−(N41) = 2.217 Å, respectively). These W−N bond lengths are compatible with the expected order of relative trans-influence: RC≡CR ≥ C≡O > C≡N$^-$.

Electrophilic Addition to the Cyanide Ligand. Addition of HBF_4 to CH_2Cl_2 solutions of **1a**−**4a** at 0 °C resulted in the production of BF_3 adducts, Tp′(CO)(CNBF$_3$)W(RC≡CR′) (**1b**−**4b**), rather than the anticipated hydrogen isocyanide complexes (eq 2). The resulting BF_3 adducts are stable both in the solid state and in solution. Addition of NEt_3 regenerates the cyanide precursors quantitatively, as measured by ^1H



1b: R = R' = H
2b: R = H, R' = Bu^n
3b: R = Ph, R' = H
3b': R = H, R' = Ph
4b: R = Ph; R' = Me

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Table 2. Selected ^{13}C NMR Data for Tp′(CO)(CNX)W(RC≡CR′) Complexes[a]

complex				CO			C_{anti}			C_{syn}			CN(X)	
	X[b]	R	R′	δ	$^1J_{WC}$	$^3J_{CH}$[c]	δ	$^1J_{WC}$	$^1J_{CH}$	δ	$^1J_{WC}$	$^1J_{CH}$	δ	$^1J_{WC}$
1a		H	H	229.1	136	6.4	214.2	52	213	204.7	12	210	150.7	140
1b[d]	BF_3	H	H	222.1	136	8.3	218.6	51	215	207.1	13	222	147.7	nd
1c[d]	Me	H	H	219.5	133	7.4	219.8	51	215	207.5	15	223	147.0	144
1d[d]	H	H	H	223.2	139	nd	217.5	nd	213	206.6	nd	221	147.6	140
2a		H	Bu	229.3	140	*e*	204.7	51	211	216.2	12		150.8	138
2b	BF_3	H	Bu	223.3	139		215.1	51	210	219.3	13		148.4	nd
2c	Me	H	Bu	220.3	140		217.0	48	210	219.5	13		150.0	nd
3a		Ph	H	230.9	135	8.3	219.2	52		202.9	11	210	152.5	138
3b	BF_3	Ph	H	225.0	134	7.5	222.5	52		204.3	11	220	150.0	nd
3c	Me	Ph	H	222.0	133	8.3	223.4	50		204.5	11	220	151.9	nd
3a′		H	Ph	231.6	134		214.8	48	200	211.1	16		150.7	138
3b′	BF_3	H	Ph	225.1	140		219.7	48	210	212.1	12		nl	nd
3c′	Me	H	Ph	216.5	nd		222.1	37	211	211.7	nd		nl	nd
4a		Ph	Me	231.5	138		215.2	53		211.3	12		152.6	138
4b	BF_3	Ph	Me	226.2	136		219.2	51		213.3	13		151.0	nd
4c	Me	Ph	Me	223.3	140		221.0	50		214.1	10		152.6	nd

[a] Chemical shift values are in ppm; coupling constant values are in hertz. Abbreviations used in table: nd = not determined, nl = not located. [b] For X = H, Me, the counterion is $O_3SCF_3^-$. [c] This is $^3J_{CHsyn}$. [d] Low-temperature data; see Experimental Section. [e] A $^3J_{CHanti}$ value of 2 Hz was recorded for **2a**.

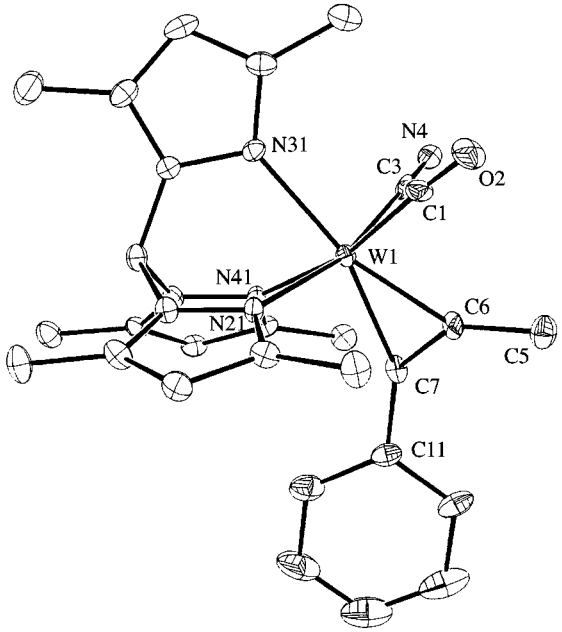


Figure 1. ORTEP representation for Tp′(CN)(CO)W(PhC≡CMe) (**4a**).

NMR. The addition of BF_3·Et_2O to a CH_2Cl_2 solution of **3a** also produced **3b**. The isomer ratio of alkyne rotamers (**3b**:**3b′**, 3:1) in the products was identical for either reaction pathway.

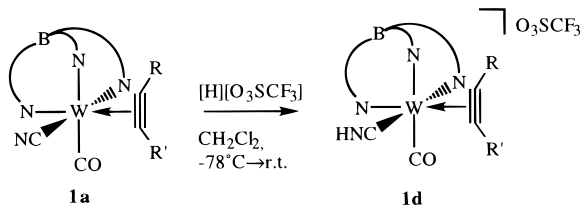
Precedent exists for this reaction. Treatment of (arene)$Mn(CO)_2CN$ complexes with HBF_4 led to isolation of BF_3 adducts.[45] Additionally, the hydroisocyanation of olefins by [Cp(dppe)Fe(CNH)][BF_4] is often compromised by formation of the unreactive Cp(dppe)-Fe($CNBF_3$) complex.[25] Direct addition of BX_3 (X = H, Cl, F) to cyanide complexes to produce the corresponding isocyanides has been explored by Shriver[46−48] and others.[22,49]

Table 3. Selected Bond Distances (Å) and Bond Angles (deg) for Tp′(CO)(CN)W(PhC≡CMe) (4a)

W(1)−C(1)	1.960 (9)	W(1)−N(41)	2.219 (10)
W(1)−C(3)	2.197 (11)	C(1)−O(2)	1.149 (11)
W(1)−C(6)	2.040 (8)	C(3)−N(4)	1.034 (14)
W(1)−C(7)	1.997 (8)	C(6)−C(7)	1.313 (12)
W(1)−N(21)	2.192 (6)	C(5)−C(6)	1.483 (12)
W(1)−N(31)	2.217 (5)	C(7)−C(11)	1.459 (12)
C(1)−W(1)−C(3)	87.4 (3)	N(31)−W(1)−N(41)	80.13 (24)
C(1)−W(1)−C(6)	70.8 (4)	C(3)−W(1)−N(41)	87.1 (3)
C(1)−W(1)−C(7)	108.2 (3)	C(6)−W(1)−N(21)	100.8 (3)
C(1)−W(1)−N(21)	96.9 (3)	C(6)−W(1)−N(31)	158.3 (3)
C(1)−W(1)−N(31)	87.6 (3)	C(6)−W(1)−N(41)	121.5 (3)
C(1)−W(1)−N(41)	166.8 (3)	C(7)−W(1)−N(21)	90.1 (3)
C(3)−W(1)−C(6)	93.9 (3)	C(7)−W(1)−N(31)	162.6 (3)
C(3)−W(1)−C(7)	101.9 (3)	C(7)−W(1)−N(41)	84.7 (3)
C(3)−W(1)−N(21)	165.4 (3)	C(6)−C(7)−C(11)	136.8 (8)
C(3)−W(1)−N(31)	85.9 (3)	C(5)−C(6)−C(7)	141.0 (9)
N(21)−W(1)−N(31)	80.33 (24)	C(6)−W(1)−C(7)	37.9 (3)
N(21)−W(1)−N(41)	85.72 (23)		

Spectroscopic evidence for a coordinated BF_3 unit was found in absorbances corresponding to B−F stretching modes near 1210, 1140, 910, and 880 cm^{-1} in the solid-state IR spectra of **1b**−**4b**. Similar features have been noted previously for organometallic cyanide−BF_3 adducts[45,48] and for related BF_3 adducts in organic systems.[50,51] A single absorbance in the range 1050−1080 cm^{-1} would be expected for an uncoordinated BF_4^- counterion.[52] Increases in $\nu_{C\equiv N}$ of about 80 cm^{-1} accompany BF_3 adduct formation. In contrast, only modest increases in $\nu_{C\equiv O}$ (25−40 cm^{-1}) were noted.

The addition of HOTf (OTf^- = $^-O_3SCF_3$) to **1a** generated a hydrogen isocyanide complex, [Tp′(CO)-(CNH)W(HC≡CH)][OTf] (**1d**), in good yield (eq 3). A



1a **1d** (3)

20 cm^{-1} increase in $\nu_{C\equiv N}$ accompanied protonation, in

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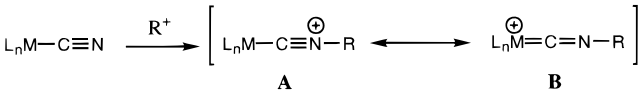
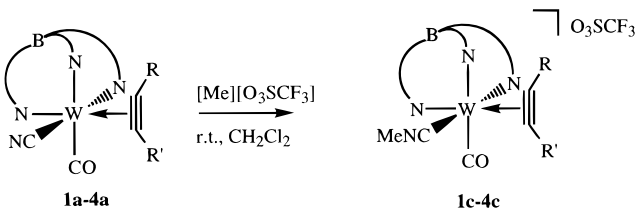
Chart 3. Resonance Forms for Isocyanide Ligands



contrast to the 78 cm^{-1} increase in $\nu_{C\equiv N}$ seen for BF_3 binding. Only a 12 cm^{-1} difference in $\nu_{C\equiv N}$ was reported for BF_3 complexation ($\nu_{C\equiv N}$ = 2153 cm^{-1}) vs protonation ($\nu_{C\equiv N}$ = 2141 cm^{-1}) of the terminal cyanide of $[Mn_2H(CN)(CO)_5(dppm)]$ ($\nu_{C\equiv N}$ = 2091 cm^{-1}; dppm = $Ph_2PCH_2PPh_2$).[22]

Treatment of **1a**−**4a** with MeOTf results in the production of methyl isocyanide complexes, **1c**−**4c** (eq 4). As with BF_3 complexation, only moderate increases



(4)

1c: R = R' = H
2c: R = H, R' = Bu^n
3c: R = Ph, R' = H
3c': R = H, R' = Ph
4c: R = Ph; R' = Me

in ν_{CO} (ca. 20 cm^{-1} for substituted alkynes) were observed upon methylation. The relative insensitivity of the carbonyl ligands suggests that resonance form **A** (Chart 3) predominates in **2b**−**4b** and **2c**−**4c**. Resonance form **B** requires a formal two-electron oxidation at the metal and is unlikely given the strong π-acids, CO and RC≡R′, in the coordination sphere. Methylation of the cyanide ligands caused 100−110 cm^{-1} increases in ν_{CN}, reflecting the stronger Lewis acidity of Me^+ when compared to BF_3 or H^+.

The ^1H and ^{13}C NMR spectra of the isocyanide complexes with substituted alkynes (**2b**−**4b**, **2c**−**4c**) are generally similar to their neutral cyanide analogues. Signals for the terminal acetylene protons were found at slightly higher frequency (14.2−13.0 ppm) with anti positions shielded relative to syn positions. In the ^{13}C NMR spectra, signals for the terminal carbonyl ligands were found at lower frequency (220−225 ppm). Chemical shifts for the alkyne carbons (203−222 ppm) were appropriate for four-electron-donor alkynes and followed the same $^1J_{WC}$ patterns observed for the cyanide complexes. Signals for the carbons of the isocyanide ligands, broadened from interaction with the quadrupolar isocyanide nitrogen, were located between 145 and 155 ppm.

Rotational Barriers for Acetylene Ligands. Cooling a CD_2Cl_2 sample to −5 °C sharpened the downfield acetylene signals of **1a**. A 15.9 kcal/mol barrier to alkyne rotation ($\Delta G^{\ddagger}_{rot}$) for **1a** was calculated from line-broadening measurements between 5 and 35 °C. In CD_2Cl_2 solution at room temperature, the isocyanide acetylene complexes, **1b**, **1c**, and **1d**, show broad signals for the acetylene protons whereas the proton resonances of the Tp′ ligand are sharp. Upon cooling of the samples to low temperature (−70 to −85 °C), well-resolved alkyne signals were obtained in the ^1H and ^{13}C NMR spectra. Other than alkyne rotation, the parent acetylene complexes are spectroscopically similar to their substituted counterparts. Low-temperature ^{13}C NMR data for **1c** and **1d** show $^1J_{WC}$ values of 144 and 140 Hz for the isocyanide ligands, respectively. In the BF_3 adduct, **1b**, a $\Delta G^{\ddagger}_{rot}$ of 13.5 kcal/mol for acetylene rotation was calculated from line-broadening measurements in the slow-exchange region. For the methyl isocyanide acetylene complex, **1c**, a $\Delta G^{\ddagger}_{rot}$ of 12.9 kcal/mol for acetylene rotation was calculated. For the hydrogen isocyanide acetylene complex, **1d**, a $\Delta G^{\ddagger}_{rot}$ of 13.3 kcal/mol for acetylene rotation was estimated from a coalescence temperature of 21.7 °C.

The barrier to acetylene rotation in structurally related Tp′(CO)(I)W(HC≡CH) has been estimated at 19 kcal/mol.[6] Variable-temperature measurements of 2-butyne rotational barriers for Tp(CO)(I)M(MeC≡CMe) (Tp = hydridotris(1-pyrazolyl)borate; M = Mo, W) complexes produce values for $\Delta G^{\ddagger}_{rot}$ near 16 kcal/mol.[53] Assuming that the lower barriers for the 2-butyne complexes result from higher ground-state energies relative to the acetylene−iodide complex, the 15.9 kcal/mol barrier for **1a** provides evidence for the participation of cyanide in lowering the barrier to acetylene rotation (see EHMO section). However, it may also be that the difference in $\Delta G^{\ddagger}_{rot}$ between **1a** and Tp′(CO)(I)W(HC≡CH) simply reflects the steric differences between the cyanide and iodide ligands.

Conversion of the cyanide into an isocyanide ligand lowers $\Delta G^{\ddagger}_{rot}$ by about 3 kcal/mol. Steric differencs should be minimal as the isocyanide substituent is too far removed from the metal to interact significantly with the small acetylene ligand. The measured $\Delta G^{\ddagger}_{rot}$ values for **1b**−**d**, therefore, represent a convenient probe of isocyanide participation in the competition for π-backbonding electrons from the metal center. The measured values are nearly independent of the positive charge on the complex and, thus, conform to the total molecular environment principle set forth by Fenske.[38]

To assess the steric effect of the Tp′ ligand on acetylene rotation, the variable-temperature ^1H NMR behavior of $[Tp'(CO)_2W(HC\equiv CH)][O_3SCF_3]$ (**5**) was studied. Complex **5** is synthesized by the abstraction of iodide from $Tp'(CO)_3WI$ with a silver salt ($AgBF_4$ or AgO_3SCF_3) in the presence of an alkyne.[42] For gaseous alkynes the alkyne is condensed prior to transfer into the solution containing the putative "$[Tp'(CO)_3W]^+$" species (eq 5).

The ^1H NMR spectrum of complex **5** in CD_2Cl_2 solution at 20 °C displays a symmetric pattern consistent with the presence of an effective mirror plane; the pyrazole protons are present in a 1:2 pattern, and the pyrazole methyl groups comprise a 3:6:3:6 set. The acetylenic protons produce a sharp singlet at 14.32 ppm with a $^2J_{WH}$ value of 5 Hz. The two carbonyl ligands are equivalent, and their signal appears at 212 ppm with a 131 Hz coupling to tungsten. The acetylene carbons appear as a slightly broadened singlet at 217 ppm with a $^1J_{CH}$ value of 230 Hz.

Upon cooling to −90 °C, **5** retains the effective mirror plane that produces the symmetric patterns in the ^1H

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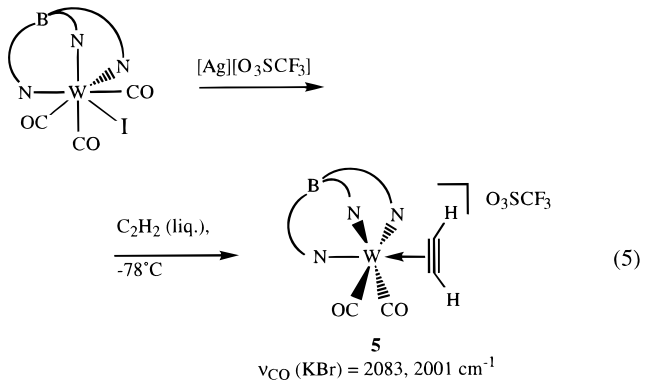

(5)

5

ν_{CO} (KBr) = 2083, 2001 cm^{-1}

and ^{13}C NMR spectra. This is consistent with structural data for [Tp′(CO)$_2$W(PhC≡CMe)][BPh$_4$] in which the alkyne ligand bisects the OC−W−CO angle.[30] EHMO calculations on cis dicarbonyl−alkyne units predict such an orientation.[30] At low temperature, two acetylene resonances appear as broad signals (half-width about 25 Hz) at 14.70 ppm for H_{syn} and 13.93 ppm for H_{anti}. An upper limit for $\Delta G^{\ddagger}_{rot}$ of 9.3 kcal/mol for **5** was estimated from a coalescence temperature of −65.8 °C. Given the lack of electronic differentiation between the π-acids cis to the acetylene ligand in **5**, it seems reasonable to propose that the 9.3 kcal/mol rotational barrier in **5** represents the intrinsic steric barrier to alkyne rotation in Tp′(CO)(L)W(RC≡CR′)$^+$ complexes.

Extended Hückel Molecular Orbital (EHMO) Calculations. In each of the models, three facially coordinating hydride ligands were used in place of the Tp′ ligand and an acetylene ligand and a carbonyl ligand were placed in mutually cis positions. To complete the models, CO, CNH, CN$^-$, and H$^-$ were placed in the remaining coordination site (Figure 2). The model complexes [H$_3$(CO)$_2$W(HC≡CH)]$^-$ (**6$_{CO}$**) and [H$_4$(CO)-W(HC≡CH)]$^{2-}$ (**6$_H$**) have been discussed in earlier publications.[30,54] For each model, EHMO calulations were performed on four geometries which differ in the relative orientation of the alkyne ligand: θ = 0° is defined with the alkyne aligned parallel to the M−CO axis (Y); θ = 45°, 90°, and 135° follow by sequential rotation toward the *X* axis.

For d^4 metal complexes containing a *cis*-carbonyl−alkyne unit, constructive interactions between the metal dπ orbitals (d$_{xy}$, d$_{xz}$, and d$_{yz}$) and the alkyne and carbonyl ligands are optimal with the alkyne aligned parallel to the metal−CO axis (Figure 3).[1] Rotation of the alkyne disrupts the 3-center, 2-electron interaction between d$_{yz}$, CO π^*_v and CC π^*_v. At θ = 90°, CO π^*_v is left facing an empty d$_{yz}$ and a global maximum results. The key feature here is that alkynes are strong enough π-acids *and* π-bases that they dictate the dπ orbital populations upon rotation. Figure 4 shows the qualitative ordering of the dπ orbitals as a result of alkyne rotation.

Placement of a carbonyl ligand in the remaining site equates the θ = 0° and 90° acetylene orientations. A low barrier to acetylene rotation of 1.6 kcal/mol was calculated for **6$_{CO}$**, supporting the hypothesis that the 9.3 kcal/mol rotational barrier measured for the acetylene ligand in [Tp′(CO)$_2$W(HC≡CH)][O$_3$SCF$_3$] (**5**) primarily results from steric interactions between the proximal pyrazole 3-methyl groups and the acetylene ligand.

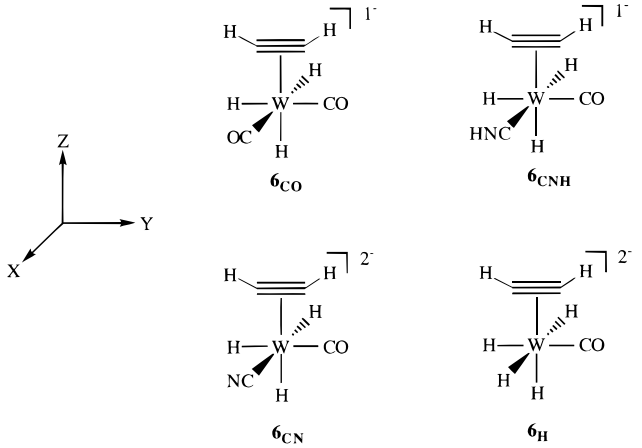

Figure 2. Coordinate system and model complexes for EHMO calculations.

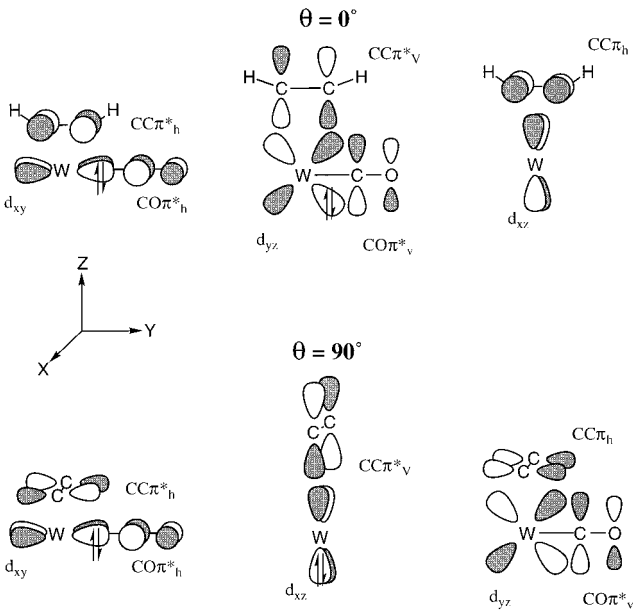

Figure 3. Metal dπ interactions for alkyne orientations of θ = 0° and 90°.

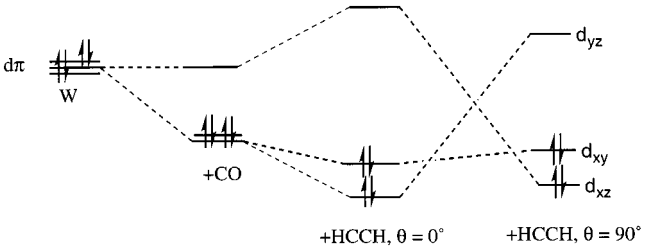

Figure 4. Qualitative molecular orbital energies for [H$_3$(CO)(HCCH)W]$^-$.

What happens with an isocyanide or a cyanide ligand? In principle, the isocyanide and cyanide ligands interact with the same metal dπ orbitals as the carbonyl ligand (Figure 5). The weaker π acidity of the isocyanide and cyanide ligands relative to the carbonyl produces calculated acetylene rotational barriers of 12.5 kcal/mol for **6$_{CNH}$** and 14.9 kcal/mol for **6$_{CN}$**. The calculated value for **6$_{CNH}$** compares well with the experimentally determined acetylene rotational barriers of 13.5, 12.9, and

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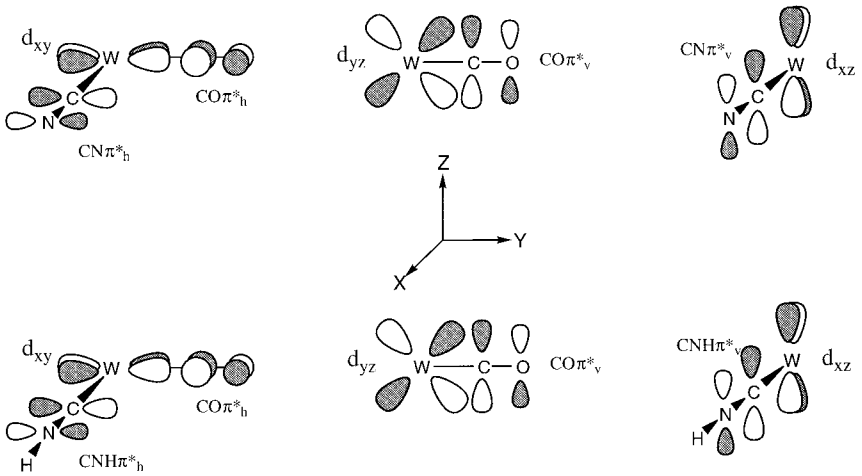


Figure 5. Metal dπ interactions with cyanide and isocyanide ligands.

Table 4. Selected EHMO Calculated Energies (Relative, kcal/mol) for $[H_3(CO)(L)W(HCCH)]^-$ Complexes

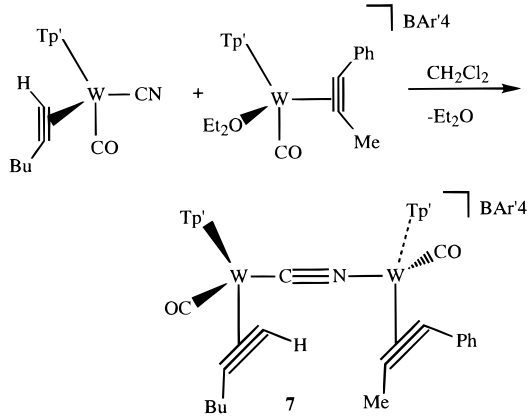
		HOMO-1				LUMO			
L	$\Delta G^{\ddagger}$	0°	45°	90°	135°	0°	45°	90°	135°
CO	1.6	0.0	−0.6	0.0	−1.3	0.0	1.4	0.0	4.0
CNH	12.5	0.0	1.8	5.0	1.6	0.0	−4.5	−11.8	−3.3
CN^-	14.9	0.0	3.0	7.7	3.3	0.0	−6.6	−15.8	−6.6
H^-	17.2	0.0	2.6	7.6	2.6	0.0	−8.3	−19.3	−8.3

13.3 kcal/mol for the isocyanide complexes **1b**, **1c**, and **1d**, respectively. Good agreement is also found between the calculated barrier for $\mathbf{6_{CN}}$ and the measured $\Delta G^{\ddagger}_{rot}$ of 15.9 kcal/mol for **1a**. Such quantitative agreement for EHMO calculations is unexpected and probably somewhat fortuitous.

A reasonable barrier to acetylene rotation of 17.2 kcal/mol was calculated for $\mathbf{6_H}$. Comparison of the alkyne rotational barriers for $\mathbf{6_{CNH}}$ and $\mathbf{6_{CN}}$ with the value for $\mathbf{6_H}$ reveals the moderating effect of the π-acidic isocyanide and cyanide ligands relative to the π-innocent hydride ligand. As the alkyne is rotated in $\mathbf{6_{CNH}}$ and $\mathbf{6_{CN}}$, the destabilization incurred by the loss of constructive overlap with COπ^*_v is diminished through stabilizing interactions with CNH π^*_v and CN π^*_v, respectively. As expected, the cyanide is an ineffective π acid, accounting for only 2 kcal/mol of stabilization relative to $\mathbf{6_H}$. The isocyanide ligand is somewhat better (4.5 kcal/mol).

It has been observed that the electronic barriers to alkyne rotation can be attributed to changes in energy within the dπ manifold.[1] As shown in Table 4, the increase in energy of the HOMO-1 orbital (primarily dπ → CC π^*_v) accounts for the bulk of the calculated barriers since two electrons occupy the HOMO-1 in all cases. A complementary drop in relative LUMO energy occurs as the alkyne rotates. Although no electrons are located in the LUMO, there will be lower lying filled orbitals which are inversely related to the LUMO in an energetic sense. The energy of these orbitals will increase in response to alkyne rotation and contribute to the overall rotation barrier.

Synthesis and Structure of a Cyanide-Bridged Bimetallic Complex. The monomeric isocyanide complexes consistently crystallized as sharp needles, frustrating attempts at X-ray crystallographic measurement. Use of a large metal complex as the Lewis acid to bind to the cyanide nitrogen was attempted. The combination of [Tp′(CO)(PhC≡CMe)W−OEt_2][BAr′$_4$][55] (Ar′ = 3,5-trifluoromethylphenyl), a Lewis acid, with **2a** in CH_2Cl_2 solution produced the cyanide-bridged bimetallic complex [Tp′(CO)(HC≡CBu^n)W−C≡N−W(PhC≡CMe)(CO)Tp′][BAr′$_4$], **7**, in moderate yield (eq 6). Single



(6)

crystals of **7** were obtained from recrystallization in CH_2Cl_2/pentane, and a crystal structure was undertaken to confirm the alkyne orientation. As shown in Figure 6, the 1-hexyne ligand aligns parallel to the W−CO axis.

The relative orientation of the two metal fragments is such that the two carbonyls are disposed nearly 180° relative to each other ({C(7)−W(2)}−{W(1)−C(1)} = 174.4°), whereas the alkyne ligands are eclipsed. The effective geometry about each metal center is distorted pseudo-octahedral. Specifically, the pyrazole rings trans to either side of the cyanide bridge form N−W−(C≡N) angles substantially less than 180° (Table 5) and the pyrazole ligands cis to the cyanide bridge form acute N−W−(C≡N) angles. Obtuse angles are found for the carbonyl and alkyne ligands in relation to the cyanide bridge. The cyanide linkage is nonlinear toward both metal centers. The overall effect is to bring the bulky Tp′ ligands closer together. We attribute the bending to constructive CH−π interactions[56] between the pyrazole rings on adjacent metal centers. In particular, note

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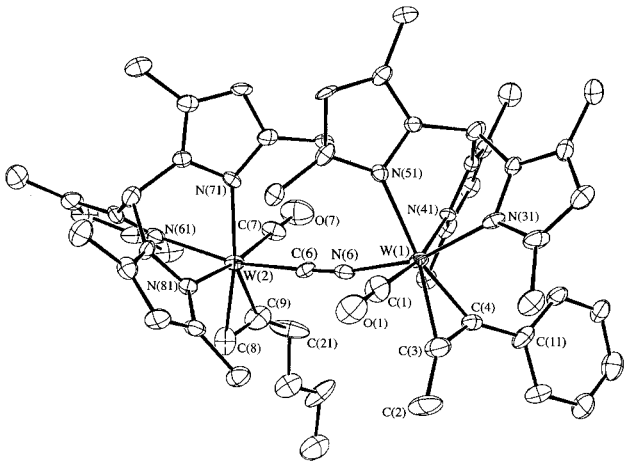
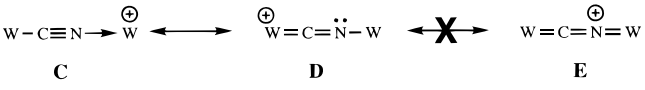


Figure 6. ORTEP representation of [Tp′(CO)(Bu^{n}C≡CMeW−C≡N−W(PhC≡CMe)(CO)Tp′][B(Ar′)$_4$] (**7**). The B(Ar′)$_4$ counterion has been omitted for clarity.

Table 5. Selected Bond Distances (Å) and Bond Angles (deg) for [Tp′(CO)(Bu^{n}C≡CMeW−C≡N−W(PhC≡CMe)(CO)Tp′][B(Ar′)$_4$] (7)

W(1)−N(6)	2.128 (8)	W(2)−C(6)	2.110 (9)
W(1)−C(1)	1.948 (10)	W(2)−C(7)	1.950 (10)
W(1)−C(3)	2.077 (10)	W(2)−C(8)	2.036 (12)
W(1)−C(4)	2.029 (9)	W(2)−C(9)	2.046 (10)
W(1)−N(6)	2.128 (8)	W(2)−C(6)	2.110 (10)
W(1)−N(31)	2.155 (8)	W(2)−N(61)	2.189 (8)
W(1)−N(41)	2.216 (7)	W(2)−N(71)	2.224 (7)
W(1)−N(51)	2.235 (7)	W(2)−N(81)	2.246 (7)
C(1)−O(2)	1.144 (13)	C(7)−O(7)	1.169 (13)
C(3)−C(4)	1.332 (15)	C(8)−C(9)	1.333 (17)
C(2)−C(3)	1.468 (16)	C(9)−C(21)	1.514 (17)
C(4)−C(11)	1.469 (14)	C(6)−N(6)	1.166 (13)
C(1)−W(1)−C(3)	70.9 (4)	C(7)−W(2)−C(8)	107.3 (4)
C(1)−W(1)−C(4)	107.9 (4)	C(7)−W(2)−C(9)	69.5 (5)
C(1)−W(1)−N(6)	92.0 (4)	C(7)−W(2)−C(6)	93.0 (4)
C(3)−W(1)−C(4)	37.8 (4)	C(8)−W(2)−C(9)	38.1 (5)
C(1)−W(1)−N(31)	95.8 (4)	C(7)−W(2)−N(61)	95.5 (4)
C(1)−W(1)−N(41)	167.2 (4)	C(7)−W(2)−N(71)	86.6 (4)
C(1)−W(1)−N(51)	86.8 (4)	C(7)−W(2)−N(81)	168.6 (4)
N(6)−W(1)−C(3)	93.9 (3)	C(6)−W(2)−C(8)	98.2 (4)
N(6)−W(1)−C(4)	101.9 (3)	C(6)−W(2)−C(9)	95.1 (4)
N(6)−W(1)−N(31)	162.9 (3)	C(6)−W(2)−N(61)	159.1 (3)
N(6)−W(1)−N(41)	82.7 (3)	C(6)−W(2)−N(71)	81.9 (3)
N(6)−W(1)−N(51)	84.8 (3)	C(6)−W(2)−N(81)	83.3 (3)
N(31)−W(1)−N(41)	86.4 (3)	N(61)−W(2)−N(71)	79.6 (3)
N(31)−W(1)−N(51)	80.5 (3)	N(61)−W(2)−N(81)	84.7 (3)
N(41)−W(1)−N(51)	81.3 (3)	N(71)−W(2)−N(81)	82.2 (3)
W(1)−N(6)−C(6)	170.5 (7)	W(1)−C(6)−N(6)	174.3 (7)
W(1)−C(1)−O(1)	177.3 (10)	W(2)−C(7)−O(7)	177.8 (10)

Chart 4. Possible Resonance Forms for 7



the "gearing" of rings N(81)−C(85) and N(71)−N(75) with rings N(51)−C(55) and N(41)−C(45).

The C≡N bond of **7** (1.166 Å) is apparently elongated relative to **4a** (C≡N = 1.034 Å), suggestive of contribution from resonance form **D** (Chart 4). However, the W−N bond distances to the pyrazole ring trans to the isocyanide ligands in each complex are nearly identical (**7**, 2.189 Å; **4a**, 2.192 Å). It may be that the cyanide carbon refines into a relatively "soft" position similar to terminal carbonyl ligand carbons.[57] Also, the high ν_{CN} value of 2128 cm^{-1} for **7** argues against form **D**. Therefore, we propose that resonance form **C** is the major contributor to complex **7**. Note that the relative orientation of the metal fragments, with eclipsed alkyne ligands, prevents full delocalization to resonance form **E** because of a filled−filled interaction between the nitrogen lone pair and the appropriate metal dπ orbital.

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Summary

The synthesis of chiral cyanide complexes containing three disparate π-acid ligands (C≡O, RC≡CR′, and C≡N$^-$) has been accomplished. Addition of electrophiles to the cyanide nitrogen produces both neutral and cationic isocyanide complexes. Variable-temperature ^{1}H NMR measurements of acetylene rotational barriers in Tp′(CO)(L)W(HC≡CH)$^{n+}$ (L = CO, CNH, CNMe {n = 1}; CN$^-$, CNBF$_3^-$ {n = 0}) complexes have provided direct experimental evidence for metal d$\pi \rightarrow$ isocyanide C≡N π^* back-bonding interactions in electron-poor complexes, even in the presence of two stronger π-acids in the coordination sphere. EHMO calculations on related models support the experimental data. Single-crystal X-ray structures of Tp′(CO)(CN)W(PhC≡CMe) and of a cyanide-bridged bimetallic complex, [Tp′(CO)-(HC≡CBu^n)W−C≡N−W(PhC≡CMe)(CO)Tp′][BAr′$_4$], show that the alkyne ligands align parallel to the W−CO axes.

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: hexanes, CH_2Cl_2, and Et_2O were degassed and passed through activated alumina; THF was distilled from Na/benzophenone; anhydrous ethyl acetate (99.8%) was obtained from Aldrich, Inc. and used as purchased. Alkyne complexes of the form Tp′(CO)(I)W(RC≡CR′) were prepared as described in the literature.[6,42] Microanalyses were performed by Atlantic Microlab, Inc., Norcross, GA.

Synthesis of Tp′(CO)(CN)W(RC≡CR′) Complexes (1a−4a). To synthesize the cyanide derivatives, Tp′(CO)(I)W(RC≡CR′) complexes were allowed to reflux in anhydrous ethyl acetate in the presence of 1−1.2 equiv of silver cyanide. After 24−48 h, the solvent was removed and the residues were chromatographed on alumina. Initial elution with 1:1 hexanes/CH_2Cl_2 allowed clean recovery of unreacted starting material. The cyanide complexes were collected as blue bands with 1:1 CH_2Cl_2/THF as the eluent. After recrystallization of both fractions from CH_2Cl_2/hexanes, the combined weight of starting material and product typically accounted for 85−90% of the initial alkyne complex. Reaction times and specific product yields are given with the spectroscopic data.

Synthesis of Tp′(CO)(CNBF$_3$)W(RC≡CR′) Complexes (1b−4b). Synthesis of the BF_3 adducts was accomplished by treatment of the corresponding cyanide complexes with 1.2 equiv of HBF_4 at 0 °C in CH_2Cl_2 followed by recrystallization from CH_2Cl_2/Et_2O or CH_2Cl_2/hexanes. In general, the reactions were complete within 5 min of HBF_4 addition as monitored by IR spectroscopy. Specific yields are given with the spectroscopic data.

Synthesis of [Tp′(CO)(CNMe)W(RC≡CR′)][O$_3$SCF$_3$] Complexes (1c−4c). Synthesis of the methyl isocyanide derivatives was accomplished by treatment of the corresponding cyanide complexes with 1 equiv of [Me][O_3SCF_3] at ambient temperature in CH_2Cl_2 followed by recrystallization from CH_2Cl_2/Et_2O or CH_2Cl_2/hexanes. Reaction times were on the order of 1−1.5 h; reaction completeness was judged by examination

of the IR spectra of reaction mixtures. Specific yields are given with the spectroscopic data.

Tp′(CO)(CN)W(HC≡CH) (1a). Blue, 48 h, 44%. IR (KBr, cm^{-1}): ν_{BH} 2555; $\nu_{C\equiv N}$ 2114; $\nu_{C\equiv O}$ 1910; $\nu_{C=N}$(Tp′) 1543. ^{1}H NMR (CD_2Cl_2, δ): 13.71 (HC≡CH_{syn}), 12.78 (H_{anti}C≡CH), 6.16, 5.93, 5.82 (Tp′C*H*), 2.78, 2.55, 2.44, 2.37, 1.67 (3:6:3:3:3, Tp′CH_3). ^{13}C NMR (CD_2Cl_2, δ): 229.1 (d, $^3J_{CH}$ = 6.4 Hz, $^1J_{WC}$ = 136 Hz, *C*O), 214.2 (dd, $^1J_{CH}$ = 213 Hz, $^2J_{CH}$ = 7.4 Hz, $^1J_{WC}$ = 52 Hz, HC_{syn}≡CH), 204.7 (dd, $^1J_{CH}$ = 210 Hz, $^2J_{CH}$ = 9.2 Hz, $^1J_{WC}$ = 12 Hz, HC≡*C*H), 155.2, 154.3, 149.0, 146.8, 146.2, 144.8 (Tp′*C*CH$_3$), 150.7 ($^1J_{WC}$ = 140 Hz, *C*N), 108.3, 108.1, 107.6 (Tp′*C*H), 16.9, 16.5, 16.3, 12.9, 12.7, 12.6 (Tp′*C*H$_3$). Anal. Calcd for $WC_{19}H_{24}N_7BO$: C, 40.67; H, 4.31; N, 17.47. Found: C, 40.53; H, 4.28; N, 17.38.

[Tp′(CO)(CNBF$_3$)W(HC≡CH)] (1b). Green, 74%. IR (KBr, cm^{-1}): ν_{BH} 2561; $\nu_{C\equiv N}$ 2192; $\nu_{C\equiv O}$ 1971; $\nu_{C=N}$(Tp′) 1545; ν_{BF} 1206, 1133, 917, 892. ^{1}H NMR (CD_2Cl_2, −69 °C, δ): 13.99 (HC≡C*H*), 13.13 (*H*C≡CH), 6.16, 5.96, 5.87 (Tp′C*H*), 2.57, 2.50, 2.41, 2.38, 2.34, 1.56 (Tp′CH_3). ^{13}C NMR (CD_2Cl_2, −69 °C, δ): 222.1 (d, $^3J_{CH}$ = 8.3 Hz, $^1J_{WC}$ = 136 Hz, *C*O), 218.6 (dd, $^1J_{CH}$ = 215 Hz, $^2J_{CH}$ = 7.4 Hz, $^1J_{WC}$ = 51 Hz, HC_{anti}≡CH), 207.1 (dd, $^1J_{CH}$ = 222 Hz, $^2J_{CH}$ = 9.2 Hz, $^1J_{WC}$ = 13 Hz, HC≡C_{syn}H), 154.4, 153.6, 148.4, 147.1, 147.1, 144.8 (Tp′*C*CH$_3$), 147.7 (br, *C*NBF$_3$), 107.9, 107.3 (2:1, Tp′*C*H), 16.1, 15.8, 15.5, 12.8, 12.4 (1:1:1:1:2, Tp′*C*H$_3$). Anal. Calcd for $WC_{19}H_{24}N_7B_2F_3O$: C, 36.29; H, 3.85; N, 15.59. Found: C, 36.44; H, 3.98; N, 15.32.

[Tp′(CO)(CNMe)W(HC≡CH)][O$_3$SCF$_3$] (1c). Dark blue, 78%. IR (KBr, cm^{-1}): ν_{BH} 2555; $\nu_{C\equiv N}$ 2225; $\nu_{C\equiv O}$ 1974; $\nu_{C=N}$(Tp′) 1543. ^{1}H NMR (CD_2Cl_2, −65 °C, δ): 14.24 (HC≡CH_{syn}), 13.30 (H_{anti}C≡CH), 6.19, 6.02, 5.88 (Tp′C*H*), 3.77 (CN*Me*), 2.51, 2.42, 2.35, 2.33, 1.55 (6:3:3:3:3, Tp′CH_3). ^{13}C NMR (CD_2Cl_2, −65 °C, δ): 219.8 (dd, $^1J_{CH}$ = 215 Hz, $^2J_{CH}$ = 7.4 Hz, $^1J_{WC}$ = 51 Hz, HC_{anti}≡CH), 219.5 (d, $^3J_{CH}$ = 7.4 Hz, $^1J_{WC}$ = 133 Hz, *C*O), 207.5 (dd, $^1J_{CH}$ = 223 Hz, $^2J_{CH}$ = 10 Hz, HC≡C_{syn}H), 154.1, 153.4, 148.5, 147.7, 147.5, 145.1 (Tp′*C*CH$_3$), 147.0 ($^1J_{WC}$ = 144 Hz, *C*N), 120.3 (q, $^1J_{CF}$ = 320 Hz, O$_3$S*C*F$_3$), 108.2, 108.0, 107.4 (Tp′*C*H), 31.33 (q, $^1J_{CH}$ = 147 Hz, CN*Me*), 16.5, 15.80, 15.76, 12.9, 12.44, 12.39 (Tp′*C*H$_3$). Anal. Calcd for $WC_{21}H_{27}N_7BF_3O_4S$: C, 34.78; H, 3.75; N, 13.53. Found: C, 34.84; H, 3.75; N, 13.59.

[Tp′(CO)(CNH)W(HC≡CH)][O$_3$SCF$_3$] (1d). A CH_2Cl_2 (20 mL) solution containing 0.110 g (0.196 mmol) of **1a** was cooled to −78 °C to form a slurry. A stoichiometric amount of HO_3SCF_3 was added. No change was noted for the solution. Upon warming to room temperature, the solution turned green and the CO stretching frequency shifted to higher energy. Broad, multiple absorptions were noted in the C≡N stretching region. The solvent volume was reduced to ca. 5 mL, and 20 mL of hexanes was layered over the dark green solution. A dark green solid resulted; 0.115 g (83%) was collected from two crops. IR (KBr, cm^{-1}) ν_{BH} 2560; $\nu_{C\equiv N}$ 2134; $\nu_{C\equiv O}$ 1945; $\nu_{C=N}$(Tp′) 1544. ^{1}H NMR (CD_2Cl_2, −85 °C, δ): 13.95 (HC≡CH_{syn}), 13.03 (H_{anti}C≡CH), 6.16, 5.95, 5.83 (Tp′C*H*), 2.53, 2.47, 2.38, 2.34, 2.32, 1.53 (Tp′CH_3). ^{13}C NMR (CD_2Cl_2, −85 °C, δ): 223.2 ($^1J_{WC}$ = 139 Hz, *C*O), 217.5 (d, br, $^1J_{CH}$ = 213 Hz, HC_{anti}≡CH), 206.6 (dd, $^1J_{CH}$ = 221 Hz, $^2J_{CH}$ = 9.2 Hz, HC≡C_{syn}H), 154.3, 153.5, 148.1, 147.0, 144.8 (1:1:1:2:1, Tp′*C*CH$_3$), 147.6 ($^1J_{WC}$ = 140 Hz, *C*NH), 119.1 (q, $^1J_{CF}$ = 320 Hz, O$_3$S*C*F$_3$), 107.7, 107.0 (2:1, Tp′*C*H), 16.2, 15.7, 15.6, 12.8, 12.4 (1:1:1:1:2, Tp′*C*H$_3$). Anal. Calcd for $WC_{20}H_{25}N_7BF_3O_4S$: C, 33.78; H, 3.53; N, 13.79. Found: C, 33.69; H, 3.85; N, 13.19.

Tp′(CO)(CN)W(HC≡CBu^n) (2a). Blue-violet, 24 h, 55%. IR (KBr, cm^{-1}): ν_{BH} 2557; $\nu_{C\equiv N}$ 2112; $\nu_{C\equiv O}$ 1910; $\nu_{C=N}$(Tp′) 1544. ^{1}H NMR (CD_2Cl_2, δ): 12.72 (H_{anti}C≡CBu^n), 6.15, 5.92, 5.81 (Tp′C*H*), 3.85, 3.67 (ea.m, HC≡CCH_2CH$_2$CH$_2$CH$_3$), 2.79, 2.55, 2.51, 2.45, 2.38, 1.58 (Tp′CH_3), 2.10−1.89 (m, HC≡CCH$_2$CH_2-CH$_2$CH$_3$), 1.57 (m, HC≡CCH$_2$CH$_2$CH_2CH$_3$), 1.05 (t, $^3J_{HH}$ = 7.4 Hz, HC≡CCH$_2$CH$_2$CH$_2$CH_3). ^{13}C NMR (CD_2Cl_2, δ): 229.3 (d, $^3J_{CH}$ = 2 Hz, $^1J_{WC}$ = 140 Hz, *C*O), 216.2 (m, $^1J_{WC}$ = 12 Hz, Bu^{n}C≡CH), 204.7 (dt, $^1J_{CH}$ = 211 Hz, $^3J_{CH}$ = 3 Hz, $^1J_{WC}$ = 51 Hz, Bu^{n}C≡*C*H), 154.9, 154.5, 150.3, 146.6, 146.1, 144.6 (Tp′*C*CH$_3$), 150.8 ($^1J_{WC}$ = 138 Hz, *C*N), 108.2, 108.0, 107.5 (Tp′*C*H), 37.5 (t, $^1J_{CH}$ = 129 Hz, H≡C*C*H$_2$CH$_2$CH$_2$CH$_3$), 33.1 (t, $^1J_{CH}$ = 128, H≡CCH$_2$*C*H$_2$CH$_2$CH$_3$), 22.9 (t, $^1J_{CH}$ = 125, H≡CCH$_2$CH$_2$*C*H$_2$CH$_3$), 16.8, 16.6, 16.2, 12.9, 12.7 (1: 1:1:1:2, Tp′*C*H$_3$), 14.0 (H≡CCH$_2$CH$_2$CH$_2$*C*H$_3$). Anal. Calcd for $WC_{23}H_{32}N_7BO$: C, 44.76; H, 5.23; N, 15.89. Found: C, 44.88; H, 5.20; N, 15.91.

[Tp′(CO)(CNBF$_3$)W(HC≡CBu^n)] (2b). Blue, 73%. IR (KBr, cm^{-1}): ν_{BH} 2569; $\nu_{C\equiv N}$ 2188; $\nu_{C\equiv O}$ 1948; $\nu_{C=N}$(Tp′) 1544; ν_{BF} 1207, 1140, 906, 880. ^{1}H NMR (CD_2Cl_2, δ): 13.01 (H_{anti}C≡CBu^n), 6.15, 5.97, 5.86 (Tp′C*H*), 3.97, 3.77 (ea.m, HC≡CCH_2-CH$_2$CH$_2$CH$_3$), 2.65, 2.55, 2.47, 2.39, 2.38, 1.55 (Tp′CH_3), 2.12−1.87 (m, HC≡CCH$_2$CH_2CH$_2$CH$_3$), 1.53 (m, HC≡CCH$_2$CH$_2$-CH_2CH$_3$), 1.05 (t, $^3J_{HH}$ = 7.4 Hz, HC≡CCH$_2$CH$_2$CH$_2$CH_3). ^{13}C NMR (CD_2Cl_2, δ): 223.3 ($^1J_{WC}$ = 139 Hz, *C*O), 219.0 (m, $^1J_{WC}$ = 13 Hz, HC≡C_{syn}Bu^n), 215.1 (d, $^1J_{CH}$ = 210 Hz, $^1J_{WC}$ = 51 Hz, HC_{anti}≡CBu^n), 154.9, 154.8, 150.5, 147.5, 147.4, 145.2 (Tp′*C*CH$_3$), 148.4 (br, *C*NBF$_3$), 108.6, 108.0 (2:1, Tp′*C*H), 38.0 (t, $^1J_{CH}$ = 129 Hz, HC≡C*C*H$_2$CH$_2$CH$_2$CH$_3$), 32.9 (t, $^1J_{CH}$ = 127, HC≡CCH$_2$*C*H$_2$CH$_2$CH$_3$), 22.8 (t, $^1J_{CH}$ = 125, HC≡CCH$_2$*C*H$_2$-CH$_2$CH$_3$), 16.5, 16.1, 13.0, 12.70, 12.66 (1:2:1:1:1, Tp′*C*H$_3$), 13.9 (HC≡CCH$_2$CH$_2$CH$_2$*C*H$_3$). Anal. Calcd for $WC_{23}H_{32}N_7B_2F_3O$: C, 40.59; H, 4.74; N, 14.41. Found: C, 40.05; H, 4.81; N, 14.00.

[Tp′(CO)(CNMe)W(HC≡CBu^n)][O$_3$SCF$_3$] (2c). Aqua, 95%. IR (KBr, cm^{-1}): ν_{BH} 2563; $\nu_{C\equiv N}$ 2211; $\nu_{C\equiv O}$ 1945; $\nu_{C=N}$(Tp′) 1544. ^{1}H NMR (CD_2Cl_2, δ): 13.19 (H_{anti}C≡CBu^n), 6.18, 6.03, 5.89 (Tp′C*H*), 3.95, 3.75 (ea.m, HC≡CCH_2CH$_2$CH$_2$CH$_3$), 3.81 (CN*Me*), 2.57, 2.55, 2.47, 2.40, 2.31, 1.53 (Tp′CH_3), 2.15−1.89 (m, HC≡CCH$_2$CH_2CH$_2$CH$_3$), 1.56 (m, HC≡CCH$_2$CH$_2$CH_2CH$_3$), 1.05 (t, $^3J_{HH}$ = 7.2 Hz, HC≡CCH_2CH$_2$CH$_2$CH_3). ^{13}C NMR (CD_2Cl_2, δ): 220.3 ($^1J_{WC}$ = 140 Hz, *C*O), 219.5 (m, $^1J_{WC}$ = 13 Hz, HC≡C_{syn}Bu^n), 217.0 (d, $^1J_{CH}$ = 210 Hz, $^1J_{WC}$ = 48 Hz, HC_{anti}≡CBu^n), 154.4, 154.3, 150.7, 148.2, 148.0, 145.6 (Tp′*C*CH$_3$), 150.0 (br, *C*NMe), 121.4 (q, $^1J_{CF}$ = 320 Hz, O$_3$S*C*F$_3$), 109.0, 108.7, 108.2 (Tp′*C*H), 38.4 (t, $^1J_{CH}$ = 131 Hz, HC≡C*C*H$_2$CH$_2$-CH$_2$CH$_3$), 33.0 (t, $^1J_{CH}$ = 130, HC≡CCH$_2$*C*H$_2$CH$_2$CH$_3$), 31.8 (q, $^1J_{CH}$ = 147 Hz, CN*Me*), 22.8 (t, $^1J_{CH}$ = 126, HC≡CCH$_2$-CH$_2$*C*H$_2$CH$_3$), 16.8, 16.2, 16.0, 13.0, 12.7, 12.6 (Tp′*C*H$_3$), 13.9 (HC≡CCH$_2$CH$_2$CH$_2$*C*H$_3$). Anal. Calcd for $WC_{25}H_{35}N_7BF_3O_4S$: C, 38.43; H, 4.51; N, 12.55. Found: C, 38.36; H, 4.48; N, 12.63.

Tp′(CO)(CN)W(PhC≡CH) (3a, 3a′). Blue-green, 81%. IR (KBr, cm^{-1}): ν_{BH} 2549; $\nu_{C\equiv N}$ 2110; $\nu_{C\equiv O}$ 1928; $\nu_{C=N}$(Tp′) 1544. ^{1}H NMR (CD_2Cl_2, δ): *Major isomer* (**3a**, 79%) 13.68 ($^2J_{WH}$ = 4.4 Hz, PhC≡CH_{syn}), 7.28 (m, 3H, *Ph*), 6.90 (m, 2H, *Ph*), 5.93, 5.78 (2:1, Tp′C*H*), 2.87, 2.58, 2.52, 2.37, 1.76, 1.46 (3H ea., Tp′CH_3); *Minor isomer* (**3a′**, 21%) 12.87 (H_{anti}C≡CPh), 7.89 (m, 2H, *Ph*), 7.63 (m, 2H, *Ph*), 7.52 (m, 1H, *Ph*), 6.14, 5.82, 5.78 (2:1, Tp′C*H*), 2.87, 2.55, 2.47, 2.44, 2.27, 1.54 (3H ea., Tp′CH_3). ^{13}C NMR (CD_2Cl_2, δ): *Major isomer* (**3a**) 230.9 (d, $^3J_{CH}$ = 8.3 Hz, $^1J_{WC}$ = 135 Hz, *C*O), 219.2 ($^1J_{WC}$ = 52 Hz, PhC_{anti}≡CH), 202.9 (d, $^1J_{CH}$ = 210 Hz, $^1J_{WC}$ = 11 Hz, PhC≡C_{syn}H), 154.9, 154.7, 148.5, 146.4, 146.3, 145.1 (Tp′*C*CH$_3$), 152.5 ($^1J_{WC}$ = 138 Hz, *C*N), 136.3 (Ph, C_{ipso}), 131.1 (Ph, C_{meta}), 130.5 (Ph, C_{para}), 129.0 (Ph, C_{ortho}), 108.4, 108.1, 107.3 (Tp′*C*H), 16.5, 16.2, 15.9, 13.0, 12.84, 12.75 (Tp′*C*H$_3$); *Minor isomer* 231.6 ($^1J_{WC}$ = 134 Hz, *C*O), 214.8 (d, $^1J_{CH}$ = 200 Hz, $^1J_{WC}$ = 48 Hz, HC_{anti}≡CH), 211.1 ($^1J_{WC}$ = 16 Hz, HC≡C_{syn}Ph), 154.9, 154.7, 150.4, 146.8, 146.4, 144.8 (Tp′*C*CH$_3$), 150.7 ($^1J_{WC}$ = 138 Hz, *C*N), 138.4 (Ph, C_{ipso}), 130.8 (Ph, C_{meta}), 130.7 (Ph, C_{para}), 129.3 (Ph, C_{ortho}), 108.3, 108.2, 107.6 (Tp′*C*H), 16.8, 16.8, 16.5, 13.0, 12.84, 12.75, 12.7 (Tp′*C*H$_3$). Anal. Calcd for $WC_{25}H_{28}N_7BO\cdot0.25CH_2Cl_2$: C, 46.06; H, 4.36; N, 14.89. Found: C, 46.41; H, 4.55; N, 14.72.

[Tp′(CO)(CNBF$_3$)W(PhC≡CH)] (3b, 3b′). Dark green, 78%. IR (KBr, cm^{-1}): ν_{BH} 2551; $\nu_{C\equiv N}$ 2185; $\nu_{C\equiv O}$ 1958; $\nu_{C=N}$(Tp′) 1543; ν_{BF} 1202, 1133, 909, 885. ^{1}H NMR (CD_2Cl_2, δ): *Major isomer* (**3b**, 76%) 13.90 ($^2J_{WH}$ = 4 Hz, PhC≡CH_{syn}), 7.68 (*Ph*$_{meta}$), 7.59 (*Ph*$_{para}$), 6.99 (*Ph*$_{ortho}$), 5.99, 5.95, 5.83 (Tp′C*H*), 2.75, 2.60, 2.56, 2.40, 1.63, 1.40 (Tp′CH_3); *Minor isomer* (**3b′**, 24%) 13.30 (H_{anti}C≡CPh), 7.93 (*Ph*$_{ortho}$), 7.39 (*Ph*$_{para}$), 7.31 (*Ph*$_{meta}$), 6.15, 5.99, 5.87 (Tp′C*H*), 2.75, 2.57, 2.50, 2.40, 2.30,

1.50 (Tp′CH_3). ^{13}C NMR (CD_2Cl_2, δ): *Major isomer* (**3b**) 225.0 (d, $^3J_{CH}$ = 7.5 Hz, $^1J_{WC}$ = 134 Hz, *C*O), 222.5 (m, $^1J_{WC}$ = 52 Hz, PhC$_{anti}$≡CH), 204.3 (d, $^1J_{CH}$ = 220 Hz, $^1J_{WC}$ = 11 Hz, PhC≡*C*$_{syn}$H), 155.2, 154.8, 148.6, 147.7, 147.0, 145.8 (Tp′*C*CH$_3$), 150.0 (br, *C*NH), 135.1 (Ph, *C*$_{ipso}$), 131.9 (Ph, *C*$_{meta}$), 131.8 (Ph, *C*$_{para}$), 129.3 (Ph, *C*$_{ortho}$), 108.8, 108.7, 107.6 (Tp′*C*H), 16.1, 15.4, 13.1, 12.8 (1:2:1:2, Tp′*C*H$_3$); *Minor isomer* (**3b′**) 225.1 ($^1J_{WC}$ = 140 Hz, *C*O), 219.7 (d, $^1J_{CH}$ = 210 Hz, $^1J_{WC}$ = 48 Hz, H$_{anti}$≡CPh), 212.1 (m, $^1J_{WC}$ = 12 Hz, HC≡*C*$_{syn}$Ph), 155.0, 154.8, 150.6, 147.7, 147.5, 145.3 (Tp′*C*CH$_3$), 137.4 (Ph, *C*$_{ipso}$), 131.9 (Ph, *C*$_{para}$), 131.1 (Ph, *C*$_{meta}$), 129.6 (Ph, *C*$_{ortho}$), 108.8, 108.6, 107.9 (Tp′*C*H), 16.6, 16.4, 16.3, 13.1, 12.7 (1:1:1:1:2, Tp′*C*H$_3$). Anal. Calcd for $WC_{25}H_{28}N_7B_2F_3O$: C, 42.59; H, 4.00; N, 13.91. Found: C, 42.22; H, 4.16; N, 13.48.

[Tp′(CO)(CNMe)W(PhC≡CH)][O$_3$SCF$_3$] (3c, 3c′). Green, 85%. IR (KBr, cm^{-1}): ν_{BH} 2560; $\nu_{C\equiv N}$ 2210; $\nu_{C\equiv O}$ 1950; $\nu_{C=N}$(Tp′) 1544. ^{1}H NMR (CD_2Cl_2, δ): *Major isomer* (**3c**, 84%) 14.10 ($^1J_{WH}$ = 5 Hz, PhC≡C*H*$_{syn}$), 7.44 (1H, *Ph*$_{para}$), 7.34 (2H, *Ph*$_{meta}$), 7.03 (*Ph*$_{ortho}$), 6.04, 5.99, 5.85 (1H ea., Tp′C*H*), 3.89 (3H, CN*Me*), 2.69, 2.62, 2.57, 2.42, 1.52, 1.36 (3H ea., Tp′C*H*$_3$); *Minor isomer* (**3c′**, 16%) 13.50 (PhC≡C*H*$_{syn}$), 8.00 (1H, *Ph*$_{ortho}$), 7.73 (2H, *Ph*$_{meta}$), 7.64 (*Ph*$_{para}$), 6.19, 6.06, 5.90 (1H ea., Tp′C*H*), 3.89 (3H, CN*Me*), 2.69, 2.57, 2.51, 2.42, 2.23, 1.47 (3H ea., Tp′C*H*$_3$). ^{13}C NMR (CD_2Cl_2, δ): *Major isomer* (**3c**) 223.4 (q, $^3J_{CH}$ = $^2J_{CH}$ = 5.6 Hz, $^1J_{WC}$ = 50 Hz, PhC$_{anti}$≡CH), 222.0 (d, $^3J_{CH}$ = 8.3 Hz, $^1J_{WC}$ = 133 Hz, *C*O), 204.5 (d, $^1J_{CH}$ = 220 Hz, $^1J_{WC}$ = 11 Hz, PhC≡*C*$_{syn}$H), 154.8, 154.2, 148.9, 148.5, 147.6, 146.3 (Tp′*C*CH$_3$), 151.9 (br, *C*NMe), 135.5 (Ph, *C*$_{ipso}$), 132.5 (Ph, *C*$_{para}$), 132.3, 129.5 (Ph, *C*$_{ortho}$, *C*$_{meta}$), 121.5 (q, $^1J_{CF}$ = 320 Hz, O$_3$S*C*F$_3$), 109.1, 108.8, 107.9 (Tp′*C*H), 31.8 (q, $^1J_{CH}$ = 147 Hz, CN*C*H$_3$), 16.3, 16.0, 15.4, 13.1, 12.8 (1:1:1:1:2, Tp′*C*H$_3$); *Minor isomer* (**3c′**) 222.1 (d, $^1J_{CH}$ = 211 Hz, $^1J_{WC}$ = 37 Hz, H*C*$_{anti}$≡CPh), 216.5 (*C*O), 211.7 (HC≡*C*$_{syn}$Ph), 154.6, 154.2, 151.0, 148.5, 148.0, 148.5 (Tp′*C*CH$_3$), 136.7 (Ph, *C*$_{ipso}$), 132.6 (Ph, *C*$_{para}$), 131.7, 129.9 (Ph, *C*$_{ortho}$, *C*$_{meta}$), 109.2, 108.7, 108.3 (Tp′*C*H), 31.9 (q, $^1J_{CH}$ = 147 Hz, CN*C*H$_3$), 16.9, 16.6, 15.4, 14.2, 12.7 (1:1:1:1:2, Tp′*C*H$_3$). Anal. Calcd for $WC_{27}H_{31}N_7BF_3O_4$: C, 40.47; H, 3.90; N, 12.24. Found: C, 40.22; H, 3.96; N, 11.97.

Tp′(CO)(CN)W(PhC≡CMe) (4a). Royal blue, 80%. IR (KBr, cm^{-1}): ν_{BH} 2554; $\nu_{C\equiv N}$ 2109; $\nu_{C\equiv O}$ 1918; $\nu_{C=N}$(Tp′) 1545. ^{1}H NMR (CD_2Cl_2, δ): 7.28 (m, 3H, *Ph*), 6.30 (m, 2H, *Ph*), 5.93, 5.88, 5.77 (Tp′C*H*), 3.61 (PhC≡C*Me*), 2.88, 2.57, 2.52, 2.38, 1.70, 1.33 (Tp′C*H*$_3$). ^{13}C NMR (CD_2Cl_2, δ): 231.5 ($^1J_{WC}$ = 138 Hz, *C*O), 215.2 ($^1J_{WC}$ = 53 Hz, PhC$_{anti}$≡CMe), 211.3 ($^1J_{WC}$ = 12 Hz, PhC≡*C*$_{syn}$Me), 154.8, 154.5, 149.7, 146.3, 146.1, 144.9 (Tp′*C*CH$_3$), 152.6 ($^1J_{WC}$ = 138 Hz, *C*N), 137.3 (Ph, *C*$_{ipso}$), 129.7 (Ph, *C*$_{para}$), 129.5, 128.9 (Ph, *C*$_{ortho}$, *C*$_{meta}$), 108.2, 108.1, 107.3 (Tp′*C*H), 22.8 (PhC≡C*Me*), 16.6, 16.0, 15.7, 13.0, 12.8, 12.7 (Tp′*C*H$_3$). Anal. Calcd for $WC_{26}H_{30}N_7BO\cdot0.75CH_2Cl_2$ (see X-ray): C, 44.94; H, 4.44; N, 13.71. Found: C, 44.91; H, 4.39; N, 13.62.

[Tp′(CO)(CNBF$_3$)W(PhC≡CMe)] (4b). Blue-green, 77%. IR (KBr, cm^{-1}): $\nu_{C\equiv N}$ 2178; $\nu_{C\equiv O}$ 1939; $\nu_{C=N}$(Tp′) 1543. ^{1}H NMR (CD_2Cl_2, δ): 7.39 (*Ph*$_{para}$), 7.31 (*Ph*$_{meta}$), 6.92 (*Ph*$_{ortho}$), 5.99, 5.91, 5.82 (Tp′C*H*), 3.71 (PhC≡C*Me*), 2.76, 2.59, 2.56, 2.40, 1.57, 1.29 (Tp′C*H*$_3$). ^{13}C NMR (CD_2Cl_2, δ): 226.2 ($^1J_{WC}$ = 136 Hz, *C*O), 219.2 ($^1J_{WC}$ = 51 Hz, PhC$_{anti}$≡CMe), 213.3 ($^1J_{WC}$ = 13 Hz, $^2J_{CH}$ = 7 Hz, PhC≡*C*$_{syn}$Me), 155.3, 154.4, 149.9, 147.5, 146.8, 145.6 (Tp′*C*CH$_3$), 151 (br, *C*NBF$_3$), 136.7 (Ph, *C*$_{ipso}$), 131.1 (Ph, *C*$_{para}$), 130.3, 129.3 (Ph, *C*$_{ortho}$, *C*$_{meta}$), 108.7, 108.5, 107.7 (Tp′*C*H), 23.7 ($^1J_{CH}$ = 130 Hz, PhC≡C*Me*), 16.3, 15.8, 15.3, 13.1, 12.8 (1:1:1:2, Tp′*C*H$_3$). Anal. Calcd for $WC_{26}H_{30}N_7B_2F_3O$: C, 43.43; H, 4.21; N, 13.64. Found: C, 43.38; H, 4.33; N, 13.58.

[Tp′(CO)(CNMe)W(PhC≡CMe)][O$_3$SCF$_3$] (4c). Green, 96%. IR (KBr, cm^{-1}): $\nu_{C\equiv N}$ 2207; $\nu_{C\equiv O}$ 1943; $\nu_{C=N}$(Tp′) 1541. ^{1}H NMR (CD_2Cl_2, δ): 7.44 (*Ph*$_{para}$), 7.34 (*Ph*$_{meta}$), 6.95 (*Ph*$_{ortho}$), 6.04, 5.94, 5.85 (Tp′C*H*), 3.86, 3.77 (CN*Me*, PhC≡C*Me*), 2.69, 2.60, 2.56, 2.42, 1.47, 1.27 (Tp′C*H*$_3$). ^{13}C NMR (CD_2Cl_2, δ): 223.3 ($^1J_{WC}$ = 140 Hz, *C*O), 221.0 ($^1J_{WC}$ = 50 Hz, PhC$_{anti}$≡CMe), 214.1 ($^1J_{WC}$ = 10 Hz, $^2J_{CH}$ = 7 Hz, PhC≡*C*$_{syn}$Me), 154.9, 153.9, 150.1, 148.4, 147.4, 146.2 (Tp′*C*CH$_3$), 152.6 (br, *C*NMe), 136.4 (Ph, *C*$_{ipso}$), 131.9 (Ph, *C*$_{para}$), 130.6, 129.5 (Ph, *C*$_{ortho}$, *C*$_{meta}$), 121.4 (q, $^1J_{CF}$ = 320 Hz, O$_3$S*C*F$_3$), 109.1, 108.7, 108.0 (Tp′*C*H), 31.9 (q, $^1J_{CH}$ = 147 Hz, CN*C*H$_3$), 24.3 ($^1J_{CH}$ = 130 Hz, PhC≡C*Me*), 16.1, 15.9, 15.2, 13.0, 12.8 (1:1:1:1:2, Tp′*C*H$_3$). Anal. Calcd for $WC_{28}H_{33}N_7BF_3O_4S$: C, 41.25; H, 4.08; N, 12.03. Found: C, 41.11; H, 4.03; N, 11.94.

[Tp′(CO)$_2$W(HC≡CH)][O$_3$SCF$_3$] (5). A solution containing 2.50 g (3.60 mmol) of Tp′(CO)$_3$WI in 40 mL of CH_2Cl_2 was prepared. A stoichiometric amount of silver triflate (AgO_3SCF_3, 0.930 g, 3.62 mmol) was added under positive nitrogen flow. While this solution was stirring, an excess of acetylene was condensed into a separate flask maintained at −78 °C. The liquid acetylene was transferred via cannula into the flask containing the Tp′(CO)$_3$WI and AgO_3SCF_3. The orange mixture was allowed to stir at room temperature for 2 h. The solution gradually turned dark green, and gas evolution was noted during this period (excess C_2H_2 and CO). The solution was filtered from the silver salts, and the volume was reduced to approximately 10 mL. The dark green CH_2Cl_2 solution was transferred by cannula into 40 mL of stirring diethyl ether, leaving a brown-violet supernatant over a green precipitate. The precipitate was isolated by filtration and recrystallized from CH_2Cl_2/Et_2O. A dark green crystalline solid was isolated (1.71 g, 67%). IR (KBr, cm^{-1}): ν_{BH} 2578; $\nu_{C\equiv O}$ 2084, 2001; $\nu_{C=N}$(Tp′) 1543. ^{1}H NMR (CD_2Cl_2, δ, ppm): *20 °C* 14.32 ($^2J_{WH}$ = 5 Hz, *H*C≡C*H*), 6.13, 6.10 (1:2, Tp′C*H*), 2.56, 2.55, 2.44, 1.94 (3:6:3:6, Tp′C*H*$_3$); *−90 °C* 14.70 (br, HC≡C*H*$_{syn}$), 13.93 (*H*$_{anti}$C≡CH), 6.08, 6.06 (1:2, Tp′C*H*), 2.48, 2.47, 2.36, 1.88 (3:6:3:6, Tp′C*H*$_3$). ^{13}C NMR (CD_2Cl_2, δ): *20 °C* 217.1 (d, br, $^1J_{CH}$ = 230 Hz, H*C*≡*C*H), 212.1 ($^1J_{WC}$ = 131 Hz, *C*O), 155.3, 152.5, 150.6, 147.8 (1:2:1:2, Tp′*C*CH$_3$), 110.1, 109.0 (1:2, Tp′*C*H), 16.9, 16.5, 13.4, 12.7 (2:1:1:2, Tp′*C*H$_3$); *−90 °C* (*^{13}C{^{1}H}*) 226.1 (br, HC≡*C*$_{syn}$H), 211.3 ($^1J_{WC}$ = 131 Hz, *C*O), 207.6 (br, H*C*$_{anti}$≡CH), 154.0, 151.4, 149.4, 146.7 (1:2:1:2, Tp′*C*CH$_3$), 119.9 (q, $^1J_{CF}$ = 320 Hz, O$_3$S*C*F$_3$), 108.8, 107.8 (1:2, Tp′*C*H), 16.3, 15.9, 13.0, 12.3 (2:1:1:2, Tp′*C*H$_3$). Anal. Calcd for $WC_{20}H_{24}N_6BF_3O_5S$: C, 33.73; H, 3.40; N, 11.80. Found: C, 33.49; H, 3.38; N, 11.76.

[Tp′(CO)(HC≡CBu^n)W−C≡N−W(MeC≡CPh)(CO)Tp′][BAr′$_4$] (7). An equimolar mixture of **2a** (0.80 g, 0.13 mmol) and [Tp′(CO)(PhC≡CMe)W−OEt$_2$][BAr′$_4$][55] (0.200 g, 0.13 mmol) was placed in a Schlenk flask, which was then evacuated and backfilled with N_2 3 times. The addition of 25 mL of CH_2Cl_2 and stirring for 15 min created a dark green solution. Removal of solvent followed by recrystallization from CH_2Cl_2/pentane produced 0.101 g (37%) of dark green crystals. IR (KBr, cm^{-1}): $\nu_{C\equiv N}$ 2128; $\nu_{C\equiv O}$ 1950, 1923; $\nu_{C=N}$(Tp′) 1546. ^{1}H NMR (CD_2Cl_2, δ): 12.84 (*H*$_{anti}$C≡CBu^n), 7.72, 7.56 (8:4, B*Ar*′$_4$), 7.25, 6.69 (3:2, m, MeC≡C*Ph*), 5.89, 5.77, 5.74, 5.72, 5.63, 5.58 (Tp′C*H*), 3.86−3.45 (m, HC≡CC*H*$_2$CH$_2$CH$_2$CH$_3$), 3.68 (*Me*C≡CPh), 2.54, 2.52, 2.50, 2.47, 2.39, 2.38, 2.27, 1.83, 1.79, 1.50, 1.48, 1.26 (Tp′C*H*$_3$), 1.94 (m, HC≡CCH$_2$C*H*$_2$CH$_2$CH$_3$), 1.51 (m, HC≡CCH$_2$-CH$_2$C*H*$_2$CH$_3$), 1.03 (t, $^3J_{HH}$ = 7.2 Hz, HC≡CCH$_2$CH$_2$CH$_2$C*H*$_3$). ^{13}C NMR (CD_2Cl_2, δ): 229.0, 225.3 (*C*O), 219.7, 212.9, 210.9 (m, *C*$_{alkyne}$), 214.4 (d, $^1J_{CH}$ = 220 Hz, H*C*≡CBu^n), 162.3 (1:1:1:1 pattern, $^1J_{BC}$ = 50 Hz, C$_{ipso}$, BAr′$_4$), 154.7, 154.0, 153.9, 153.6, 150.6, 150.4, 147.7, 147.6, 147.0, 146.6, 145.0, 144.9 (Tp′*C*CH$_3$), 136.6 (C$_{ipso}$, MeC≡C*Ph*), 135.3 (C$_{ortho}$, BAr′$_4$), 130.5, 129.5, 129.3 (C$_{para}$, C$_{meta}$, C$_{ortho}$, MeC≡C*Ph*), 129.4 (q, $^2J_{CF}$ = 40 Hz, C$_{meta}$, BAr′$_4$), 125.1 (q, $^1J_{CF}$ = 270 Hz, BAr′$_4$−*C*F$_3$), 117.9 (C$_{para}$, BAr′$_4$), 108.8, 108.6, 108.5, 108.4, 108.1, 108.0 (Tp′*C*H), 38.3 (t, $^1J_{CH}$ = 128 Hz, HC≡C*C*H$_2$CH$_2$CH$_2$CH$_3$), 33.6 (t, $^1J_{CH}$ = 127 Hz, HC≡CCH$_2$*C*H$_2$CH$_2$CH$_3$), 23.0 (t, $^1J_{CH}$ = 127 Hz, HC≡CCH$_2$CH$_2$*C*H$_2$CH$_3$), 23.1 (q, $^1J_{CH}$ = 130 Hz, *Me*C≡CPh), 16.1, 16.0, 15.5, 15.0, 14.3, 14.1, 13.3, 12.9, 12.8, 12.7, 12.5 (1:1:1:1:1:1:1:2:2:1, Tp′*C*H$_3$). The carbon of the isocyanide bridge was not located. Anal. Calcd for $W_2C_{80}H_{74}N_{13}B_3F_{24}O_2$: C, 45.63; H, 3.54; N, 8.65. Found: C, 45.39; H, 3.62; N, 8.49.

Variable-Temperature ^{1}H NMR Experiments. Probe temperatures were obtained by the use of a 100% methanol standard. All spectra were recorded in CD_2Cl_2. Site exchange

rate constants (k_{ex}) in the slow-exchange regions were calculated from the slow-exchange approximation $k_{ex} = \pi(\delta\omega)$, where $\delta\omega$ is the corrected line width. Corrected line widths were obtained by subtracting the average of the natural line widths from the average of the measured line widths of the acetylenic protons. The site exchange rate constants at coalescence were obtained by $k_{ex} = \pi(\nu_a - \nu_x)/\sqrt{2}$; where ν_a and ν_x are the chemical shifts of the higher frequency and lower frequency acetylene protons, respectively. Line widths in all cases were those reported by the Felix for Windows (v1.02) program. Barriers to alkyne rotation ($\Delta G^{\ddagger}_{rot}$) were calculated from the Eyring equation ($k_{ex} = (kT/h)\exp[-\Delta G^{\ddagger}_{rot}/RT]$).

Extended Hückel Molecular Orbital (EHMO) Calculations. The Extended Hückel program and the Alvarez collected parameters on the CAChe (release 3.5) system were used. Bond distances in the $[H_3(CO)W(HCCH)]^-$ fragment were set as follows: W−C(O) = 1.95 Å, W−H = 1.70 Å, and C−O = 1.15 Å. All intraligand angles for the metal fragment were fixed at 90°. The alkyne C≡C bond distance for all models was set at 1.25 Å with the midpoint of the alkyne 1.95 Å from tungsten along the *z* axis. A bent acetylene geometry was idealized with C−C−H bond angles of 135° and acetylene C−H bond distances of 1.00 Å. For $\mathbf{6_{CO}}$, the second CO ligand was constructed identical to the first. For $\mathbf{6_{CN}}$, the W−C distance was set at 2.20 Å and the C−N distance at 1.03 Å. For $\mathbf{6_{CNH}}$, bond distances for the linear isocyanide ligand were as follows: W−C = 2.15 Å, C−N = 1.15 Å, and N−H = 0.97 Å.

X-ray Diffraction Data Collection. 4a: Diffraction data were collected on a Rigaku diffractometer. Forty-four centered reflections found in the region 30.0° < 2θ < 40.0° were refined by least-squares calculations to indicate a triclinic unit cell. Diffraction data were collected in the hemisphere $\pm h, +k, \pm l$ under the conditions specified in Table 6. The data were corrected for Lorentz−polarization effects during the final stages of refinement. **7:** Diffraction data were collected on a Siemens SMART diffractometer. Centered reflections (8192) found in the region 3.00° < 2θ < 50.0° were refined by least-squares calculations to indicate a triclinic unit cell. Diffraction data were collected in the hemisphere $\pm h, +k, \pm l$ under the conditions specified in Table 6. The data were corrected for Lorentz−polarization effects during the final stages of refinement.

Solution and Refinement of the Structures. The positions of the tungsten atoms were deduced from the three-dimensional Patterson functions. The positions of the remaining non-hydrogen atoms were determined through subsequent Fourier and difference Fourier calculations. All non-hydrogen atoms were refined anisotropically. Hydrogen atom locations 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. The final residuals are given in Table 6.

Table 6. Crystallographic Data Collection Parameters

	4a	**7**
empirical formula	$WC_{26}H_{30}N_7OB\cdot 0.75(CH_2Cl_2)$	$W_2C_{83}H_{81}B_3F_{24}O_2N_{13}$
fw, g/mol	714.92	2148.70
cryst dimens, mm	0.25 × 0.25 × 0.30	0.15 × 0.15 × 0.20
space group	$P\bar{1}$	$P\bar{1}$
cell params		
a, Å	10.961(4)	12.6344(6)
b, Å	11.210(3)	17.9230(9)
c, Å	13.624(5)	20.3426(10)
α, deg	86.14(3)	79.3250(10)
β, deg	70.03(2)	77.1710(10)
γ, deg	69.927(23)	20.3426
vol, Å^3	1475.4(8)	4386.4(4)
Z	2	2
density calcd, g/cm^3	1.609	1.627
Collection and Refinement Parameters		
radiation (wavelength, Å)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
monochromator	graphite	graphite
linear abs coeff, cm^{-1}	40.9	27.3
scan type	$\theta/2\theta$	ω
2θ limit, deg	46.0	50.0
quadrants collected	$\pm h, +k, \pm l$	$\pm h, +k, \pm l$
total no. of reflns	4194	14 955
data with $I \geq 2.5\sigma(I)$	3530	10 333
R,[a] %	3.8	5.9
R_w,[a] %	4.7	5.9
GOF	1.56	1.77
no. of params	347	1171
largest param shift (shift/error ratio)	0.004	0.042

[a] $R_{unweighted} = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$, and $R_{weighted} = [\Sigma\omega(|F_o| - |F_c|)^2/\Sigma\omega F_o^2]^{1/2}$.

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Supporting Information Available: ORTEP representations showing complete numbering scheme and complete tables of bond lengths and bond angles, atomic coordinates, and U_{ij} values for **4a** and **7** (14 pages). Ordering information is given on any masthead page.

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