E/*Z*-Isomerization Dynamics in Molybdenum and Tungsten η^1-Ketone Complexes

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A series of tungsten(II) and molybdenum(II) iodide complexes of the type {Tp}M(CO)(RC≡CR′)I ({Tp} = Tp, Tp′; M = Mo, W; R, R′ = Ph, Me) (**5a**−**g**) have been synthesized by utilizing hydridotris(1-pyrazolyl)borate (Tp) and hydridotris(3,5-dimethylpyrazolyl)borate (Tp′) ligands and 1-phenyl-1-propyne, 2-butyne, and diphenylacetylene alkynes. Reacting the iodide complexes **5a**−**g** with either $LiCuMe_2$ or Me_2Mg formed the corresponding methyl complexes {Tp}M(CO)(RC≡CR′)Me (**7a**−**g**), which serve as Lewis acid precursors in these systems. Protonation of the methyl complexes with $HBAr'_4{\cdot}2OEt_2$ (BAr'_4 = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate), loss of methane, and addition of a ketone (acetone, 2-butanone, 3-methyl-2-butanone, acetophenone, or pinacolone) gave the η^1-ketone complexes. The ketone complexes exhibit different conformational preferences about the M−O bond. The *E*/*Z*-isomerization barriers of the ketone complexes were calculated using coalescence temperatures from low-temperature ^{1}H NMR spectra. Differences in *E*/*Z*-isomerization barriers between Tp and Tp′ tungsten and molybdenum systems are analyzed in terms of an isomerization mechanism involving a linear M←O═C transition state. The vacant dπ orbital of the d^4 metal and the versatility of the alkyne $\pi_\perp$ donation into the dπ-orbital enhances accessibility of the linear transition state for *E*/*Z*-isomerization.

Introduction

Lewis acid coordination influences the structural, electronic, and conformational preferences of bound organic carbonyls.[1] Carbonyl coordination mode (σ/π) and *E*/*Z*-isomerization (*syn*/*anti*) binding preferences have a significant affect on the reactivity of organic carbonyls bound to Lewis acids.

Aldehyde complexes of the $[CpRe(NO)(PPh_3)]^+$ fragment exist as a mixture of σ and π isomers.[2,3] The $[TpW(CO)(MeC{\equiv}CMe)]^+$ Lewis acid fragment also exhibits ambichelic σ- and π-binding of aldehydes.[4] In contrast, aldehydes are exclusively σ-bound to the $[TpMo(CO)(MeC{\equiv}CMe)]^+$ fragment[4] and to the $[Tp'W(CO)(PhC{\equiv}CMe)]^+$ fragment.[5] Other tungsten and molybdenum organic carbonyl complexes have been synthesized.[6]

Although halogenated ketones may be sufficiently π-acidic to π-bind to Lewis acids,[7,8] alkyl ketones are generally σ-bound. A central issue for σ-bound ketone complexes is *E*/*Z*-isomerization.[9] Ketone adducts of $[Tp'W(CO)(PhC{\equiv}CMe)]^+$ are exclusively σ-bound to the metal with relatively high barriers to *E*/*Z*-isomerization ($\Delta G^{\ddagger}$ =11−15 kcal/mol).[5] In this paper, a series of tungsten and molybdenum hydridotris(1-pyrazolyl)borate (Tp) and hydridotris(3,5-dimethylpyrazolyl)-

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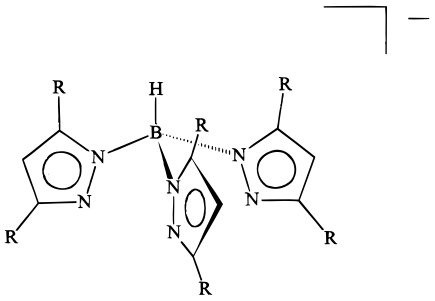


Figure 1. Hydridotris(pyrazolyl)borate ligands: Tp = hydridotris(1-pyrazolyl)borate (R = H; cone angle = 184°); Tp′ = hydridotris(3,5-dimethylpyrazolyl)borate (R = Me; cone angle = 224°).

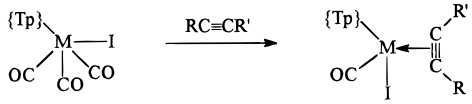
borate (Tp′)[10] Lewis acids have been synthesized in order to probe ketone binding (Figure 1). Lewis acids with the Tp′ ligand in the coordination sphere are sterically encumbered and electron-rich relative to Tp. Tungsten complexes are more electron-rich than their molybdenum analogues, and comparison provides a probe for electronic factors in metal−ketone binding.

Conformational preferences are responsible for determining the stereochemical outcome of reactions involving Lewis acid bound organic carbonyls. Therefore, identifying characteristics of the Lewis acid that control *E*/*Z*-isomerization is central to understanding the origins of stereoselectivity. The Lewis acids reported here serve as a probe of these binding and conformational preferences of tungsten and molybdenum pyrazolylborate ketone complexes.

We report (1) syntheses of tungsten and molybdenum methyl derivatives that differ with respect to the pyrazolylborate ligand and the alkyne, (2) syntheses of ketone complexes from tungsten and molybdenum methyl precursors, (3) variable-temperature NMR studies which reflect dynamic phenomena of the bound ketones.

Results

Alkyne Iodide Complexes, {Tp}M(CO)(R′C≡CR)I. The alkyne iodide complexes {Tp}M(CO)(RC≡CR′)I (**5a**−**g**) were synthesized from the tricarbonyl iodide complexes **1**−**4** (eq 1, Table 1).[11] The Tp′ molybdenum



(1)

1; {Tp} = Tp′; M = W
2; {Tp} = Tp′; M = Mo
3; {Tp} = Tp; M = W
4; {Tp} = Tp; M = Mo

5a-g

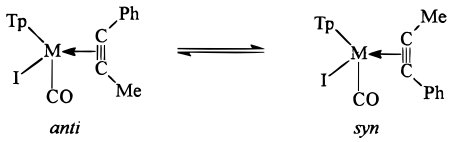
complex **2** is not isolable due to spontaneous loss of one carbonyl ligand to generate the reactive 16-electron species Tp′Mo(CO)$_2$I.[12] The successful synthesis of **5d** exemplifies the more accessible metal environment of Tp complexes relative to Tp′ since attempts to synthesize Tp′W(CO)(PhC≡CPh)I by refluxing **1** in the presence of diphenylacetylene gave Tp′W(CO)$_2$I exclusively.[11] Presumably diphenylacetylene is incompatible with the bulky tridentate ligand in the Tp′ tungsten complex.

Table 1. Selected Data for Alkyne Iodide Complexes

complex	color	ν(C≡O) (cm^{-1}, CH_2Cl_2)	^{13}C NMR (*C*≡*C*, ppm)[a]
Tp′W(CO)(PhC≡CMe)I (**5a**)[b]	green	1907	208.9, 206.5
TpW(CO)(PhC≡CMe)I (**5b**)	green	1927	216.4, 210.5 (225.0, 205.0)[c]
TpW(CO)(MeC≡CMe)I (**5c**)	blue	1921	220.6, 207.6
TpW(CO)(PhC≡CPh)I (**5d**)	green	1938	219.2, 207.4
Tp′Mo(CO)(PhC≡CMe)I (**5e**)	amber	1930	211.6, 211.3
TpMo(CO)(PhC≡CMe)I (**5f**)	green	1953	220.8, 217.0 (230.1, 209.0)[c]
TpMo(CO)(MeC≡CMe)I (**5g**)	green	1942	228.1, 214.3

[a] Spectra obtained in CD_2Cl_2. [b] See ref 11. [c] Minor isomer listed in parentheses.

Scheme 1



anti *syn*

Pyrazolylborate ligands promote polarization of the metal orbitals into an octahedral arrangement.[13] Three nonequivalent pyrazole rings in the ^{1}H and ^{13}C NMR spectra of **5a**−**g** indicate chirality at the metal center. Table 1 lists selected IR and ^{13}C NMR data for the alkyne iodide complexes. The Tp complexes have C≡O absorbances that are approximately 20 cm^{-1} higher than their Tp′ analogues, indicating that Tp′ is a better electron donor than Tp. Additionally, the C≡O absorbances of molybdenum complexes are approximately 20 cm^{-1} higher than the more electron-rich tungsten analogues. Infrared C≡O absorbances of the 1-phenyl-1-propyne complexes (**5b,f**) are 6−11 cm^{-1} higher than the 2-butyne analogues (**5c,g**).

Complexes **5a**−**g** are formally 16-electron complexes, but donation from the alkyne $\pi_\perp$ effectively makes these complexes 18-electron species.[14] A parallel alkyne and M−CO orientation maximizes the π-acid and π-donor components of the alkyne bonding. Complexes **5a**−**g** exhibit typical four-electron donor alkyne resonances in ^{13}C NMR (Table 1).[15]

The 1-phenyl-1-propyne Tp complexes **5b,f** exist as two rotamers. The *syn* and *anti* rotamers shown in Scheme 1 refer to the placement of the alkyne phenyl substituent relative to the C≡O ligand. The two rotamers exist in a 7:1 and 5:1 ratio (CD_2Cl_2) for **5b** and **5f**, respectively, where the *anti* rotamer is the major isomer. The alkyne methyl resonance in ^{1}H NMR is farther downfield in the *anti* rotamer than in the *syn* rotamer. Rotamers of Tp′ complexes were not detected by NMR suggesting that the thermodynamic difference between the *anti* and *syn* isomers increases from Tp to Tp′.[11,16]

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Table 2. Alkyne Rotational Barriers in Alkyne Iodide Complexes

complex	$\Delta G^{\ddagger}$ (kcal/mol)[a]
Tp′W(CO)(PhC≡C(CH₂)₄)I[b]	20.0
Tp′W(CO)(HC≡CH)I[c]	19.0
TpW(CO)(PhC≡CMe)I (**5b**)	16.2
TpW(CO)(MeC≡CMe)I (**5c**)	16.1
TpMo(CO)(PhC≡CMe)I (**5f**)	16.2
TpMo(CO)(MeC≡CMe)I (**5g**)	15.8

[a] Error margin: ±0.1 kcal/mol. [b] See ref 16a. [c] See ref 16b.

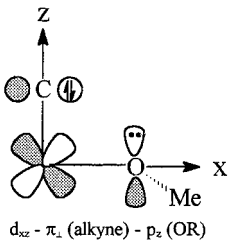
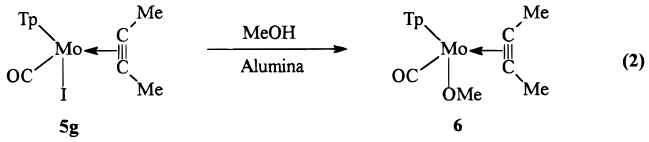


Figure 2. Orbital description of the competitive methoxide p_z and alkyne $\pi_\perp$ donation to the metal d_{xz}-orbital.

Ring interactions between the pyrazolylborate ligand and the phenyl substituent of the alkyne may contribute to the energy profile for alkyne rotation. The alkyne phenyl substituent(s) in the structurally characterized Tp′W(CO)(PhC≡CMe)I (**5a**)[11] and Tp′(CO)₂W≡CCH₂W-(CO)(PhC≡CPh)Tp[17] complexes are oriented to maximize ring interactions with the pyrazolylborate ligands. Alknye rotational barriers were calculated on the basis of ^{1}H NMR line broadening data as a function of temperature for compounds **5b,c,f,g** (Table 2).

Methoxide Complexes. The TpMo(CO)(MeC≡CMe)I complex **5g** is only slightly soluble in THF. Chromatography on alumina with methanol resulted in methanolysis to form a blue complex, TpMo(CO)(MeC≡CMe)-(OMe) (**6**) (eq 2).[18] Alumina promotes the methanolysis



5g **6** (2)

reaction, since **5g** cannot be converted to **6** using methanol exclusively. The C≡O absorption at 1885 cm^{-1} in the IR spectrum is much lower than that of the iodide complex **5g** (1942 cm^{-1}), indicating substantial donation from the methoxide ligand to molybdenum. A three-center four-electron bond (Figure 2) involving d_{xz}, alkyne $\pi_\perp$, and methoxide p_z reduces alkyne $\pi_\perp$ donation, resulting in upfield shifts of the alkyne carbon resonances of **6** in ^{13}C NMR (187.5, 173.2 ppm). The C≡O absorbance of **6** is 35 cm^{-1} higher than that of the corresponding Tp′ methoxide complex, Tp′W(CO)(Ph-C≡CMe)(OMe).[5]

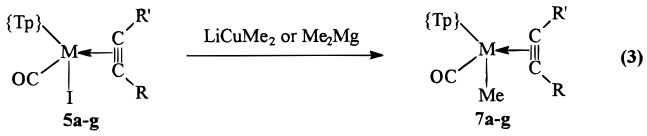
Methyl Complexes. Methyl complexes **7a**−**e** were synthesized from the iodide complexes **5a**−**e** with $LiCuMe_2$, while **7f,g** formed from methylation of **5f,g** with

Table 3. Selected Data for Methyl Complexes

complex	color	ν(C≡O) (cm^{-1}, CH_2Cl_2)	^{13}C NMR (C≡C, ppm)[a]
Tp′W(CO)(PhC≡CMe)Me (**7a**)[b]	purple	1869	207.5, 204.1
TpW(CO)(PhC≡CMe)Me (**7b**)	purple	1892	210.4, 206.5 (216.4, 203.4)[c]
TpW(CO)(MeC≡CMe)Me (**7c**)	purple	1884	210.4, 202.8
TpW(CO)(PhC≡CPh)Me (**7d**)	green	1905	215.2, 206.4
Tp′Mo(CO)(PhC≡CMe)Me (**7e**)	green	1892	205.9, 203.6
TpMo(CO)(PhC≡CMe)Me (**7f**)	blue	1904	208.8, 205.7 (216.3, 201.6)[c]
TpMo(CO)(MeC≡CMe)Me (**7g**)	blue	1896	210.9, 202.6

[a] Spectra obtained in CD_2Cl_2. [b] See ref 5. [c] Minor isomer listed in parentheses.

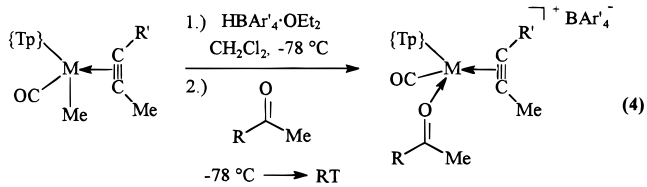
dimethylmagnesium (eq 3, Table 3). Significant alkyne



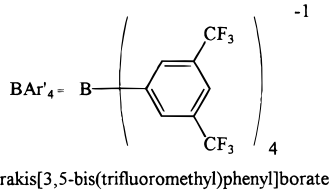
5a-g **7a-g** (3)

$\pi_\perp$ donation creates acidic propargyl sites[19] in **5a**−**g**, so that basic methylating reagents such as methyl lithium cannot be used. The alkyne methyl complexes were characterized by IR, ^{1}H NMR, and ^{13}C NMR. The C≡O absorbances of the methyl complexes are lower than those of the corresponding iodide complexes **5a**−**g**. The methyl protons of tungsten complexes **7a**−**d** exhibit two-bond coupling of approximately 7.0 Hz to tungsten (^{183}W 14%, $I = {}^1/_2$).[20]

Ketone Complexes. Ketone complexes in other systems have been prepared by displacement of labile triflate or BF_4 ligands,[6g,h,i] but these ligands are not labile in our system. Tungsten ketone complexes have been prepared by protonation of the Tp′W(CO)(Ph-C≡CMe)Me complex **7a** with HBF_4·OMe_2 in the pres-



(4)



Tetrakis[3,5-bis(trifluoromethyl)phenyl]borate

ence of excess ketone, but complications arose from competitive coordination of $[BF_4]^-$.[5] To avoid counterion interference, $HBAr'_4$·$2OEt_2$ (BAr′$_4$ = tetrakis[3,5-bis-

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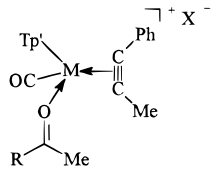
Table 4. Selected Data for Ketone Complexes (Chart 1)

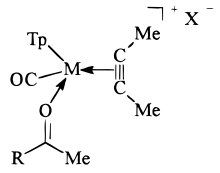
entry no.	complex	R	IR ν(C═O) (cm^{-1}, CH_2Cl_2)[a]	IR ν(C≡O) (cm^{-1}, CH_2Cl_2)	^{13}C NMR: η^1-O═*C*Me(R) (ppm)[b]	T_c (°C)[c]	$\Delta G^{\ddagger}$ (kcal/mol)[d,e]
1[f]	**8a**	Me	1635[g]	1925[g]	226.7	−71	9.8
2	**9a**	Me	1635	1937	225.2	−58	10.6
3	**10a**	Me	1653	1958	226.9	−80	9.0
4	**11a**	Me		1952	224.5	−138	6.0
5	**12a**	Me	1655	1968	226.7	<−150	
6[f]	**8b**	Et	1635[g]	1921[g]	229.4	−55	11.0
7	**9b**	Et		1935	228.2	−54	11.1
8	**10b**	Et	1652	1957	229.9	−88	9.9
9	**11b**	Et	1631	1950	227.6	<−148	
10	**12b**	Et	1652	1967	229.7	<−148	
11	**9c**	^{i}Pr	1622	1934	231.3	−48	11.4
12	**11c**	^{i}Pr	1621	1949	230.8	<−148	
13	**12c**	^{i}Pr	1642	1972	232.9	<−148	
14[f]	**8c**	Ph		1915[g]	203.4, 202.7[h]	28	15.1
15	**10c**	Ph	1571	1958	211.0, 210.0[h]	−16	13.0
16	**11d**	Ph	1550	1952	209.2	−126	6.9
17	**12d**	Ph	1569	1970	212.6	−146	6.0
18[f]	**8d**	^{t}Bu		1932[g]	233.1, 232.3[h]	25	14.9
19	**11e**	^{t}Bu		1952	232.8	<−148	

[a] C═O absorbances not listed were obscured by the C═C stretch of the $[BAr'_4]^-$ counterion (1610 cm^{-1}). [b] In CD_2Cl_2. [c] With the exception of entry 1, all spectra were recorded in CD_2Cl_2 at temperatures above −95 °C. All other spectra were taken in $CDFCl_2$. [d] All complexes decoalesced as 1:1 *E*/*Z* isomer ratios except **11d** and **12d**, where approximate $\Delta G^{\ddagger}$ values were calculated assuming 1:1 ratios. [e] Error margin: ±0.1 kcal/mol. [f] See ref 5. [g] KBr value. [h] Resonances of *E*- and *Z*-isomers from low-temperature ^{13}C NMR.

Chart 1. Structures of Tungsten and Molybdenum Ketone Complexes (Table 4)



8: M = W; X = BF_4
9: M = W; X = BAr'_4
10: M = Mo; X = BAr'_4



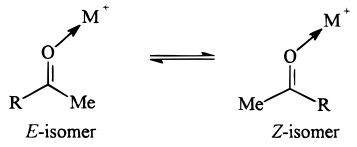
11: M = W; X = BAr'_4
12: M = Mo; X = BAr'_4

(trifluoromethyl)phenyl]borate)[21] is the preferred acid (eq 4). The large, noncoordinating anion $[BAr'_4]^-$ generates salts that are more stable, easier to recrystallize, and more soluble in low-polarity solvents than the $[BF_4]^-$ analogues.

The methyl complexes **7a**−**g** were protonated with $HBAr'_4 \cdot 2OEt_2$ in CH_2Cl_2 at −78 °C to generate a methylene chloride complex as an intermediate.[22] Subsequent addition of acetone, 2-butanone, 3-methyl-2-butanone, acetophenone, or pinacolone generated the methyl ketone complexes **9**−**12** (eq 4, Chart 1, Table 4). Synthesis of the $[BF_4]^-$ complexes **8** has been reported previously.[5] The ketone complexes generated from methyl complexes **7a,c,e,g** were obtained as analytically pure crystals in 60−90% yield after workup.

Isolation complications occurred with the Tp complexes **7b,f**. Although IR spectra of the reaction products of **7b,f** indicated formation of ketone complexes, the ^1H NMR spectra were complicated by decomposition. To test the hypothesis that alkyne rotational isomers complicate the reactivity of the 1-phenyl-1-propyne complexes **7b,f**, the 2-butyne and diphenylacetylene tungsten analogues **7c,d** were synthesized. Ketone complexes can be generated from the 2-butyne complex **7c** in high yield, but considerable decomposition accompanied formation of ketone complexes from the diphenylacetylene complex **7d**. Therefore, it is likely that the *syn* rotamers of **7b,f** complicate clean adduct formation (Scheme 1). To maintain consistency between Lewis acids and to avoid rotamer complications, the 2-butyne Tp complexes **7c,g** and the 1-phenyl-1-propyne Tp′ complexes **7a,e** were utilized exclusively for the remainder of this study.

Scheme 2



E-isomer *Z*-isomer

The ketone complexes **8**−**12** were characterized by IR, ^1H and ^{13}C NMR, and microanalysis (Chart 1, Table 4). Both IR and ^{13}C NMR were diagnostic for the σ-mode of coordination for the bound ketones.[1a] The ketone C═O absorbances of **8**−**12** were red shifted 50−90 cm^{-1} relative to the corresponding absorbances of the free ketones. The ketone carbonyl carbons in ^{13}C NMR resonated within the range of the free ketones (200−240 ppm). The alkyne carbons of complexes **8**−**12** resonate in a range expected for four-electron donating alkyne ligands.[15]

Conformational Equilibria. Two geometrical isomers are possible for asymmetric ketone complexes (Scheme 2). The *E*-isomer has the larger ketone substituent *trans* to the metal fragment about the C═O unit, while the *Z*-isomer has the metal and the larger substituent in a *cis* relationship. In ambient-temperature ^1H and ^{13}C NMR spectra, the asymmetric ketone complexes reported here appear to exist as single isomers. Therefore, the *E*/*Z*-isomers are either rapidly interconverting or the ketone complexes exist as a single isomer in solution.

(21) (a) Nishida, H.; Takada, N.; Yoshimura, M.; Sonoda, T.; Kobayashi, H. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 2600. (b) Brookhart, M.; Grant, B.; Volpe, A. F. *Organometallics* **1992**, *11*, 3920.
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The barriers to *E*/*Z*-isomerization ($\Delta G^{\ddagger} = 11-15$ kcal/mol) of the acetone, 2-butanone, acetophenone, and pinacolone complexes [Tp′W(CO)(PhC≡CMe)L][BF_4] (**8a**−**d**) were determined previously[5] and are large relative to other η^1-ketone complexes.[1a,3] In order to explore this dynamic phenomenon further, low-temperature NMR experiments were undertaken. Coalescence temperatures below −95 °C were obtained in $CDFCl_2$.[23] The calculated $\Delta G^{\ddagger}$ values for complexes **8**−**12** (Table 4) indicate that the molybdenum complexes have lower barriers to *E*/*Z*-interconversion than their tungsten analogues, and the Tp complexes **11** and **12** have lower $\Delta G^{\ddagger}$ values than the Tp′ complexes **8**−**10**.

Discussion

Solution-State Structures. The ketone C═O IR absorbances of the complexes reported here are within the range expected for σ-bound ketones.[1a] Although aldehydes can form π adducts with the [TpW(CO)(MeC≡CMe)]$^+$ fragment,[4] ketones are bulkier and less π-acidic[24] and form σ complexes. Back-bonding to the σ-bound ketone π*-orbital in tungsten complexes is more extensive than in the molybdenum complexes. Consequently, the C═O absorbances of tungsten complexes are lowered approximately 80 cm^{-1} from the free ketone while molybdenum complexes are lowered by approximately 60 cm^{-1}. Little difference in the C═O absorbances is observed between ketone Tp and Tp′ complexes. The downfield shift of 10−30 ppm observed for the ketone carbonyl resonance in the ^{13}C NMR spectra is also indicative of σ-bound complexes.[1a]

Ketones that are σ-bound to transition metal Lewis acids usually adopt a bent ground-state M−O−C geometry. A linear geometry would involve rehybridization of the oxygen to give two nonequivalent lone pairs, where the sp-hybridized lone pair coordinates to the Lewis acid and the other lone pair is in a higher energy p-orbital.[1b,25] In a linear geometry, the oxygen p-hybridized lone pair would be positioned to donate competitively with the alkyne to the empty metal dπ orbital in our systems, resulting in upfield shifts for the alkyne carbons in ^{13}C NMR (Figure 2). However, the ketone complexes reported here have four-electron alkyne carbon chemical shifts compatible with a bent ground-state geometry for the σ-bound ketones.

***E*/*Z*-Isomerization.** Alkyne rotation is not the cause of geometric isomerization in 1-phenyl-1-propyne Tp′ complexes since the alkyne rotational barriers in Tp′ complexes are high, typically near 20 kcal/mol (Table 2).[11,16] More definitive is the fact that Tp complexes with the symmetrical 2-butyne ligand exhibit isomers. Another potential source of isomers is restricted M−O rotation to generate NMR detectable conformers. However, the barriers for isomer interconversion in the Tp′ complexes are unusually high for rotamer interconversion. Finally, an intermolecular *E*/*Z*-isomerization due to exchange of free and coordinated ketone is not operative in our system since exchange with free ketone was not observed on the NMR time scale. Thus, we conclude that *E*/*Z*-isomerization is the dynamic process responsible for our NMR observations.

It has been suggested that the unusually high *E*/*Z*-isomerization barriers ($\Delta G^{\ddagger} = 11-15$ kcal/mol) in Tp′ complexes are a result of the d^4 nature of the metal.[5] The metal center presents one empty and one filled dπ-orbital to the η^1-ketone. Since the Tp complexes are also d^4, yet they have low barriers to isomerization, this electronic explanation for the high barriers no longer seems attractive. Many of the Tp complexes appear as single isomers in ^1H NMR spectra at −150 °C, presumably due to rapid interconversion. Low-temperature broadening of the α-methyl substituent resonance is observed for these Tp complexes and supports the conclusion that *E*/*Z*-isomerization is occurring with very low barriers. Moreover, it seems unlikely that the less sterically-demanding Tp complexes would have a higher thermodynamic isomer preference than the analogous Tp′ complexes.

The barriers to *E*/*Z*-isomerization in the Tp′ systems conform to expectations based on steric arguments. As the alkyl substituent of the methyl ketone becomes larger, the barrier to interconversion increases. The acetone complexes **8a** and **9a** have the lowest barriers while the acetophenone and pinacolone complexes **8c,d** have the highest barriers. Conversely, in the Tp series, the acetone complexes **11a** and **12a** have high barriers. Similar disparities exist in the literature. While resonances of *trans*-[$PtCl_2$py(η^1-O═CR(R′))] complexes decoalesce at −74 °C for acetone and −80 °C for 3-pentanone, the 2-butanone complex did not decoalesce above −90 °C.[26] For BF_3 adducts, the 2-butanone complex does not decoalesce above −110 °C while the 3-pentanone complex reaches coalescence at −101 °C ($\Delta G^{\ddagger} = 8.3$ kcal/mol).[9a]

The isomerization behavior of the Tp′ and Tp systems can be explained by an *E*/*Z*-isomerization mechanism involving a linear intermediate. Theoretical studies of BF_3 ketone complexes show that the linear form corresponds to the transition state for *E*/*Z*-isomerization.[9b] Mechanisms involving rehybridization of the oxygen lone pairs between the *E*- and *Z*-isomers with a linear sp-hybridized transition state have been described (Scheme 3).[6b,9b,26,27] Rotation about either the M−O or the C−O bond at any point along this rehybridization continuum interconverts the *E*- and *Z*-isomers.

The Lewis acids in our systems have a vacant dπ-orbital after adduct formation, where interaction with the remaining heteroatom lone pair can occur along the isomerization coordinate (Scheme 3, structure II). Lone pair p-orbital donation into the empty metal d_{xz}-orbital in [Tp′W(CO)(PhC≡CMe)]$^+$ nitrene, azavinylidene, amido, and alkoxide complexes has been observed. In the stepwise reduction of acetonitrile coordinated to the [Tp′W(CO)(RC≡CMe)]$^+$ fragment (R = Ph, Me), the azavinylidene, imine, amido, and amine metal complexes have been isolated and characterized (Figure 3).[28] Three-electron donating alkyne ligands in complexes I

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

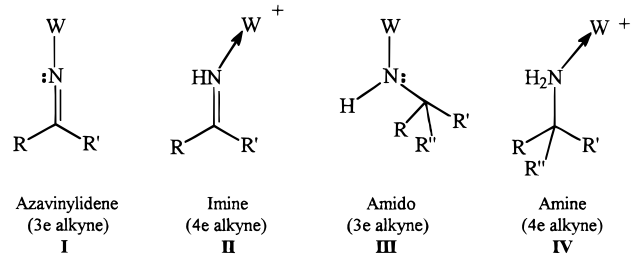
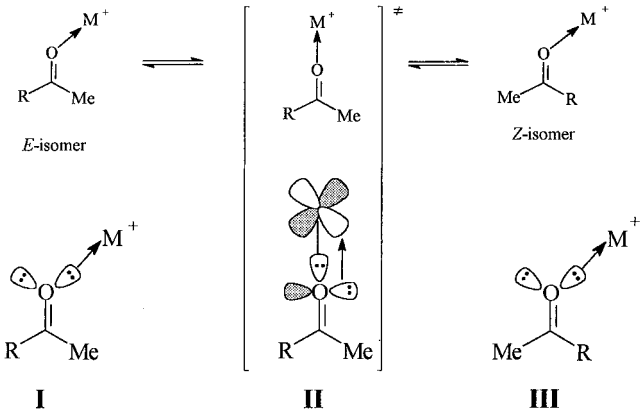


Figure 3. π-Donor capabilities of nitrogen ligands in competition with alkyne $\pi_\perp$ donation.

Scheme 3



and III indicate competitive p-hybridized lone pair donation from the heteroatom to the metal dπ-orbital (Figure 2). The azavinylidene complex Tp′W(CO)(PhC≡CMe)(N=CMePh) has been structurally characterized,[29] and the ground-state geometry is a linear M−N−C backbone with an orientation that allows nitrogen lone pair donation into the empty metal dπ-orbital. In contrast, lone pair donation is not possible from the imine and amine ligands in II and IV, and these complexes have four-electron donating alkynes. Similar phenomena are observed for isolated intermediates in the stepwise oxidation of benzylamine coordinated to the $[Tp'W(CO)(PhC{\equiv}CMe)]^+$ fragment.[30] Nitrene[31] (M=NR) and alkoxide[5] complexes have p-hybridized lone pair donation to the metal dπ-orbital as well, as exemplified by TpMo(CO)(MeC≡CMe)(OMe) (**6**) (*vide supra*).

These examples demonstrate that the vacant dπ-orbital of the d^4 metal and the versatility of alkyne $\pi_\perp$ donation allow heteroatoms to utilize a lone pair in a p-hybridized orbital for donation to the empty metal dπ-orbital in our systems. More basic heteroatoms (*i.e.* higher energy lone pairs) facilitate lone pair donation to the metal center. The energy required to access the linear transition state may explain the *E*/*Z*-isomerization barriers of the ketone complexes in our systems. Methyl ketones with more alkyl substituents have higher-energy oxygen lone pairs due to inductive effects. As with alkoxide, azavinylidene, amido, and nitrene complexes, increased basicity at the heteroatom facilitates p-hybridization of one of the heteroatom lone pairs and promotes donation into the empty d_{xz}-orbital. This is the optimal hybridization for the linear transition state of ketone *E*/*Z*-isomerization shown in structure II of Scheme 3. Thus, donation from a ketone substituent decreases the *E*/*Z*-isomerization barrier by favoring the linear transition state. Given that azavinylidene complexes adopt a ground-state linear M−N−C backbone,[29] the isoelectronic ketone complexes could certainly access this linear geometry along an isomerization coordinate.

In Tp Lewis acids where steric factors are less significant, these electronic factors may control the barrier. Therefore, complexes with more substituted ketones (*e.g.* **11c,e**) have a lower barrier than the acetone complex **11a**. While the electronic effects that control access to the linear transition state would apply for both Tp and Tp′ complexes, steric factors play a larger role in controlling the *E*/*Z*-isomerization barrier in the Tp′ systems.

The acetophenone complexes **11d** and **12d** have the highest barriers among the Tp complexes. Aromatic aldehyde complexes of Tp′ and Tp Lewis acids exhibit broad *ortho* and *meta* aryl resonances in ^{1}H and ^{13}C NMR at ambient temperature reflecting restricted rotation about the aryl−formyl single bond due to π-delocalization from the aryl group to the aldehyde C=O moiety.[4] However, analogous aryl resonances in the acetophenone Tp complexes **11d** and **12d** are sharp to −80 °C. Therefore, aryl donation is minimal in these acetophenone complexes, and the low energy of the ketone oxygen lone pairs raises the barrier to *E*/*Z*-isomerization.

The difference in *E*/*Z*-isomerization barriers for molybdenum compared to tungsten can be explained in terms of π-basicity of the metal. Back-bonding to the ketone π^* orbital to form a partial metal−ligand multiple bond is probably more significant in tungsten complexes than in molybdenum complexes. Such back-bonding would increase the barrier to rotation about the M−O bond and could account for the slightly larger *E*/*Z*-barriers of tungsten complexes relative to molybdenum complexes.

Other Conformational Issues. Although the 2-butanone Tp-complexes **11b** and **12b** are chiral, the methylene protons in both cases appear as quartets in the ^{1}H NMR spectra, reflecting either a fluxional process or coincidental chemical shifts for the methylene protons. Dissociation of the ketone could result in a quartet either by rapid formation of an achiral metal intermediate after dissociation or by migration of the dissociated ketone to a metal center of opposite chirality. However, the ^{1}H and ^{13}C NMR spectra show nine separate resonances for the pyrazole ligand, negating any possibility of an achiral intermediate on the NMR time scale. Migration of 2-butanone between metal centers can also be excluded since sharp and separate signals for free and bound ketone are seen upon addition of excess 2-butanone to the NMR samples of **11b** and **12b**.

Variable-temperature ^{1}H NMR and homonuclear decoupling experiments indicate that the anomalous quartets in **11b** and **12b** are simply due to coincidental chemical shifts. The singlet in the decoupled spectra splits into two singlets without significant broadening of the original singlet. Figure 4 shows the spectra for complex **11b**. This implies that a temperature-depend-

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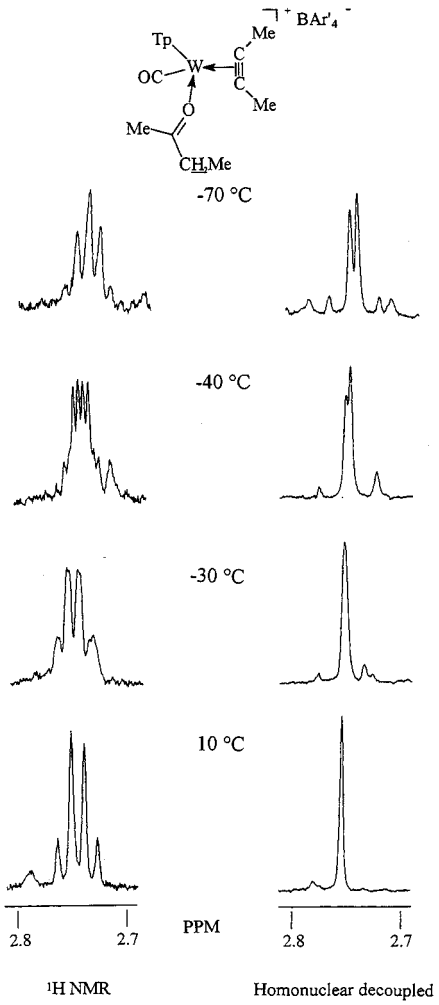
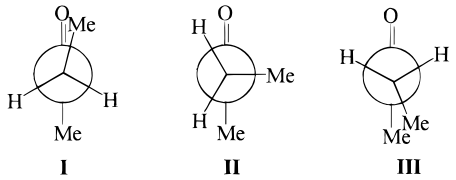


Figure 4. Selected variable-temperature ^{1}H NMR and homonuclear decoupled spectra of **11b**, [TpW(CO)(MeC≡CMe)(η¹-O=CMe(Et))][BAr′$_4$].

Scheme 4



ent chemical shift phenomenon is occurring rather than a fluxional process. The quartet phenomenon in Tp complexes **11b** and **12b** is not related to the *E*/*Z*-interconversion, since there is no doubling of 2-butanone resonances as observed with low-temperature decoalescence of the *E*- and *Z*-isomers of the 2-butanone Tp′ complexes **(8−10)b**.

Conformational preferences of organic carbonyls coordinated to Lewis acids are dependent on both the steric environment and the Lewis acidity of the metal fragment. Rotamer preferences and barriers to internal rotation about sp^2−sp^3 bonds adjacent to the C=O can be affected by the Lewis acid.[27a,32] Scheme 4 gives Newman projections of uncoordinated 2-butanone viewed down the sp^2−sp^3 methylene−acetyl bond. *Ab initio* calculations of free 2-butanone predict that the eclipsed conformer (I) is more stable than either the gauche (II) or trans (III) conformers.[33] It is believed that the stability of the eclipsed conformer (I) is due to a dipole-induced dipole interaction between the α-alkyl substituents and the polar C=O bond. Certainly differences in the polarity of the ketone C=O bond and in the steric environment about the metal would exist between Tp and Tp′ systems. These differences will alter populations of the rotational conformers between the two systems and directly influence the chemical shifts of the diastereotopic α methylene protons in ^{1}H NMR. The rotational barriers about sp^2−sp^3 α bonds are expected to be low, and only average couplings and chemical shifts of the rotamers are observed.[34] The shift from a quartet to a multiplet at low temperatures in **11b** and **12b** presumably reflects perturbation of rotamer populations as a function of temperature.

Summary

A series of chiral molybdenum(II) and tungsten(II) pyrazolylborate methyl derivatives that differ with respect to the pyrazolylborate ligand and the alkyne has been synthesized. The methyl complexes can be converted to ketone complexes via protonation, loss of methane, and subsequent ketone coordination. Comparison of the *E*/*Z*-isomerization barriers of different Lewis acids (Tp or Tp′, Mo or W) suggests an isomerization mechanism involving a linear transition state. The barriers to *E*/*Z*-isomerization in Tp′ complexes are dominated by the steric environment. In Tp complexes, steric factors are substantially diminished and electronic factors determine the barriers. The unusually low barriers in Tp complexes relative to many other reported Lewis acids may be due to both the d^4 configuration of the metal center and the versatility of alkyne $\pi_\perp$ donation. Both factors favor accessibility of the linear transition state.

Experimental Section

General Procedures. Reactions were carried out under a purified nitrogen atmosphere using standard Schlenk techniques. Solvents were purified as follows: Hexanes, tetrahydrofuran (THF), and diethyl ether (Et_2O) were distilled from sodium benzophenone ketyl; methylene chloride was distilled from phosphorus pentoxide; acetonitrile and propionitrile were distilled from calcium hydride. Pentane and methanol were used without purification. Ketones were dried over 4 Å molecular sieves prior to use. CD_2Cl_2 was degassed and dried over 4 Å molecular sieves. $CDFCl_2$[23] was distilled prior to storing over 4 Å molecular sieves at 0 °C. HBAr′$_4$·2OEt$_2$ (BAr′$_4$ = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate),[21] $LiCuMe_2$,[5] and Me_2Mg[35] were prepared according to the literature. Complexes **1**,[11] **2**,[12] **4**,[36] **5a**,[11] and **7a**[5] were prepared according to the literature. Complex **3** was synthesized according to the literature procedure for the synthesis of complex **1**, where the $TpW(CO)_3I$ complex was synthesized from KTp[10a] and $(EtCN)_3W(CO)_3$[37] in THF at ambient temperature.

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^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC 200 (200 MHz), a Bruker WM 250 (250 MHz), or a Varian XL 400 (400 MHz) spectrometer. The $\Delta G^{\ddagger}$ values were calculated from ^{1}H NMR coalescence temperatures. All complexes decoalesced into 1:1 *E*/*Z* isomer ratios except **11d** and **12d**, where approximate $\Delta G^{\ddagger}$ values were calculated assuming 1:1 ratios.

Infrared spectra were collected on a Mattson Polaris FTIR spectrometer. Elemental analyses were performed by Atlantic Microlab, Norcross, GA.

NMR Data. Full ^{1}H and ^{13}C NMR data are reported only for complexes **5b,e** as representative data. ^{1}H and ^{13}C NMR data for the $[BAr'_4]^-$ counterion is reported separately for simplicity. Complete NMR details are available for all complexes in the Supporting Information.

Representative [BAr′$_4$]$^-$. ^{1}H NMR (CD_2Cl_2): δ 7.77 (br, 8 H, *o*-Ar′), 7.60 (br, 4 H, *p*-Ar′). ^{13}C{H} NMR (CD_2Cl_2): δ 162.2 (q, $^1J_{BC}$ = 50 Hz, *ipso*), 135.3 (*o*-C), 129.4 (qq, $^2J_{CF}$ = 30 Hz, $^4J_{CF}$ = 5 Hz, *m*-C), 125.1 (q, $^1J_{CF}$ = 270 Hz, *C*F$_3$), 117.9 (m, *p*-C).

Synthesis of TpW(CO)(RC≡CR′)I Complexes (5b−d). To a THF solution (200 mL) of $TpW(CO)_3I$ (4.0 g, 6.6 mmol) was added excess alkyne in one portion (2 equiv) for 1-phenyl-1-propyne and diphenylacetylene derivatives (**5b,d**) and portionwise (8 equiv) during reflux for the 2-butyne derivative (**5c**). The solution was refluxed until solution FTIR in the ν_{CO} region indicated that the reaction was complete. The solvent was removed by rotary evaporation, and the crude product was chromatographed on alumina using CH_2Cl_2/hexanes (**5b,d**) or THF (**5c**). Excess alkyne was removed by washing the solid with hexanes. The product was recrystallized at 0 °C with CH_2Cl_2/hexanes (**5b,d**) and at ambient temperature with THF/hexanes (**5c**).

TpW(CO)(PhC≡CMe)I (5b). 3.8 g, 5.7 mmol, 86% yield. Two alkyne rotamers of complex **5b** were observed in a 7:1 ratio by ^{1}H NMR at ambient temperature. Detectable resonances in NMR for the minor isomer are listed separately. IR (CH_2Cl_2): 1927 ν(C≡O) cm^{-1}. Major rotamer: ^{1}H NMR (CD_2Cl_2) δ 8.30 (d, 1 H, $^3J_{HH}$ = 1.8 Hz, 3,5-Tp *H*), 7.92, 7.71 (each a m, each 2 H, 3,5-Tp *H*), 7.31−7.17 (m, 3 H, ≡C*Ph*), 6.62−6.52 (m, 2 H, ≡C*Ph*), 6.50 (d, 1 H, $^3J_{HH}$ = 2.0 Hz, 3,5-Tp *H*), 6.27 (m, 2 H, 4-Tp *H*), 6.05 (t, 1 H, $^3J_{HH}$ = 2.2 Hz, 4-Tp *H*), 3.57 (s, 3 H, ≡C*Me*); ^{13}C{H} NMR (CD_2Cl_2) δ 231.9 ($^1J_{WC}$ = 140 Hz, *C*≡O), 216.4 ($^1J_{WC}$ = 60 Hz, ≡*C*Ph), 210.5 ($^1J_{WC}$ = 20 Hz, ≡*C*Me), 149.3, 148.2, 143.8 (Tp-*C*), 137.4 (*ipso* of ≡C*Ph*), 136.8, 135.8, 135.4 (Tp-*C*), 128.9 (*p* of ≡C*Ph*), 128.7, 128.3 (*o*, *m* of ≡C*Ph*), 106.9, 106.8, 106.8 (Tp-*C*), 23.4 (≡C*Me*). Minor rotamer: ^{1}H NMR (CD_2Cl_2) δ 3.09 (s, 3 H, ≡C*Me*); ^{13}C{H} NMR (CD_2Cl_2) δ 234.3 (*C*≡O), 225.0, 205.0 (Ph*C*≡*C*Me), 19.7 (≡C*Me*). Anal. Calcd: C, 34.17; H, 2.72; N, 12.58. Found: C, 34.25; H, 2.69; N, 12.58.

TpW(CO)(MeC≡CMe)I (5c). 3.4 g, 5.6 mmol, 85% yield. Anal. Calcd: C, 27.75; H, 2.66; N, 13.87. Found: C, 27.91; H, 2.69; N, 13.84.

TpW(CO)(PhC≡CPh)I (5d). 4.42 g, 6.1 mmol, 92% yield. Anal. Calcd: C, 39.49; H, 2.76; N, 11.51. Found: C, 39.41; H, 2.77; N, 11.54.

Tp′Mo(CO)(PhC≡CMe)I (5e). The brown $Tp'Mo(CO)_3I$ intermediate (**2**) was prepared from $[Et_4N][Tp'Mo(CO)_3]$ (15.7 g, 26.0 mmol) and iodine (7.9 g, 31 mmol) in acetonitrile (250 mL) according to the literature. The solvent was removed by rotary evaporation, and the brown residue was redissolved in 200 mL of THF. Addition of 1-phenyl-1-propyne (4.6 mL, 37 mmol) and purification of **5e** were performed as described for complexes **5b,d**: 15.6 g, 23.5 mmol, 90% yield. ^{1}H NMR (CD_2Cl_2): δ 7.34−7.13, 6.79−6.69 (each a m, 3:2 H, ≡C*Ph*), 5.86, 5.79, 5.67 (each a s, each 1 H, Tp′-*H*), 3.51 (s, 3 H, ≡C*Me*), 2.89, 2.59, 2.50, 2.38, 1.51, 1.17 (each a s, each 3 H, Tp′-*Me*). ^{13}C{H} NMR (CD_2Cl_2): δ 234.7 (*C*≡O), 211.6 (≡*C*Ph), 211.3 (≡*C*Me), 154.5, 153.6, 148.2, 145.8, 145.1, 144.3 (Tp′-*C*-*Me*), 136.2 (*ipso* of ≡C*Ph*), 129.3, 128.5, 127.8 (*p*, *o*, *m*, respectively, of ≡C*Ph*), 108.1, 107.7, 107.0 (Tp′-*C*-*H*), 23.3 (≡C*Me*), 17.9, 17.4, 15.0, 12.8, 12.7, 12.7 (Tp′-*Me*). Anal. Calcd based on $MoC_{25}H_{30}N_6BO\cdot 0.5CH_2Cl_2$ (as determined by ^{1}H NMR): C, 43.34; H, 4.42; N, 11.89. Found: C, 43.97; H, 4.63; N, 11.82.

TpMo(CO)(PhC≡CMe)I (5f). To 6.0 g of $Mo(CO)_6$ (23 mmol) in freshly distilled and degassed acetonitrile (200 mL) was added 5.73 g (22.7 mmol) of KTp. A bright yellow solution of $[K][TpMo(CO)_3]$ formed during reflux, as determined by solution FTIR. The acetonitrile solution was cooled to 0 °C, and freshly crushed elemental iodine (5.9 g, 23 mmol) was added portionwise to generate a reddish-orange solution of $TpMo(CO)_3I$ (**4**). Solvent was removed by rotary evaporation, and the orange residue was redissolved in 200 mL of THF. Addition of 1-phenyl-1-propyne (4.3 mL, 34 mmol) and purification of **5f** were performed as described for complexes **5b,d**. Two alkyne rotamers of **5f** were observed in a 5:1 ratio by ^{1}H NMR at ambient temperature: 8.83 g, 15.2 mmol, 66% yield. Anal. Calcd: C, 39.34; H, 3.13; N, 14.49. Found: C, 39.50; H, 3.19; N, 14.32.

TpMo(CO)(MeC≡CMe)I (5g). Complex **5g** was prepared according to the procedure described for **5f** with portionwise addition of 2-butyne (5.3 mL, 68 mmol). Workup of complex **5g** was performed as described for **5c**: 6.2 g, 12 mmol, 52% yield. Anal. Calcd: C, 32.46; H, 3.11; N, 16.22. Found: C, 32.33; H, 3.14; N, 16.10.

TpMo(CO)(MeC≡CMe)(OMe) (6). During chromatography of complex **5g** (2.0 g, 3.9 mmol) on alumina with MeOH, the color of the solution changed from light green to royal blue. The solvent was removed by rotary evaporation, and the blue solid was recrystallized from CH_2Cl_2/hexanes to give blue crystals of **6**. Complex **6** is stable for approximately 1 month in air: 1.14 g, 2.70 mmol, 69% yield. Anal. Calcd: C, 42.68; H, 4.54; N, 19.91. Found: C, 42.72; H, 4.57; N, 20.01.

Synthesis of {Tp}M(CO)(RC≡CR′)Me Complexes. In a typical experiment, freshly prepared $LiCuMe_2$ (2.0 equiv) was added to {Tp}M(CO)(RC≡CR′)I (2.5 mmol) dissolved in THF (100 mL).[5] Complexes **7f,g** were prepared using Me_2Mg (0.6 equiv). Workup of complexes **7b−g** was performed as described for **5b,d**.

TpW(CO)(PhC≡CMe)Me (7b). 92% yield. Two alkyne rotamers of **7b** were observed in a 7:1 ratio by ^{1}H NMR at ambient temperature. Detectable resonances in NMR for the minor isomer are listed separately: IR (CH_2Cl_2): 1892 ($\nu_{C\equiv O}$) cm^{-1}. Major rotamer: ^{1}H NMR (CD_2Cl_2) δ 3.37 (s, 3 H, ≡C*Me*), 0.35 (s, 3 H, $^2J_{WH}$ = 6.8 Hz, W−*Me*); ^{13}C{H} NMR (CD_2Cl_2) δ 245.4 ($^1J_{WC}$ = 140 Hz, *C*≡O), 210.4 ($^1J_{WC}$ = 50 Hz, ≡*C*Ph), 206.5 ($^1J_{WC}$ = 10 Hz, ≡*C*Me), 21.8 (≡C*Me*), 20.4 ($^1J_{WC}$ = 82 Hz, W−*Me*). Minor rotamer: ^{1}H NMR (CD_2Cl_2) δ 3.08 (s, 3 H, ≡C*Me*), 0.47 (s, 3 H, $^2J_{WH}$ = 6.9 Hz, W−*Me*); ^{13}C{H} NMR (CD_2Cl_2) δ 249.3 (*C*≡O), 216.4, 203.4 (Ph*C*≡*C*Me), 20.5 ($^1J_{WC}$ = 81 Hz, W−*Me*), 18.3 (≡C*Me*). Anal. Calcd: C, 43.20; H, 3.81; N, 15.11. Found: C, 43.20; H, 3.83; N, 14.96.

TpW(CO)(MeC≡CMe)Me (7c). 72% yield. Anal. Calcd: C, 36.47; H, 3.88; N, 17.01. Found: C, 36.19; H, 3.83; N, 16.86.

TpW(CO)(PhC≡CPh)Me (7d). The product was recrystallized at 0 °C with CH_2Cl_2/pentane: 67% yield. Anal. Calcd: C, 48.58; H, 3.75; N, 13.60. Found: C, 48.46; H, 3.73; N, 13.54.

Tp′Mo(CO)(PhC≡CMe)Me (7e). 64% yield. Anal. Calcd: C, 56.54; H, 6.02; N, 15.22. Found: C, 56.59; H, 6.07; N, 15.30.

TpMo(CO)(PhC≡CMe)Me (7f). 76% yield. Two rotamers of complex **7f** were observed in a 7:1 ratio by ^{1}H NMR at ambient temperatures. Anal. Calcd: C, 51.31; H, 4.52; N, 17.92. Found: C, 51.16; H, 4.50; N, 17.82.

TpMo(CO)(MeC≡CMe)Me (7g). 70% yield. Anal. Calcd: C, 44.36; H, 4.72; N, 20.69. Found: C, 44.09; H, 4.75; N, 20.56.

Synthesis of [{Tp}M(CO)(RC≡CR′)(η^1-ketone)][BAr′$_4$] Complexes. In a typical experiment, {Tp}M(CO)(RC≡CR′)-Me (0.10 g) in CH_2Cl_2 (10 mL) was cooled to −78 °C. In a separate Schlenk flask, a CH_2Cl_2 solution (5 mL) of HBAr′$_4$·

$2OEt_2$ (1 equiv) was cooled to −78 °C. The two solutions were mixed at −78 °C, ketone (0.3 mL) was added, and the reaction mixture was allowed to warm to ambient temperature. The solution was stirred for 5 min before the solvent was removed *in vacuo*. The residue was triturated with hexanes and recrystallized from layered CH_2Cl_2/hot hexanes.

[Tp′W(CO)(PhC≡CMe)(η^1-O=CMe$_2$)][BAr′$_4$] (9a). Green crystals; 75% yield; IR (CH_2Cl_2) 1937 ($\nu_{C\equiv O}$), 1635 ($\nu_{C=O}$) cm^{-1}; ^1H NMR (CD_2Cl_2) δ 2.20 (s, 6 H, O=C*Me*(*Me*)); $^{13}C\{H\}$ NMR (CD_2Cl_2) δ 225.2 (*C*=O), 29.8 (O=C*Me*(*Me*)). Anal. Calcd: C, 46.60; H, 3.13; N, 5.43. Found: C, 46.64; H, 3.21; N, 5.49.

[Tp′W(CO)(PhC≡CMe)(η^1-O=CMe(Et))][BAr′$_4$] (9b). Green crystals; 72% yield; IR (CH_2Cl_2) 1935 ($\nu_{C\equiv O}$) cm^{-1}; ^1H NMR (CD_2Cl_2) δ 2.85−2.65 (m, 2 H, O=CMe(C*H*$_2$Me), 1.92 (s, 3 H, O=C*Me*(Et)), 0.80 (t, 3 H, $^3J_{HH}$ = 7.5 Hz, O=CMe(CH$_2$*Me*)); $^{13}C\{H\}$ NMR (CD_2Cl_2) δ 228.2 (*C*=O), 37.9 (O=CMe(*C*H$_2$Me), 26.8 (O=C*Me*(Et)), 7.9 (O=CMe(CH$_2$*Me*)). Anal. Calcd based on $WC_{61}H_{50}N_6B_2O_2F_{24}\cdot CH_2Cl_2$ (as determined by ^1H NMR): C, 45.26; H, 3.19; N, 5.11. Found: C, 45.50; H, 3.42; N, 5.27.

[Tp′W(CO)(PhC≡CMe)(η^1-O=CMe(^{i}Pr))][BAr′$_4$] (9c). Green crystals; 78% yield; IR (CH_2Cl_2) 1934 ($\nu_{C\equiv O}$), 1622 ($\nu_{C=O}$) cm^{-1}; ^1H NMR (CD_2Cl_2) δ 2.77 (sep, 1 H, $^3J_{HH}$ = 7.0 Hz, O=CMe(C*H*Me$_2$)), 1.87 (s, 3 H, O=C*Me*(^{i}Pr)), 0.96, 0.94 (each a d, 3 H each, $^3J_{HH}$ = 7.0 Hz each, O=CMe(CH*Me*$_2$)); $^{13}C\{H\}$ NMR (CD_2Cl_2) δ 231.3 (*C*=O), 43.4 (O=CMe(*C*HMe$_2$), 24.6 (br, O=C*Me*(^{i}Pr), 18.4, 18.2 (O=CMe(CH*Me*$_2$). Anal. Calcd: C, 47.29; H, 3.33; N, 5.34. Found: C, 47.43; H, 3.32; N, 5.35.

[Tp′Mo(CO)(PhC≡CMe)(η^1-O=CMe$_2$)][BAr′$_4$] (10a). Green crystals; 80% yield; IR (CH_2Cl_2) 1958 ($\nu_{C\equiv O}$), 1653 ($\nu_{C=O}$) cm^{-1}; ^1H NMR (CD_2Cl_2) δ 2.00 (s, 6 H, O=C*Me*(*Me*)); $^{13}C\{H\}$ NMR (CD_2Cl_2) δ 226.9 (*C*=O), 30.4 (O=C*Me*(*Me*)). Anal. Calcd: C, 49.41; H, 3.32; N, 5.76. Found: C, 49.54; H, 3.37; N, 5.79.

[Tp′Mo(CO)(PhC≡CMe)(η^1-O=CMe(Et))][BAr′$_4$] (10b). Green crystals; 76% yield; IR CH_2Cl_2) 1957 ($\nu_{C\equiv O}$), 1652 ($\nu_{C=O}$) cm^{-1}; ^1H NMR (CD_2Cl_2) δ 2.65−2.20 (m, 2 H, O=CMe(C*H*$_2$-Me), 1.72 (s, 3 H, O=C*Me*(Et)), 0.83 (t, 3 H, $^3J_{HH}$ = 7.2 Hz, O=CMe(CH$_2$*Me*); $^{13}C\{H\}$ NMR (CD_2Cl_2) δ 229.9 (*C*=O), 38.6 (O=CMe(*C*H$_2$Me)), 27.2 (O=C*Me*(Et)), 7.8 (O=CMe(CH$_2$*Me*)). Anal. Calcd: C, 49.75; H, 3.42; N, 5.71. Found: C, 49.78; H, 3.46; N, 5.79.

[Tp′Mo(CO)(PhC≡CMe)(η^1-O=CMe(Ph))][BAr′$_4$] (10c). Trituration with hexanes gave a green powder: 79% yield; IR (CH_2Cl_2) 1958 ($\nu_{C\equiv O}$), 1571 ($\nu_{C=O}$) cm^{-1}; ^1H NMR (CD_2Cl_2) δ 7.68−7.60, 7.50−7.22, 6.85−6.76 (each a m, 2:6:2 H, O=CMe-(*Ph*), ≡C*Ph*), 2.37, 2.15 (each br, each 3 H, O=C*Me*(Ph), Tp′-*Me*). Resonances for both the *E*- and *Z*-isomers were detected in ^{13}C NMR at −40 °C: $^{13}C\{H\}$ NMR (CD_2Cl_2; −40 °C) δ 226.8, 226.2 (*C*≡O), 216.4, 216.2, 213.1, 212.4 (Ph*C*≡*C*Me), 211.0, 210.0 (*C*=O), 152.9, 152.5, 150.8, 150.7, 149.5, 149.1, 147.8, 147.7, 147.2, 146.7, 146.0, 145.7 (Tp′-*C*-*Me*), 137.0, 136.7, 131.4, 131.0 (*p* of 2 Ph), 134.0, 133.9, 133.4, 133.3 (*ipso* of 2 Ph), 129.6, 129.4, 129.4, 128.9, 128.8, 128.7, 128.6, 128.5 (*o*, *m* of 2 Ph), 107.9, 107.8, 107.8, 107.8, 107.8, 107.6 (Tp′-*C*-*H*), 24.4, 24.2, 23.7, 21.3 (≡C*Me*, O=C*Me*(Ph)), 15.4, 15.3, 15.2, 15.1, 13.3, 13.1, 13.1, 13.0, 12.8, 12.7, 12.7, 12.6 (Tp′-*Me*). Anal. Calcd: C, 51.34; H, 3.31; N, 5.53. Found: C, 51.37; H, 3.34; N, 5.63.

[TpW(CO)(MeC≡CMe)(η^1-O=CMe$_2$)][BAr′$_4$] (11a). Purple crystals, 78% yield; IR (CH_2Cl_2) 1952 ($\nu_{C\equiv O}$) cm^{-1}; ^1H NMR (CD_2Cl_2) δ 2.18 (s, 6 H, O=C*Me*(*Me*)); $^{13}C\{H\}$ NMR (CD_2Cl_2) δ 224.5 (*C*=O), 29.8 (O=C*Me*(*Me*)). Anal. Calcd based on $WC_{49}H_{34}N_6B_2O_2F_{24}\cdot 0.5CH_2Cl_2$ (as determined by ^1H NMR): C, 41.21; H, 2.45; N, 5.83. Found: C, 40.95; H, 2.57; N, 6.28.

[TpW(CO)(MeC≡CMe)(η^1-O=CMe(Et))][BAr′$_4$] (11b). Purple crystals, 69% yield; IR (CH_2Cl_2) 1950 ($\nu_{C\equiv O}$), 1631 ($\nu_{C=O}$) cm^{-1}; ^1H NMR (CD_2Cl_2) δ 2.80 (q, 2 H, $^3J_{HH}$ = 7.3 Hz, O=CMe(C*H*$_2$Me)), 1.93 (s, 3 H, O=C*Me*(Et)), 0.69 (s, 3 H, $^3J_{HH}$ = 7.3 Hz, O=CMe(CH$_2$*Me*)); $^{13}C\{H\}$ NMR (CD_2Cl_2): δ 227.6 (*C*=O), 38.0 (O=CMe(*C*H$_2$Me)), 27.2 (O=C*Me*(Et)), 7.9 (O=CMe-(CH$_2$*Me*)). Anal. Calcd based on $WC_{50}H_{36}N_6B_2O_2F_{24}\cdot 0.5CH_2Cl_2$ (as determined by ^1H NMR): C, 41.63; H, 2.56; N, 5.77. Found: C, 41.52; H, 2.57; N, 6.17.

[TpW(CO)(MeC≡CMe)(η^1-O=CMe(^{i}Pr))][BAr′$_4$] (11c). Purple crystals, 72% yield; IR (CH_2Cl_2) 1949 ($\nu_{C\equiv O}$), 1621 ($\nu_{C=O}$) cm^{-1}; ^1H NMR (CD_2Cl_2) δ 2.84 (sep, 1 H, $^3J_{HH}$ = 7.0 Hz, O=CMe(C*H*Me$_2$)), 1.89 (s, 3 H, O=C*Me*(^{i}Pr)), 0.86, 0.84 (each a d, $^3J_{HH}$ = 7.0 Hz each, O=CMe(CH*Me*$_2$)); $^{13}C\{H\}$ NMR (CD_2Cl_2) δ 230.8 (*C*=O), 42.9 (O=CMe(*C*HMe$_2$), 25.3 (br, O=C*Me*(^{i}-Pr), 18.4, 18.2 (O=CMe(CH*Me*$_2$). Anal. Calcd based on $WC_{51}H_{38}N_6B_2O_2F_{24}\cdot 0.5CH_2Cl_2$ (as determined by ^1H NMR): C, 42.10; H, 2.67; N, 5.71. Found: C, 42.38; H, 2.69; N, 6.04.

[TpW(CO)(MeC≡CMe)(η^1-O=CMe(Ph))][BAr′$_4$] (11d). Red crystals, 82% yield; IR (CH_2Cl_2) 1952 ($\nu_{C\equiv O}$), 1550 ($\nu_{C=O}$) cm^{-1}; ^1H NMR (CD_2Cl_2) δ 7.51−7.41, 7.28−7.18 (each a m, 3:2 H, O=CMe(*Ph*)), 2.30 (s, 3 H, O=C*Me*(Ph)); $^{13}C\{H\}$ NMR (CD_2Cl_2) δ 209.2 (*C*=O), 137.3 (*p* of Ph), 133.2 (*ipso* of Ph), 129.9, 129.7 (*o*, *m* of Ph), 22.0 (O=C*Me*(Ph)). Anal. Calcd: C, 44.35; H, 2.48; N, 5.75. Found: C, 44.10; H, 2.52; N, 5.93.

[TpW(CO)(MeC≡CMe)(η^1-O=CMe(^{t}Bu))][BAr′$_4$] (11e). Purple crystals, 74% yield; IR (CH_2Cl_2) 1952 ($\nu_{C\equiv O}$) cm^{-1}; ^1H NMR (CD_2Cl_2) δ 1.83 (s, 3 H, O=C*Me*(^{t}Bu)), 0.91 (s, 9 H, O=CMe(C*Me*$_3$)); $^{13}C\{H\}$ NMR (CD_2Cl_2) δ 232.8 (*C*=O), 46.4 (O=CMe(*C*Me$_3$)), 26.5 (O=CMe(C*Me*$_3$)), 22.9 (O=C*Me*(^{t}Bu)). Anal. Calcd based on $WC_{52}H_{40}N_6B_2O_2F_{24}\cdot 0.5CH_2Cl_2$ (as determined by ^1H NMR): C, 42.46; H, 2.78; N, 5.66. Found: C, 42.60; H, 2.73; N, 5.91.

[TpMo(CO)(MeC≡CMe)(η^1-O=CMe$_2$)][BAr′$_4$] (12a). Blue crystals, 71% yield; IR (CH_2Cl_2) 1968 ($\nu_{C\equiv O}$), 1655 ($\nu_{C=O}$) cm^{-1}; ^1H NMR (CD_2Cl_2) δ 2.00 (s, 6 H, O=C*Me*(*Me*)); $^{13}C\{H\}$ NMR (CD_2Cl_2) δ 226.7 (*C*=O), 30.5 (O=C*Me*(*Me*)). Anal. Calcd: C, 44.85; H, 2.61; N, 6.40. Found: C, 45.01; H, 2.67; N, 6.52.

[TpMo(CO)(MeC≡CMe)(η^1-O=CMe(Et))][BAr′$_4$] (12b). Blue crystals, 69% yield; IR (CH_2Cl_2) 1967 ($\nu_{C\equiv O}$), 1652 ($\nu_{C=O}$) cm^{-1}; ^1H NMR (CD_2Cl_2) δ 2.56 (q, 2 H, $^3J_{HH}$ = 7.2 Hz, O=CMe(C*H*$_2$Me)), 1.79 (s, 3 H, O=C*Me*(Et)), 0.72 (s, 3 H, $^3J_{HH}$ = 7.2 Hz, O=CMe(CH$_2$*Me*)); $^{13}C\{H\}$ NMR (CD_2Cl_2) δ 229.7 (*C*=O), 38.5 (O=CMe(*C*H$_2$Me)), 27.8 (O=C*Me*(Et)), 7.7 (O=CMe-(CH$_2$*Me*)). Anal. Calcd: C, 45.28; H, 2.74; N, 6.34. Found: C, 45.11; H, 2.77; N, 6.56.

[TpMo(CO)(MeC≡CMe)(η^1-O=CMe(^{i}Pr))][BAr′$_4$] (12c). Blue crystals, 70% yield; IR (CH_2Cl_2) 1972 ($\nu_{C\equiv O}$), 1642 ($\nu_{C=O}$) cm^{-1}; ^1H NMR (CD_2Cl_2) δ 2.65 (sep, 1 H, $^3J_{HH}$ = 7.0 Hz, O=CMe(C*H*Me$_2$)), 1.76 (s, 3 H, O=C*Me*(^{i}Pr)), 0.87, 0.85 (each a d, 3 H each, $^3J_{HH}$ = 7.0 Hz each, O=CMe(CH*Me*$_2$)); $^{13}C\{H\}$ NMR (CD_2Cl_2) δ 232.9 (*C*=O), 43.5 (O=CMe(*C*HMe$_2$)), 26.0 (O=C*Me*(^{i}Pr)), 18.1, 17.9 (O=CMe(CH*Me*$_2$)).

[TpMo(CO)(MeC≡CMe)(η^1-O=CMe(Ph))][BAr′$_4$] (12d). Green crystals, 65% yield; IR (CH_2Cl_2) 1970 ($\nu_{C\equiv O}$), 1569 ($\nu_{C=O}$) cm^{-1}; ^1H NMR (CD_2Cl_2) δ 7.68−7.60, 7.49−7.31 (both a m, 1:4 H, O=CMe(*Ph*)), 2.13 (s, 3 H, O=C*Me*(Ph)); $^{13}C\{H\}$ NMR (CD_2Cl_2) δ 212.6 (*C*=O), 137.4 (*p* of Ph), 134.1 (*ipso* of Ph), 129.9 (*o*, *m* of Ph), 23.3 (O=C*Me*(Ph)). Anal. Calcd: C, 47.19; H, 2.64; N, 6.11. Found: C, 47.44; H, 2.68; N, 6.37.

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Supporting Information Available: Text giving full characterization data for the complexes (12 pages). Ordering information is given on any current masthead page.

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