The Uncommon Reactivity of Dihapto-Coordinated Nitrile, Ketone, and Alkene Ligands When Bound to a Powerful π-Base

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A series of complexes of the form TpM(NO)(L′)(η^2-L) are prepared (where L is a nitrile, ketone, or alkene, M = W or Mo, L′ = PMe₃, MeIm, Tp = hydridotris(pyrazolyl)borate). These complexes are subjected to various electrophiles (e.g., alkyl halides, Brønsted acids) to systematically probe the ability of the π-basic transition metal to affect the reactivity of the dihapto-coordinated ligand. Alkylation is observed at the heteroatom of the ketone and the nitrile, but depending on the reagent, alkylation of the nitrosyl ligand or addition to the complexed π-bond also occurs. The structures of several nitrilium complexes and a rare example of an η^2-acetonium complex are also reported.

Introduction

Nitriles, carbonyls, and alkenes play a central role in modern synthetic chemistry, and their chemical transformations are often facilitated by the action of Lewis-acidic metals, as is portrayed in Scheme 1.[1]

Our long-standing interest in the ability of π-basic metals[2] to promote novel organic reactions with unsaturated organic molecules[3,4] led to our speculation that a nitrile, carbonyl, or alkene coordinated to such a π-base may show a markedly enhanced reactivity with carbon electrophiles, either at a lone pair or at the π-bond (Scheme 2).

Results and Discussion

Over the years, our group has explored the chemistry of osmium,[5] rhenium,[4] tungsten,[6] and molybdenum[7] π-bases, focusing primarily on their ability to activate aromatic molecules. For the present investigation, we chose the two group 6 π-bases {TpMo(NO)(MeIm)}[7] and {TpW(NO)(PMe₃)},[6] as both are known to form π-complexes with an unusually broad range of unsaturated ligands including alkenes, ketones, esters, and amides.[6,8]

Ketones. The acetone complexes **1** and **2** were prepared from their corresponding tungsten(I) or molybdenum(I) precursors,

Scheme 1

Scheme 2
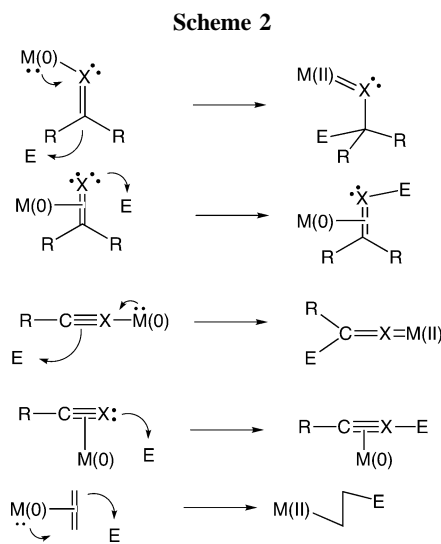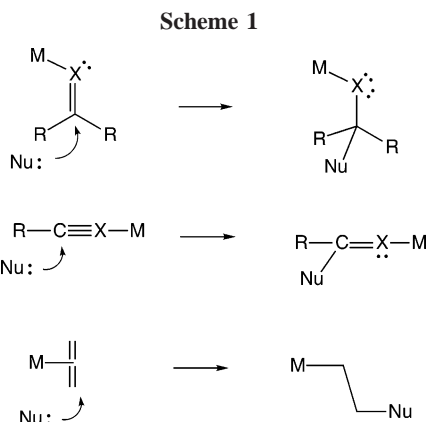
according to previously published methods.[6,7] The molybdenum acetone complex **1** is prepared as a single coordination diastereomer, with the oxygen oriented toward the imidazole ligand. When **1** was treated with methyl triflate, the *O*-methylated

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† University of Virginia.
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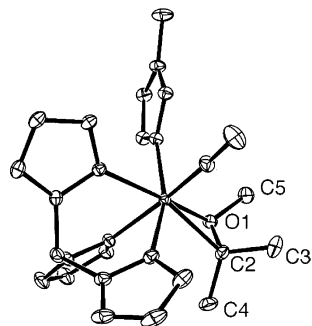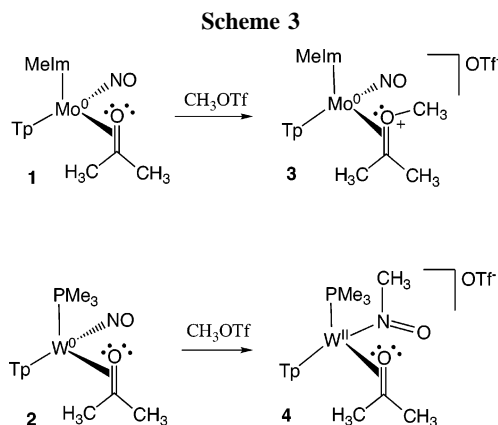(8) Meiere, S. H.; Ding, F.; Friedman, L.; Sabat, M.; Harman, W. D. *J. Am. Chem. Soc.* **2002**, *124*, 13506.

Figure 1. ORTEP diagram (30% ellipsoids) for the acetonium complex **3** (triflate not shown). Selected bond lengths (Å) and angles (deg): Mo−N9, 1.757; Mo−O1, 2.126; Mo−C2, 2.181; O1−C5, 1.457; O1−C2, 1.436; C4−C2−C3, 114.2; C2−O1−C5, 121.6; O1−C2−Mo, 68.46.

Scheme 3

acetonium complex (**3**) (i.e., a Mo(II) 2-(2-methoxypropyl) complex) is cleanly formed.

Supporting evidence for this assignment of **3** includes new methyl signals in the proton and carbon NMR spectra at 4.28 and 66.7 ppm, respectively. In addition a significant blue-shift in the NO stretch (from 1538 cm^{-1} to 1626 cm^{-1}) and a shift in the anodic peak current (from $E_{p,a}$ = 0.71 V to $E_{p,a}$ > 1.5 V) indicate the formation of a molybdenum complex that is much less electron-rich than its precursor. Crystals of **3** were grown, and the structure of this complex was determined by X-ray diffraction. The corresponding ORTEP diagram is shown in Figure 1. The carbonyl O−C2 bond length of 1.44 Å is practically the same as the O−CH$_3$ bond length (1.46 Å), indicating a complete loss of double-bond character. While the crystal structure of the molybdenum ketone complex **1** has not been determined, the C−O bond in the tungsten analogue **2** is 1.35 Å,[9] a value more in line with other dihapto-coordinated carbonyl complexes.[9,10]

The Mo(0) acetonium complex **3** is remarkably stable in solution, even in the presence of water (0.1% in acetone), but when it is subjected to an amine base (e.g., DBU, Et$_3$N), it readily demethylates, returning complex **1**. In an effort to develop a procedure to prepare mixed acetals, we attempted to oxidatively decomplex the acetonium ligand in the presence of an alcohol. In a typical experiment, **3** and methanol were combined in solution and treated with an oxidant (CAN, DDQ, AgOTf), and the solution was heated (60 °C). Oxidants such as silver triflate failed to react with complex **3**. The more

powerful oxidants CAN and DDQ reacted with **3** to give a complex mixture of products. When the reaction mixture was analyzed by mass spectrometry, a major peak was present at 104 (*m/z*), the mass of the anticipated parent ion corresponding to (CH$_3$)$_2$C(OMe)$_2$; however, none of this acetal could be detected by ^{1}H NMR spectroscopy. Furthermore, when the experiment was repeated without the addition of the oxidant, the same feature at *m/z* = 104 was present. These observations suggest that the high temperature (250 °C) of the injection port likely played a more important role in liberation of the acetonium ion than the oxidant.

Examples in which an η^2-bound aldehyde or ketone is alkylated are rare,[10,11] and **3** appears to be the first example in which a product of such a reaction has been structurally characterized. The only other crystallographic report of a nonchelated η^2-ketonium complex comes from Erker et al., in which a lithiated benzhydryl methyl ether combines with zirconocene.[12]

We next explored the reactivity of the tungsten ketone complex **2** with methyl triflate. To our surprise, alkylation at the ketone oxygen was pre-empted by the nitrosyl ligand. NMR spectra of this product, **4**, resemble those of **3**, with a single additional signal in both the carbon and proton spectrum, corresponding to the new methyl group. However, IR data failed to show a nitrosyl stretch in the expected region, and NOE data were inconsistent with carbonyl alkylation. Instead, an NOE interaction with the new methyl group and the pyrazole ring *trans* to the acetone suggested that the nitrosyl nitrogen was alkylated to form nitrosomethane, according to Scheme 3. Two other examples of nitrosomethane complexes have appeared in the literature; both were derived from nitrosylium ion, as either a salt or complex.[13,14] In these examples, the nitrosyl adds into a metal−methyl bond. A similar mechanism for **4**, in which methyl triflate oxidatively adds to the tungsten of **2** prior to insertion, may be operative, but the direct electrophilic addition to the nitrosyl nitrogen is also plausible.

Nitriles. The *N*-bound coordination mode for nitriles is easily identified by a strong absorption in the infrared spectrum. For π-basic metals, this stretch is typically red-shifted by about 50 cm^{-1} from that of the free nitrile. For example, the osmium and rhenium π-bases that we have worked with form the pedestrian *N*-bound complexes [Os(NH$_3$)$_5$(CH$_3$CN)]$^{2+}$ and TpRe(CO)(MeIm)(CH$_3$CN). Preliminary experiments with tungsten were more promising. An acetonitrile solution of the complex TpW(NO)(PMe$_3$)(η^2-benzene) was prepared and allowed to stand for 5 h. The precipitate resulting from the addition of pentane (41% yield) contained a mixture of four diamagnetic species, according to ^{1}H and ^{31}P NMR data.
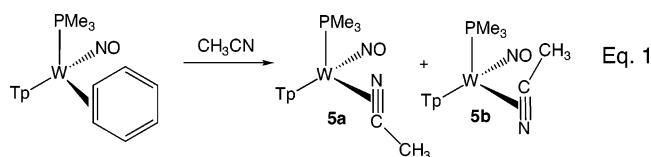
The two major components (**5a** and **5b**, eq 1) each show a single methyl group, a set of nine Tp signals, and a PMe$_3$ doublet. ^{31}P chemical shifts for **5a** and **5b** at −7.91 and −8.26

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(11) Spera, M. L.; Chen, H. Y.; Moody, M. W.; Hill, M. M.; Harman, W. D. *J. Am. Chem. Soc.* **1997**, *119*, 12772.
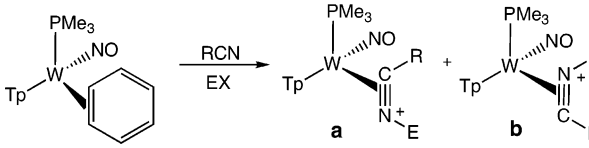
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Table 1. Preparation of the Tungsten Nitrilium Complexes, 6−11

EX	dr (a:B)	R	% yield	cpd
BnBr	10:1	Me	91	**6**
n-BuI	10:1	Me	39	**7**
C_3H_5Br	2:1	Me	61	**8**
CH_3I	1:1	Me	90	**9**
HOTf (Ph$_2$NH)	2:1	Me	50	**10**
BnBr	1:4	Et	73	**11**

ppm are similar to dihapto-coordinated alkene complexes of this tungsten metal fragment.[5] HMBC (heteronuclear multiple-bond correlation) data indicate that the methyl peaks at 2.84 and 2.34 ppm correlate to carbon shifts at 177.5 and 184.1 ppm, respectively, values that are consistent with other examples of η^2-coordinated nitriles.[15] Furthermore, the IR absorption spectrum of **5** shows a nitrosyl signal at 1540 cm^{-1} and a nitrile stretch at 1735 cm^{-1}, which is in agreement with other reports of η^2-coordinated acetonitrile complexes.[15]

A third component, **5c**, shows a doublet ($J_{PH} = 112.5$ Hz) in the proton spectrum at 8.72 ppm with tungsten satellites ($J_{WH} = 27$ Hz), a feature that indicates a tungsten hydride complex.[9] Further evidence for a hydride species include a ^{31}P signal at 1.13 ppm and a nitrosyl stretching signal in the IR absorption spectrum of **5c** at 1587 cm^{-1}, values similar to those observed for the complex TpW(NO)(PMe$_3$)(H)(OAc).[9] Of note, a weak signal is also present for **5c** at 2197 cm^{-1}, which we originally mistook for an η^1-nitrile stretch. But the lack of other data supporting this hypothesis leads us to tentatively attribute this feature to a W−H stretch.[16]

Unfortunately, attempts to purify the η^2-nitrile complex (**5a** and **5b**) by either recrystallization or chromatography resulted in its decomposition. However, when TpW(NO)(PMe$_3$)(η^2-benzene) was dissolved in a nitrile solvent along with an alkyl halide, W(0) nitrilium complexes (i.e., W(II) iminoacyl complexes) were isolated in 39−91% yield. The range of electrophiles added is summarized in Table 1.

The following analysis of the benzylacetonitrilium complex **6a** is typical. The corresponding ^{1}H NMR spectrum features diastereotopic methylene protons at 5.31 and 5.24 ppm ($J_{HH} = 12.4$ Hz) and a CH$_3$ at 3.46 ppm. The second diastereomer (**6b**) shows features similar to **6a**.

When propionitrile is used as the solvent, similar results were observed. The ^{1}H NMR spectrum for a sample of the crude reaction mixture showed a 4:1 ratio of diastereomers along with the formation of several side products. Treatment of the reaction mixture with hexanes precipitated predominantly one diastereomer, **11b**. Though attempts to purify this material by chromatography failed, several small crystals of this product were ultimately grown by vapor diffusion of hexanes into a solution of ether. An ORTEP diagram resulting from an X-ray diffraction study confirmed that **11** was an η^2-propionitrilium complex (Figure 2).

The parent nitrilium complex, **10**, was prepared by protonation of the acetonitrile complex **5** with Ph$_2$NH$_2$OTf as a 3:1

(15) Shin, J. H.; Savage, W.; Murphy, V. J.; Bonanno, J. B.; Churchill, D. G.; Parkin, G. *Dalton Trans.* **2001**, *11*, 1732.

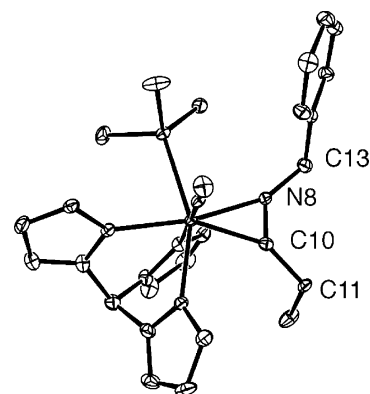(16) A fourth component (**5d**) appears to be associated with a ^{31}P signal at 36.96 ppm.

Figure 2. ORTEP diagram (30% ellipsoids) of the benzylpropionitrilium complex (**11b**) (Br$^-$ not shown). Selected bond lengths (Å) and angles (deg): W−C10, 2.08; W−N8, 2.15; N8−C10, 1.25; O1−N7, 1.22; C13−N8−C10, 132; N8−C10−C11, 133.
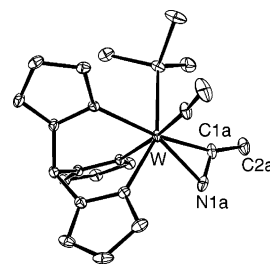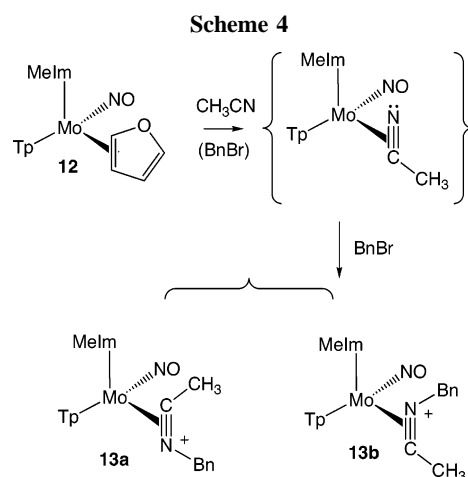

Figure 3. ORTEP diagram (30% ellipsoids) of the acetonitrilium complex (**10**) (OTf$^-$ not shown). Selected bond lengths (Å) and angles (deg): N1a−C1a, 1.25, N1a−C1a−C2a: 130.

Scheme 4

mixture of diastereomers. However, a better synthetic route came from an unexpected reaction. In an unrelated study, the dimethylthiophene complex [TpW(NO)(PMe$_3$)(4,5-η^2-(2-methylthiophene)] (**13**) was treated with TBSOTf in CH$_3$CN. The isolated product was found to be a single isomer of the acetonitrilium complex [TpW(NO)(PMe$_3$)(η^2-CH$_3$CNH)]OTf (**10a**, Table 1). Apparently, the reaction of adventitious water and TBSOTf is the proton source for this reaction. Crystals of **10** were obtained, and the corresponding ORTEP diagram is shown in Figure 3.

Attempts to cleanly prepare a molybdenum η^2-nitrile complex with the {TpMo(NO)(MeIm)} fragment have been unsuccessful. However, when the furan complex **12** was heated at 50 °C in a solution of acetonitrile and benzyl bromide, the corresponding benzylacetonitrilium complex, **13**, was obtained in 77% yield, as a 4:1 mixture of coordination diastereomers (Scheme 4). Characteristic features of the major isomer include diastereotopic
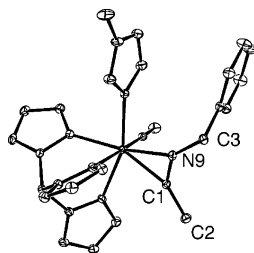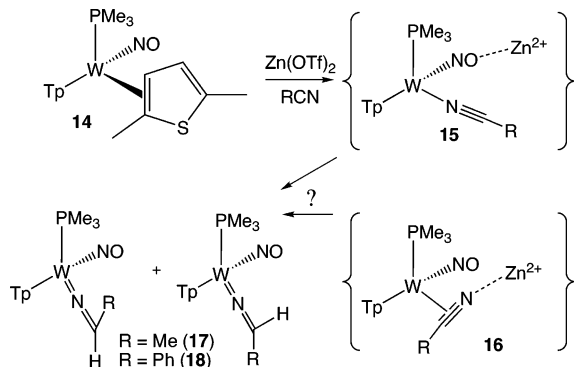
Figure 4. ORTEP diagram (30% ellipsoids) for the molybdenum benzylnitrilium complex (**13b**) (Br⁻ not shown). Selected bond lengths (Å) and angles (deg): Mo−N9, 2.13; Mo−C1, 2.12; N9−C1, 1.24; N9−C1−C2, 136.

Scheme 5.   A Possible Mechanism for the Formation of the Proposed Azavinylidine Complexes 17 and 18

methylene protons at 5.52 ppm and a single methyl group at 2.15 ppm. Crystals of **13** were obtained from an acetone/pentane solution, and the structure was determined. The corresponding ORTEP diagram is shown in Figure 4.

ORTEP diagrams of **10a**, **11b**, and **13** all show a lengthening of the nitrile CN bond (1.24−1.25 Å) compared to that of free acetonitrile (1.16 Å). This reflects the decrease in triple-bond character due to π-back-bonding. The lengthening of the CN bond and the departure from linearity of the C−C−N bond angle are features common to other nitrilium complexes.[17]

While η^2-iminoacyl (i.e., η^2-nitrilium) ligands have been observed for a number of organometallic complexes, we know of only two other reports in which a dihapto-coordinated nitrile is alkylated. Parkin et al. have demonstrated nitrogen methylation and ethylation of the complex [(η^5-C₅H₄Buᵗ)₂Mo(η^2-NCMe)],[15] and Templeton et al. have recently reported the methylation of the W(IV) η^2-nitrile complex [Tp′W(O)(I)-(NCCH₃)] using methyl triflate.[18]

In contrast to the chemistry described above for η^2-nitrile complexes, Young et al.[19] and more recently Pombeiro et al.[20] have demonstrated that η^1-nitrile ligands can undergo β-electrophilic addition (addition at carbon; see Scheme 2). Relevant to these reports, we have isolated in low yield several species that appear to be products of nitrile carbon protonation. When the 2,5-dimethyl thiophene complex **14** was treated with Zn-(OTf)₂ in acetonitrile, a small amount of a new complex (**17**) was isolated that we tentatively assign as an η^1-acetonitrilium (an azavinylidine) (2:1 ratio of diastereomers **17a**:**17b**). A key feature for isomer **A** that supports this assignment is a

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(20) Fatima, M.; Guedes da Silva, C.; Frausto da Silva, J. J. R.; Pombeiro, A. J. L. *Inor. Chem.* **2002**, *41*, 219.
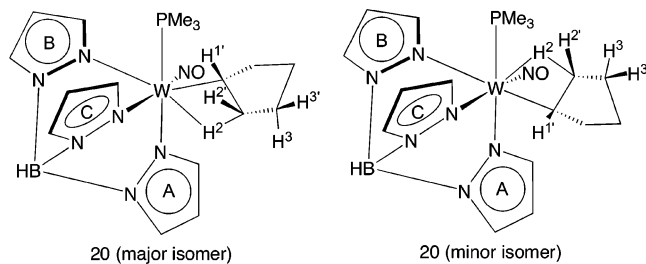

Figure 5. Proposed isomers for the agostic cyclopentanyl complex **20**.

methyl resonance at 2.22 ppm coupled to a proton signal at 8.07 ppm. A similar set of peaks at 1.91 and 8.45 ppm appear for diastereomer **17b**. These data are similar to those reported for the complex [Cr(NCHMe)₂(dmpe)₂]²⁺.[7] A similar reaction appears to occur with benzonitrile to generate the phenyl derivative **18** (¹H NMR characterization only), but our attempts to produce and isolate either of these complexes in pure form were unsuccessful.

The mechanism for the formation of **17** or **18** is unknown; however, we note that without the addition of Zn(OTf)₂ no reaction occurs between the thiophene complex **14** and aceto-nitrile. The Zn²⁺ not only facilitates the displacement of the heterocycle by a nitrile (e.g., **15**), possibly by coordination of the nitrosyl (see Scheme 5), but prevents the nitrile from undergoing *N*-protonation. This could be accomplished either by inducing η^1-nitrile coordination (**15**) or by forming an adduct with the η^2-nitrile (e.g., **16**).
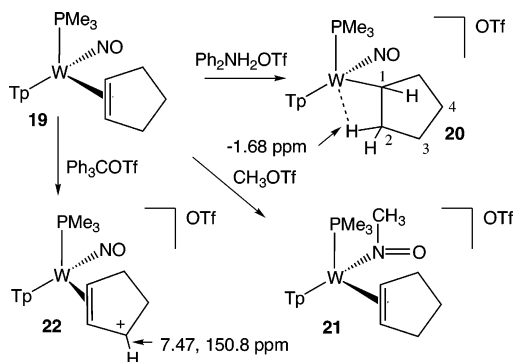
Alkenes. In the final part of this study, we compared the nucleophilic nature of the η^2-nitrile and ketone ligands in **1**, **2**, and **5** with that of an alkene, a π-coordinated ligand without the ability to react at a lone-pair of a heteroatom. The cyclopentene complex **19** was prepared by ligand substitution of the benzene complex TpW(NO)(PMe₃)(η^2-benzene) (82%). Spectroscopic features for **19** include a full set of eight intra-coupled protons ranging from 1.47 to 3.04 ppm and IR and electrochemical data similar to the benzene precursor. When the cyclopentene complex, **19**, is protonated with the Brønsted acid Ph₂NH₂OTf, a new product is obtained (**20**), which appears by ¹H NMR to consist of two diastereomers in a 5:1 ratio (**20a**:**20b**). The major diastereomer (**20a**), in addition to Tp resonances and a strong doublet assigned to the PMe₃, shows eight single proton resonances in the range 1.5−4.5 ppm, plus one more at −1.53 ppm. HSQC (heteronuclear single quantum correlation) and COSY spectra revealed four methylenes and one methine among those nine resonances. The resonance at −1.53 ppm was determined to be part of a methylene group, and its J_{C-H} of 93 Hz is considerably less than those of the other eight protons, which range from 121 to 148 Hz. (The J_{C-H} values were determined by examination of a *coupled*-HSQC spectrum.) Further examination of the COSY spectrum revealed a series of coupling connections consistent with an intact five-membered ring connected to tungsten, and a NOESY spectrum provided evidence that the ring is oriented such that the methine proton is close to the PMe₃ moiety. The NOESY spectrum also shows that the PMe₃ protons are close in space to two of the pyrazole protons, presumably those in the 3-position on pyrazole rings B and C. The methine proton at 4.26 (H¹) shows an NOE correlation with one of those pyrazole peaks, presumably from the C ring, while the methylene proton at −1.53 ppm (H²) shows a correlation with a different pyrazole proton, presumably from the A ring (Figure 5).

Taken together, this information suggests to us that the fixed cyclopentanyl ring is attached to the metal via a bond between

Table 2. Crystal and Structure Refinement Data

empirical formula	$C_{15}H_{23}BN_8O_4F_3PSW$	$C_{18}H_{25}BF_3MoN_9O_5S$	$C_{22}H_{26}BBrMoN_{10}O$	$C_{22}H_{31}BBrN_8OPW$
cpd no.; fw	**10**, 694.1	**3**; 643.3	**13b**, 633.2	**11b**, 729.1
crystal	monoclinic	monoclinic	monoclinic	orthorhombic
space group	$P2(1)/c$	$P2(1)/n$	Pn	$Pca2(1)$
a (Å)	20.333(1)	7.9609(4)	10.0685(6)	18.2222(11)
b (Å)	13.0569(7)	13.6846(7)	7.6424(5)	9.7499(6)
c (Å)	19.096(1)	24.5781(13)	17.0127(10)	15.4929(10)
β (deg)	102.624(1)	93.831(1)	99.351(1)	90
volume (Å^3)	4947.1	2671.6(2)	1291.69(14)	2752.5(3)
Z	8	4	2	4
T (K)	153(2)	153(2)	153(2)	153(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073
R/R_w ($I > 2\sigma(I)$)	0.0311/0.0774	0.0447/0.1012	0.0313/0.0759	0.0370/0.0748
no. of reflns/params	17 825/709	9139/444	8109/430	8802/324
gof	0.968	1.043	1.074	0.937

Scheme 6

tungsten and the methine carbon *and* by an agostic interaction between the tungsten and a CH bond on an adjacent carbon.[21] A similar observation was reported by Spencer et al.[22] for the ethyl group in the complex Pt(L−L)(Et) (where L−L = a bidentate phosphine), which is also prepared from the protonation of an alkene precursor. The formation of **20** is likely to occur by the protonation of tungsten followed by hydride insertion into the alkene bond.

The NOESY evidence suggests that the orientation of the cyclopentanyl ring in the major diastereomer places the methine carbon up toward the PMe$_3$ and the agostic CH down, with those two groups still set roughly orthogonal to the metal−NO bond (see Figure 5). While we were not able to extract a complete set of signals for the minor diastereomer, we were able to observe resonances from all but one of the Tp protons, the PMe$_3$, and, at about −2.5 ppm, a signal from what we assume is its agostic proton. Noting that (a) the agostic proton of **20b** shows a significantly wider signal, consistent with one or more coupling constants being much larger, and (b) its agostic proton also shows an NOE correlation with the minor diastereomer's PMe$_3$ protons, we conclude that the minor diastereomer is similar to the major diastereomer, except with the agostic proton oriented toward the PMe$_3$ (Figure 5). Confirmation of the large J_{PH} for **20b** was obtained from a ^{31}P-decoupled proton NMR spectrum (Supporting Information).

When methyl triflate was used as the electrophile, a net alkylation of the nitrosyl was observed, similar to what was reported above for the acetone complex, **2**. Evidence for the nitrosomethane ligand in **21** comes from proton and carbon data corresponding to the methyl group at 4.14 and 66.7 ppm, respectively, and a correlated set of cyclopentene protons, each shifted downfield from those found in **19**.

Finally, treatment of the cyclopentene complex (**19**) with the hydride extractor Ph$_3$COTf resulted in the allyl complex **22**.[23] Judging from proton and carbon NMR data, the binding in the allyl ligand is highly asymmetric. Two of the allylic protons are at 4.59 and 4.86 ppm, while the third is at 7.47 ppm, with a corresponding carbon signal at 150.8 ppm. The analogous situation was observed previously for the molybdenum allyl complex [TpMo(NO)(MeIm)(η^2-C$_5$H$_7$)]$^+$, in which a crystal structure revealed Mo−C bond lengths of 2.33, 2.33, and 2.64 Å.[24] Leibeskind et al. observed a similar distortion in the "η^2-allyl" complex [TpMo(NO)(CO)(C$_3$H$_5$)]$^+$.[25] There appear to be only two other reports of hydride abstraction from an alkene to form a π-allyl complex. Rosenblum et al.[26] reported such a reaction for an Fe(0) system, and most recently, Casey et al. reported extraction of a hydride from the complexes CpRe(CO)$_2$-(propene) and CpRe(CO)$_2$(butene).[27] In none of the above reactions of **18** with electrophiles was the {TpWPMe$_3$} fragment altered.

Concluding Remarks

Previous reports of the π-bases {TpMo(NO)(L)}, {TpW(NO)-(L)}, {TpRe(CO)(L)}, and {Os(NH$_3$)$_5$}$^{2+}$ have focused primarily on the ability of these metals to affect the chemistry at *uncoordinated* double bonds that are integral to dihapto-coordinated aromatic systems. In this study, we have sought to provide a comprehensive survey of the ligand-centered reactions for coordinated carbonyls, nitriles, and alkenes, where no uncoordinated double bond is present, other than the ancillary ligands. While most of the reaction types reported in this paper have sporadically been documented, they represent unusual examples of electrophilic addition to functional groups that when coordinated to a transition metal are more commonly observed to react with nucleophiles. We know of no other report in which this set of elementary reactions has been systematically investigated for a single metal or family of complexes.

Experimental Section

General Methods. NMR spectra were obtained on a 300 or 500 MHz Varian INOVA (UVA) or Bruker Avance (UR) spectrometer. All chemical shifts are reported in ppm and are referenced to

(21) Shultz, L. H.; Brookhart, M. *Organometallics* **2001**, *20*, 3975.

(22) Carr, N.; Mole, L.; Orpen, A. G.; Spencer, J. L. *J. Chem. Soc., Dalton Trans.* **1992**, 2653.

(23) Complex **22** was also prepared by the protonation of the corresponding cyclohexadiene complex.

(24) Mocella, C. J.; Delafuente, D. A.; Keane, J. M.; Warner, G. R.; Friedman, L. A.; Sabat, M.; Harman, W. D. *Organometallics* **2004**, *23*, 3772.

(25) Villanueva, L. A.; Ward, Y. D.; Lachicotte, R.; Liebeskind, L. S. *Organometallics* **1996**, *15*, 4190.

(26) Margulis, T. N.; Schiff, L.; Rosenblum, M. *J. Am. Chem. Soc.* **1965**, *87*, 3269.

(27) Casey, C. P.; Yi, C. S. *Organometallics* **1990**, *9*, 2413.

tetramethylsilane (TMS) utilizing residual ^1H or ^{13}C signals of the deuterated solvents as an internal standard. Coupling constants (J) are reported in hertz (Hz). ^{31}P NMR spectra are reported using the reported literature value versus H_3PO_4 for triphenyl phosphate (J = −16.58 ppm), which is used as the internal standard. All Tp coupling constants ($J_{H,H}$) are about 2 Hz. Infrared spectra (IR) were recorded on a MIDAC Prospect Series (Model PRS) spectrometer as a glaze on a horizontal attenuated total reflectance (HATR) accessory (Pike Industries). Electrochemical experiments were performed under a dinitrogen atmosphere using a BAS Epsilon EC-2000 potentiostat. Cyclic voltammetric data were taken at ambient temperature at 100 mV/s in a standard three-electrode cell from +1.7 to −1.7 V with a glassy carbon working electrode, *N,N*-dimethylacetamide (DMA) solvent, and tetrabutylammonium hexafluorophosphate (TBAH) electrolyte (∼0.5 M). All potentials are reported versus NHE (normal hydrogen electrode) using cobaltocenium hexafluorophosphate ($E_{1/2}$ = −0.78 V) or ferrocene ($E_{1/2}$ = 0.55 V) as an internal standard. The peak-to-peak separation was less than 100 mV for all reversible couples. Mass data were obtained on either a JEOL JMS600 using FAB$^+$ or a Finnagan MAT TSQ7000 using ESI$^+$, and no counterions were observed. Elemental analyses (EA) were performed with a Perkin-Elmer 2400 Series II CHNS/O analyzer or obtained from Atlantic Microlabs, Inc. Unless otherwise noted, all synthetic reactions and electrochemical experiments were performed under a dry nitrogen atmosphere. CH_2Cl_2, benzene, THF (tetrahydrofuran), and hexanes were purged with nitrogen and purified by passage through a column packed with activated alumina. Other solvents and liquid reagents were thoroughly purged with nitrogen prior to use. Deuterated solvents were used as received from Cambridge Isotopes. Compounds **1**,[7] **2**,[9] **12**,[7] and **14**[28] have been reported previously.

[TpMo(NO)(MeIm)(η^2-methyl acetonium)]OTf (3). [TpMo-(NO)(MeIm)(η^2-acetone)] (546 mg, 1.14 mmol) was dissolved in CH_2Cl_2 (∼1.5 mL), then methyl triflate (204 mg, 1.25 mmol) was added. The mixture was stirred at room temperature for 10 min. The reaction mixture was then added to 50 mL of pentane, and the precipitate was collected on a fritted glass funnel and washed with ether to give a brown solid (338 mg, 0.704 mmol, 62% yield). ^1H NMR (acetone-d_6): 8.26 (1H, s, Im), 8.21 (1H, d, Tp), 8.09 (1H, d, Tp), 8.05 (1H, d, Tp), 7.94 (1H, d, Tp), 7.91 (1H, d, Tp), 7.70 (1H, d, Tp), 7.53 (1H, t, Im), 7.15 (1H, t, Im), 6.49 (1H, t, Tp), 6.46 (1H, t, Tp), 6.28 (1H, t, Tp) 3.95 (3H, s, (N-Me)), 2.60 (3H, s, Me), 1.02 (3H, s, Me,), 4.07 (3H, s, Me (OMe). ^{13}C NMR (acetone-d_6): 143.5, 142.9, 142.8, 141.2, 137.8, 137.6, 136.4 (s, 6 Tp, 1Im), 128.6 (s, Im), 123.4 (s, Im), 107.1 (s, Tp), 106.9 (s, Tp), 106.7 (s, Tp), 34.7 (s, N-Me), 22.9 (s, Me), 24.5 (s, Me), 62.6 (s, Me), 104.1 (s, CO). FTIR (HATR, glaze): ν_{NO} = 1651 cm^{-1}.

[TpW(NOMe)(PMe₃)(η^2-acetone)]OTf (4). [TpW(NO)(PMe₃)-(η^2-acetone)] (523 mg, 0.933 mmol) was dissolved in CH_2Cl_2 (∼1.5 mL), then methyl triflate (168 mg, 1.03 mmol) was added. The mixture was stirred at room temperature for 10 min. The reaction mixture was then added to 50 mL of pentane, and the precipitate was collected on a fritted glass funnel and washed with ether to give a light yellow powder (239 mg, 0.415 mmol, 45% yield). ^1H NMR (acetone-d_6): 8.52 (1H, d, Tp), 8.46 (1H, d, Tp), 8.22 (1H, d, Tp), 8.15 (1H, d, Tp), 8.13 (1H, d, Tp), 7.88 (1H, d, Tp), 6.66 (1H, t, Tp), 6.59 (1H, t, Tp), 6.49 (1H, t, Tp), 4.30 (3H, s, Me), 2.74 (3H, s, Me), 1.48 (3H, d (*J*), 1), Me), 1.60 (9H, d (*J*) 10.0), PMe3). ^{13}C NMR (acetone-d_6): 146.7 (s, Tp), 146.3 (s, Tp), 145.3 (s, Tp), 139.3 (s, Tp), 138.6 (s, Tp), 138.5 (s, Tp), 108.9 (s, Tp), 108.4 (s, Tp), 107.9 (s, Tp), 95.5 (s, CO), 67.7 (s, Me), 34.0 (s, Me), 25.4 (s, Me), 11.5 (d (*J*) 120), PMe3). FTIR (HATR, glaze): 1645 cm^{-1} (w).

[TpW(NO)(PMe₃)(η^2-CH₃CN)] (5). [TpW(NO)(PMe₃)(η^2-benzene)] (107 mg, 0.183 mmol) was dissolved in acetonitrile

(5.213 g), where a brown color was observed. After 5 h, the solvent was evaporated and the resulting brown oil was dissolved in THF and added to hexanes, where a light brown solid precipitated. The solid was collected and dried in vacuo to give a light brown solid (41 mg, 41.0%). Four compounds were seen in ∼3:1:1:1 ratio. Attempts to separate this mixture on silica or alumina resulted in decomposition. Compound **1**: ^1H NMR (acetone-d_6): δ 8.32, 8.18, 8.00, 7.81, 7.74, 7.08 (1H each, each a d, 6 Tp 3,5); 6.32, 6.26, 6.13 (1H each, each a t, 3 Tp 4); 2.34 (d, 3H, *J* = 0.9 Hz, CH₃); 1.49 (9H, buried, PMe₃). Compound **2**: ^1H NMR (acetone-d_6): δ 8.08, 8.00, 7.99, 7.95, 7.77, 7.17 (1H each, each a d, 6 Tp 3,5); 6.38, 6.28, 6.11 (1H each, each a t, 3 Tp 4); 2.85 (d, 3H, *J* = 0.9 Hz, CH₃); 1.49 (9H, buried, PMe₃). FTIR (HATR, glaze): ν_{NO} = 1546 cm^{-1}, ν_{BH} = 2499 cm^{-1}. HRMS (*m/z*, (I)): found 543.13018 (2.2), 544.13574 (2.0), 545.13004 (2.2), 546.13807 (1.0), 547.14027 (2.4); calc 543.13108 (2.4), 544.13366 (2.1), 545.13334 (2.7), 546.13793 (1), 547.13665 (2.3).

[TpW(NO)(PMe₃)(C,N-η^2-CH₃CN(CH₂C₆H₅))](Br) (6). [TpW-(NO)(PMe₃)(η^2-benzene)] (102 mg, 0.180 mmol) was dissolved in acetonitrile (3.042 g). Benzyl bromide (26 mg, 0.152 mmol) was then added, resulting in a green color. After 14 h, the green solution was evaporated down to a green oil, dissolved in CH_2Cl_2, and added to hexanes, where a green solid precipitated. The solid was collected on a fritted glass funnel and dried in vacuo to give a light green solid in a 10:1 ratio of **A:B** (89 mg, 91%). Diastereomer **A**: ^1H NMR (acetone-d_6): δ 8.31, 8.18, 8.08, 8.01, 7.98, 7.37, 6.55, 6.41, 6.16, 7.08 (m, 5H, C₆H₅), 5.38 (t, 1H, *J* = 12.4, H2), 5.24 (d, 1H, *J* = 12.4, H2), 3.48 (s, 3H, H1), 1.8 (d, 9H, *J* = 9.9, PMe₃). ^{13}C NMR (acetone-d_6): 205.6 (C2), 146.3 (Tp), 145.5 (Tp), 145.3 (Tp), 140.0 (Tp), 138.1 (Tp), 138.0 (Tp), 134.7 (C4), 129.4 (C6), 128.7 (C5), 128.5 (C7), 108.6 (Tp), 108.0 (Tp), 107.9 (Tp), 51.2 (C3), 20.2 (C1), 14.6 (PMe₃). Diastereomer **B**: ^1H NMR (acetone-d_6): 8.35, 8.21, 8.10, 8.03, 7.95, 7.42, 6.20, 6.52, 6.42, 6.03 (d, 1H, *J* = 15.3, H2), 5.92 (d, 1H, *J* = 15.3, H2), 2.90 (s, 3H, H1), 1.28 (d, 9H, *J* = 9.9, PMe₃). FTIR (HATR, glaze): ν(NO) = 1609 cm^{-1}, ν(BH) = 2510 cm^{-1}. Anal. Calcd for C₂₁H₂₉BN₈OPWBr: C, 35.52; H, 4.29; N, 11.60. Found: C, 35.02; H, 3.93; N, 11.97.

[TpW(NO)(PMe₃)(η^2-CH₃CN((CH₂)₃CH₃))](I) (7). [TpW(NO)-(PMe₃)(η^2-benzene)] (100 mg, 0.172 mmol) was dissolved in acetonitrile (5.284 g), and iodobutane (157 mg, 0.887 mmol) was then added. After 14 h, the solvent was evaporated and the green oil was dissolved in THF. The green solution was added to *n*-pentane, and a green solid precipitated. The solid was filtered and dried in vacuo to give a light green solid in a 10:1 ratio of **A:B** (47 mg, 38.5%). Attempts to purify this salt on silica or alumina resulted in decomposition. Diastereomer **A**: ^1H NMR (acetone-d_6): δ 8.31 (2H), 8.21 (2H), 8.10 (2H), 7.62, 6.57, 6.53, 6.37, 4.26 (m, 1H, H3), 3.98 (m, 1H, H3), 3.37 (s, 3H, NCH₃), 1.65 (d, 9H, *J* = 9.9, PMe₃), 0.83 (m, 4H, CH₂), 0.55 (t, 3H, *J* = 6.9, CH₃). ^{13}C NMR (acetone-d_6): 203.5 (d, *J* = 28.4 Hz, C2), 146.4 (Tp), 145.2 (Tp), 145.1 (Tp), 140.0 (Tp), 138.4 (Tp), 138.2 (Tp), 108.6 (Tp), 108.1 (Tp), 108.0 (Tp), 47.6 (C3), 30.0 (HMBC, C4), 20.4 (C5), 19.6 (C1), 14.7 (d, *J* = 32.1 Hz, PMe₃), 13.6 (C6). Diastereomer **B** (select resonances): ^1H NMR (acetone-d_6): δ 8.27, 8.17, 8.15, 8.10, 8.03, 8.00, 6.60, 6.50, 6.49, 3.66 (m, 1H, H3); 3.57 (m, 1H, H3); 2.83 (s, 1H, H1); 1.37 (d, 9H, *J* = 9.9, PMe₃), 0.94 (t, 3H, *J* = 7.0, H6). CV: $E_{p,a}$ = +0.59 V, +0.94 V. FTIR (HATR, glaze): ν_{NO} = 1609 cm^{-1}, ν_{BH} = 2515 cm^{-1}. ^{31}P NMR (acetone-d_6): δ 8.99 (d, *J* = 320 Hz). HRMS (*m/z*, (I)): found 598.19615 (1.0), 599.19249 (5.0), 600.19725 (5.2), 601.19963 (8.0), 602.20704 (4.8), 603.20484 (8.0), 604.21173 (2.4); calc 598.19643 (1.0), 599.19374 (4.7), 600.19630 (4.2), 601.19607 (5.5), 602.20041 (2.1), 603.19934 (4.5), 604.20174 (1.0).

[TpW(NO)(PMe₃)(C,N-η^2-CH₃CN(CH₂CHCH₂))](Br) (8). [TpW(NO)(PMe₃)(η^2-benzene)] (103 mg, 0.151 mmol) was dis-

(28) Delafuente, D. A.; Myers, W. H.; Sabat, M.; Harman, W. D. *Organometallics* **2005**, *24*, 1876.

solved in acetonitrile (5 g), and allyl bromide (96 mg, 0.807 mmol) was then added, resulting in a blue color. After 17 h, the solvent was evaporated and the blue oil was dissolved in 2:1 THF/CH$_2$Cl$_2$. The blue solution was added to *n*-pentane, where a blue solid precipitated. The solid was filtered and dried in vacuo to give a light blue solid in a 2:1 ratio of **A:B** (70 mg, 61.0%). Attempts to purify this salt on silica or alumina resulted in decomposition. Diastereomer **A** (select resonances): ^{1}H NMR (acetone-d_6): δ 8.33, 8.21 (2H), 8.09, 8.06, 7.10, 6.30, 6.51, 6.37, 5.43 (m, 1H, H5), 4.95 (m, 1H, H4), 4.76 (dd, 1H, $J = 9.8, 15.4$, H3′), 4.63 (dd, 1H, $J = 9.8, 15.4$, H3), 3.37 (s, 1H, H1); 1.65 (d, 9H, $J = 10.2$, PMe$_3$). ^{13}C NMR (acetone-d_6): 205.6 (HMBC, C2), 146.3 (Tp), 145.7 (Tp), 145.1 (Tp), 140.0 (Tp), 138.3 (Tp), 138.1 (Tp), 130.9 (C4), 118.5 (C5), 108.7 (Tp), 108.0 (2 carbons, 2 Tp), 49.5 (C3), 20.1 (C1), 14.6 (d, $J = 32.1$ Hz, PMe$_3$). Diastereomer **B** (select resonances): ^{1}H NMR (acetone-d_6): δ 8.42, 8.41, 8.02, 7.70, 6.61, 6.39, 2.87 (s, 1H, H1); 1.55 (d, 9H, $J = 9.6$, PMe$_3$). ^{13}C NMR (acetone-d_6): 214.6 (HMBC, C2), 145.7 (buried, HMBC, Tp), 145.4 (Tp), 144.9 (Tp), 139.5 (Tp), 138.7 (Tp), 137.9 (Tp), 132.7 (C5), 118.0 (C4), 108.8 (Tp), 108.2 (Tp), 107.8 (Tp), 52.2 (C3), 13.2 (d, $J = 31.2$ Hz, PMe$_3$). CV: $E_{p,a} = 1.08$ V. FTIR (HATR, glaze): ν(NO) = 1605 cm^{-1}, ν(BH) = 2515 cm^{-1}. ^{31}P NMR (acetone-d_6): δ 8.29 (d, $J = 261$ Hz); 7.49 (d, $J = 270$ Hz).

[TpW(NO)(PMe$_3$)(η^2-CH$_3$CN(CH$_3$))](I) (9). [TpW(NO)(PMe$_3$)-(η^2-benzene)] (103 mg, 0.151 mmol) was dissolved in acetonitrile (5 g), and methyl iodide (135 mg, 1.00 mmol) was then added, resulting in a green color. After 24 h, the solvent was evaporated and the green oil was dissolved in 1:1 THF/CH$_2$Cl$_2$. The green solution was added to *n*-pentane, where a green solid precipitated. The solid was filtered and dried in vacuo to give a light green solid in a 1:1 ratio of **A:B** (84 mg, 89.4%). ^{1}H NMR (acetone-d_6): δ 8.40, 8.35 (2H), 8.31, 8.23, 8.21, 8.08 (3H), 8.00, 7.64, 7.52, 6.59 (2H), 6.53, 6.48, 6.39, 6.36, 4.12 (s, 3H), 3.54 (d, 3H), 3.35 (s, 3H), 2.84 (s, 3H), 1.64 (d, 9H, $J = 9.9$, PMe$_3$), 1.63 (d, 9H, $J = 9.9$, PMe$_3$). ^{13}C NMR (acetone-d_6): 211.5 (HMBC, C2B), 202.9 (HMBC, C2A), 146.5 (Tp), 145.7 (Tp), 145.6 (Tp), 145.4 (Tp), 144.8 (Tp), 144.1 (Tp), 140.0 (Tp), 139.6 (Tp), 138.8 (Tp), 138.6 (Tp), 138.3 (Tp), 137.8 (Tp), 108.7 (Tp, 2C), 108.1 (Tp, 2C), 108.0 (Tp), 107.8 (Tp), 38.6 (C3B), 34.1 (C3A), 19.3 (C1A), 15.8 (C1B). FTIR (HATR, glaze): $\nu_{NO} = 1609$ cm^{-1}, $\nu_{BH} = 2527$ cm^{-1}. Anal. Calcd for C$_{15}$H$_{25}$BIN$_8$OPW: C, 26.26; H, 3.67; N, 16.34; Found: C, 26.19; H, 3.88; N, 16.31.

[TpW(NO)(PMe$_3$)(η^2-acetonitrilium)](OTf) (10). Method A: [TpW(NO)(PMe$_3$)(4,5-η^2-2-methylthiophene)] (208 mg, 0.344 mmol) was added to 2 mL of acetonitrile followed by TBSOTf (102 mg, 0.386 mmol), and the reaction was allowed to stir for 2 days. The reaction mixture was then evaporated to dryness and redissolved in minimal methylene chloride. The product was precipitated into diethyl ether, filtered, and dried in vacuo to yield a pale brown solid (193 mg, 80.4%). Attempts to purify this salt on silica or alumina resulted in decomposition. Diastereomer A: ^{1}H NMR (acetone-d_6): δ 14.19 (s, H3), 8.32, 8.23 (2H), 8.06, 8.00, 7.46, 6.61, 6.46, 6.34, 3.43, (s, 3H, H1), 1.60 (d, 9H, $J = 9.9$, PMe$_3$). ^{13}C NMR (acetone-d_6): δ 146.2 (Tp), 145.4 (Tp), 144.3 (Tp), 139.8 (Tp), 138.4 (Tp), 137.7 (Tp), 108.7 (Tp), 107.8 (Tp), 107.8 (Tp), 21.5 (s, C1), 14.4 (d, PMe$_3$). CV: $E_{p,c} = -1.75$ V, $E_{p,a} = +1.04$ V. IR: 1611 cm^{-1}. LRMS: calcd 545.0; found 544.9.

Method B: [TpW(NO)(PMe$_3$)(η^2-benzene)] (102 mg, 0.176 mmol) was dissolved in acetonitrile (1.060 g) and stirred for 5 h. A green color was observed. Diphenylammonium triflate (70 mg, 0.219 mmol) was then added, resulting in a red solution. After 1 h, the solvent was evaporated down to a red oil, which was dissolved in CH$_2$Cl$_2$. This solution was added to diethyl ether, where an oil developed. The excess solvent was decanted, and the oil was dissolved in CH$_2$Cl$_2$. The solution was added to *n*-pentane, where a brown solid precipitated. The solid was filtered and dried in vacuo

to yield a brown solid in a 2:1 ratio of **A:B** (61 mg, 50.3%). Diastereomer **B**: ^{1}H NMR (acetone-d_6): δ 8.40, 8.38, 8.18, 8.03, 7.98, 7.53, 6.58, 6.48, 6.53, 2.92 (d, 3H, $J = 0.9$, H1), 1.58 (d, 9H, $J = 9.9$, PMe$_3$).

[TpW(NO)(PMe$_3$)(C,N-η^2-CH$_3$CH$_2$CN(CH$_2$C$_6$H$_5$))](Br) (11). [TpW(NO)(PMe$_3$)(η^2-anisole)] (103 mg, 0.167 mmol) was dissolved in propionitrile (5.324 g), and benzyl bromide (33 mg, 0.193 mmol) was then added. A green color was observed. After 5 h, the solvent was evaporated down to a green oil, which was dissolved in CH$_2$Cl$_2$. The solution was added to hexanes, where a green solid precipitated. The solid was filtered and dried in vacuo to give a light green solid. The yellow filtrate was evaporated, and the yellow solid was dissolved in THF. The product was precipitated in hexanes, filtered, and dried in vacuo to yield a light brown solid (78 mg, 73%). Major diastereomer: ^{1}H NMR (acetone-d_6): δ 8.42, 8.36, 8.21, 8.12, 8.05, 7.97, 7.47 (m, 5H, H6, H7, H8), 6.20, 6.52, 6.42 (Tp H4 coupling constants are about 2 Hz), 6.04 (d, 1H, $J = 7.8$, H4), 5.93 (d, 1H, $J = 7.8$, H4), 3.40 (m, 1H, H2), 3.20 (m, 1H, H2), 1.49 (d, 9H, $J = 9.0$, PMe$_3$), 0.43 (t, 3H, $J = 7.5$, H1). IR (HATR, glaze): ν(NO) = 1614 cm^{-1}.

TpMo(NO)(Im)(C,N-η^2-benzylacetonitrilium) (13). A test tube was charged with TpMo(NO)(Im)(η^2-furan) (100 mg, 0.204 mmol), then benzyl bromide (500 mg, 2.92 mmol) and acetonitrile (1.0 mL) were added. The mixture was capped and stirred in an oil bath at 50 °C overnight. The reaction mixture was then added to 50 mL of *n*-pentane, and the product oiled and stuck to the sides of the container. The solution was decanted, and the remaining oil was dissolved in 1 mL of CH$_2$Cl$_2$. The solution was added into 50 mL of diethyl ether, and the precipitate was filtered, washed with diethyl ether (10 mL × 3), and dried in vacuo. A light yellow solid (102 mg, 77% yield) was obtained as a 4:1 (**A:B**) mixture of two isomers. The major isomer (**13A**) is much less soluble in acetone then the minor isomer. Pure major isomer can be obtained as a white solid by washing the mixture with acetone. Attempts to purify this salt on silica resulted in decomposition. Major isomer (**13A** 80%): ^{1}H NMR (CDCl$_3$): δ 7.93, 7.84, 7.61, 7.75, 7.64, 7.62 (6H, 1:1:1:1:1:1, each a d, $J = 1.5$ Hz or fine dd with $J = 0.9$ Hz, Tp 3, 5), 7.41 (1H, d, $J = 1.8$ Hz, Im), 7.27 (5H, m, Ph), 6.95, 6.72 (2H, 1:1, each a t, $J = 1.5$ Hz, Im), 6.39, 6.29, 6.12 (3H, 1:1:1, each a t, $J = 2.4$ Hz, Tp 4), 5.52 (2H, 1:1, 2 d, $J = 15$ Hz, CH$_2$), 3.85 (3H, s, N−CH$_3$), 2.46 (3H, s, CH$_3$). ^{13}C NMR (CDCl$_3$, 75 MHz): δ 200.9 (CN), 143.8, 143.5, 141.8, 140.1, 136.5, 136.3 (Tp 3, 5), 135.3 (Im), 133.6 (Ph, C), 128.7, 128.6 (Ph, 5 CHs), 128.1, 122.1 (Im), 106.9, 106.6, 106.0 (Tp 4), 52.9 (CH$_2$), 35.5 (N-CH$_3$), 15.4 (CH$_3$). Minor isomer (**13B**, 20%): ^{1}H NMR (CDCl$_3$): δ 7.93, 7.84, 7.61, 7.75, 7.64, 7.62 (underneath the signals of major isomer, Tp 3, 5), 7.17 (5H, m, Ph), 6.94, 6.70, 6.68 (3H, 1:1:1, br, Im), 6.39 (underneath the signal of major isomer, Tp 4), 6.36 (1H, br t, Tp 4), 6.12 (underneath the signal of major isomer, Tp 4), 4.88 (2H, 1:1, 2 d, $J = 15$ Hz, CH$_2$), 3.96 (3H, s, N-CH$_3$), 2.15 (3H, s, CH$_3$). ^{13}C NMR (CDCl$_3$, 75 MHz, 25 °C): δ 202.6 (CN), 144.0, 143.5 (underneath the signal of major isomer), 142.0, 140.1 (underneath the signal of major isomer), 136.6, 136.0 (Tp 3, 5), 135.8 (Im), 132.8 (Ph, C), 127.8 (Ph, 5 CHs), 128.3, 122.9 (Im), 106.9 (underneath the signal of major isomer), 106.8, 106.2 (Tp 4), 53.4 (CH$_2$), 35.5 (underneath the signal of major isomer, N-CH$_3$), 15.0 (CH$_3$). IR (HATR, glaze): $\nu_{NO} = 1640$ cm^{-1}. CV: $E_{p,c} = -1.69$ V, $E_{p,a} = 0.78$ V.

[TpW(NO)(PMe$_3$)(η^1-acetonitrilium)](OTf) (17). [TpW(NO)-(PMe$_3$)(4,5-η^2-2-methylthiophene)] (454 mg, 0.826 mmol) was added to 4 mL of acetonitrile followed by Zn(OTf)$_2$ (464 mg, 1.25 mmol) and stirred overnight. The solution was added to 125 mL of diethyl ether, and the product oiled to the sides. The solution was decanted, and the remaining oil was dissolved in 1 mL of THF. The product was precipitated into diethyl ether, then filtered and dried in vacuo. An orange solid (588 mg) was isolated in a 2:1 ratio of isomers (**A:B**). Diastereomer **A**: ^{1}H NMR (acetone-d_6): δ

8.34, 8.27, 8.25, 8.16, 8.11, 8.07, 8.07 (d, 1H, buried Hz, 1HA), 6.61, 6.52, 6.51, 2.22 (d, 3H, $J = 6.2$, Me), 1.73 (d, 9H, $J = 10.3$, PMe$_3$). Diastereomer **B**: ^{1}H NMR (acetone-d_6): 8.45, 8.28, 8.26, 8.24, 8.11, 6.46, 1.91 (d, 3H, $J = 6.1$, Me), 1.66 (d, 9H, $J = 10.8$, PMe$_3$). ^{13}C NMR (acetone-d_6): δ 12.7 (1H A), 145.9 (Tp), 145.8 (Tp), 145.0 (Tp), 139.9 (Tp), 138.6 (Tp), 138.6 (Tp), 109.0 (Tp), 108.2 (Tp), 108.2 (Tp), 19.8 (Me A), 18.9 (Me B), 14.5 (d, PMe$_3$ A), 13.4 (d, PMe$_3$ B). IR (HATR, glaze): 1644 cm^{-1}. CV: $E_{p,c} = -1.25$ V.

[TpW(NO)(PMe$_3$)(η^1-benzylideneamine)] (18). [TpW(NO)-(PMe$_3$)(4,5-η^2-2-methylthiophene)] (100 mg, 0.165 mmol) was added to 1.5 mL of dry benzonitrile followed by Zn(OTf)$_2$ (91 mg, 0.251 mmol), and the mixture was stirred overnight. The product was added to diethyl ether, where an orange solid precipitated. The solid was collected and dried in vacuo. An orange solid (84 mg) (about 80% clean; the other 20% may be a diastereomer or side product) was obtained. ^{1}H NMR (acetone-d_6): δ 9.12 (d, 1H, $J = 10.1$, CH), 8.55, 8.37, 8.34, 8.30, 8.19, 7.51, 8.20 (s, br, 1H, PhH), 7.54 (t, 1H, $J = 1.3, 1.5$, PhH), 7.48 (t, 1H, $J = 1.7, 1.5$, PhH), 7.44 (t, 1H, $J = 1.3, 0.9$, PhH), 7.41 (t, 1H, $J = 1.7, 1.5$, PhH), 6.63 (dt, 2H), 6.50 (Tp H4 coupling constants are about 2 Hz), 1.75 (d, 9H, $J = 10.7$, PMe$_3$).

TpW(NO)(PMe$_3$)(η^2-cyclopentene)(19). To a solution of [TpW-(NO)(PMe$_3$)(η^2-benzene)] (1.10 g, 1.89 mmol) and cyclopentene (4 mL) were added pentane (8 mL) and THF (1 mL). The resulting heterogeneous mixture was stirred for 3 days. The reaction mixture was then added to 75 mL of pentane, and the resulting precipitate was collected on a fritted glass funnel and dried in vacuo to give **19** (870 mg, 81%) as a light brown powder. ^{1}H NMR (acetone-d_6): δ 8.27, 8.11, 7.93, 7.87, 7.778, 7.54, 6.40, 6.28, 6.25, 3.42 (m, 1H, H5), 3.31 (m, 1H, H3), 3.04 (ddd, 1H, $J = 5.6, 7.9, 13.5$, H1), 2.82 (m, 1H, H3), 2.52 (dd, 1H, $J = 8.5, 11.7$, H5), 1.91 (m, 1H, H4), 1.63 (ddd, 1H, $J = 2.6, 5.3, 7.9$, H2), 1.47 (m, 1H, H4), 1.25 (d, 9H, $J = 8.1$, PMe$_3$). ^{13}C NMR (acetone-d_6): δ 143.9 (Tp), 143.0 (Tp), 142.0 (Tp), 137.3 (Tp), 136.5 (Tp), 136.1 (Tp), 107.0 (Tp), 106.5 (Tp), 106.3 (Tp), 62.1 (d, $J = 12.0$, C1), 60.7 (C2), 37.6 (d, $J = 2.4$, H5), 36.7 (C3), 24.4 (C4), 13.8 (d, $J = 27.6$, PMe$_3$). IR (HATR glaze): $\nu_{NO} = 1541$ cm^{-1}. CV: $E_{1/2} = +0.35$ V. HRMS (m/z, (I)): found 569.16788 (6), 570.16565 (10), 571.16899 (10), 572.16899 (14), 573.17270 (8). calc 569.16988 (3) 570.16718 (13), 571.16976 (12), 572.16949 (15), 573.17396 (5).

[TpW(NO)(PMe$_3$)(η^2-cyclopentanyl)]OTf (20). To [TpW(NO)-(PMe$_3$)(η^2-cyclopentene)] (100 mg, 0.175 mmol) were added THF (1 mL) and diphenylammonium triflate (61 mg, 0.193 mmol). The resulting solution was stirred for 20 min. The reaction mixture was then added to 50 mL of diethyl ether, and the resulting precipitate was collected on a fritted glass funnel and dried in vacuo to yield **20** (99 mg, 80%) as an off-white powder. ^{1}H NMR (**20a**, acetone-d_6): δ 8.58, 8.32, 8.30, 8.24, 8.19, 8.12, 6.69, 6.59 (dt, 2H), 4.28 (ddd, 1H, $J = 7.9, 9.0, 16.7$ Hz, H1), 3.62 (m, 1H, H5), 3.15 (dd, 1H, $J = 7.9, 13.9$ Hz, H5′), 2.77 (m, 1H, H3′), 2.44 (m, 1H, H3), 1.86 (m, 1H, H4), 1.78 (m, 1H, H4′), 1.55 (m, 1H, H2′), 1.39 (d, 9H, $J = 10.0$, PMe$_3$), −1.53 (m, 1H, H2). ^{13}C NMR (acetone-d_6):

δ 148.2 (Tp), 146.3 (Tp), 143.2 (Tp), 141.0 (Tp), 140.3 (Tp), 139.6 (Tp), 109.9 (Tp), 109.0 (Tp), 108.9 (Tp), 81.3 (C1, $J_{CP} = 19.0$ Hz) 35.9 (C5), 29.5 (C3), 26.6 (C4), 13.9 (C2, $J_{CH} = 83$ Hz) 13.0 (d, $J_{CP} = 33.4$, PMe$_3$). ^{31}P NMR (acetone-d_6): δ −2.56 ppm ($J_{WP} = 287$ Hz). IR (HATR glaze): $\nu_{NO} = 1640$ cm^{-1}. CV: $E_{p,a} = +1.07$ V. LRMS: $m/z = 572.1$. (calc 572.2)

[TpW(NOMe)(PMe$_3$)(η^2-cyclopentene)](OTf) (21). To [TpW-(NO)(PMe$_3$)(η^2-cyclopentene)] (175 mg, 0.306 mmol) was added CH$_3$CN (1 mL) along with MeOTf (10 drops). The resulting solution was stirred for 10 min. To the solution was added diethyl ether (10 mL), and an oil separated. The solvent was evaporated, and the residue was dissolved in dichloromethane (3 mL). The solution was then added to diethyl ether (50 mL), and the resulting precipitate was then collected on a fritted glass funnel, rinsed with diethyl ether (15 mL), and dried in vacuo to give **21** (167 mg, 69%) as a light brown powder. Diastereomer **A**: ^{1}H NMR (acetone-d_6): δ 8.66, 8.35, 8.18, 8.11, 8.06, 7.84, 6.63, 6.55, 6.43, 4.41 (m, 1H, H2), 4.14 (s, 3H, Me), 3.96 (m, 1H, H3-anti), 3.92 (m, 1H, H5-anti), 3.18 (dd, 1H, $J = 8.5, 13.5$ Hz, H5-syn), 2.85 (dd, 1H, $J = 13.7, 8.5$ Hz, H3-syn), 2.77 (m, 1H, H1), 1.75 (m, 1H, H4-anti), 1.51 (buried, 1H, H4-syn), 1.49 (d, 9H, $J = 9.6$ Hz, PMe$_3$). ^{13}C NMR (acetone-d_6): δ 144.8 (Tp), 145.7 (Tp), 143.7 (Tp), 139.8 (Tp), 138.5 (Tp), 138.5 (Tp), 108.9 (Tp), 108.3 (Tp), 108.2 (Tp), 72.8 (d, $J = 8.5$, C2), 70.1 (C1), 66.7 (d, $J = 1.7$, Me), 38.3 (C5), 38.2 (d, $J = 1.7$, C3), 22.4 (C4), 14.1 (d, $J = 32.0$, PMe$_3$). IR (HATR glaze): $\nu_{NO} = 1698$ (w) cm^{-1}, 1621 (br) cm^{-1}. CV: $E_{p,a} = +1.18$ V, $E_{p,c} = -1.70$ V. LRMS: $m/z = 587.9$ (calc 586.2)

[TpW(NO)(PMe$_3$)(η^2-cyclopentadienium)](OTf) (22). To [TpW(NO)(PMe$_3$)(η^2-cyclopentene)] (300 mg, 0.525 mmol) were added THF (2 mL) and tritylium triflate (227 mg, 0.577 mmol). The resulting solution was stirred for 15 min. The resulting precipitate was then collected on a fritted glass funnel, then rinsed with diethyl ether (15 mL) and dried in vacuo to give **22** (260 mg, 69%) as a yellow powder. ^{1}H NMR (acetone-d_6): δ 8.59, 8.38, 8.34, 8.19, 8.17, 7.96, 7.47 (t, 1H, (br), H2), 6.64, 6.63, 6.40, 4.86 (t, 1H, $J = 3.6, 3.6$, H1), 4.59 (dt, 1H, $J = 15.6, 4.9, 4.9$, H5), 3.84 (m, 1H, H4), 3.24 (m, 2H, H3, H3′), 2.47 (dd, 1H, $J = 13.8, 5.6$, H4′), 1.35 (d, 9H, $J = 9.8$, PMe$_3$). ^{13}C NMR (acetone-d_6): δ 150.8 (C2), 148.6 (Tp), 146.6 (Tp), 144.2 (Tp), 139.4 (Tp), 139.3 (Tp), 139.3 (Tp), 109.5 (Tp), 109.0 (Tp), 108.1 (Tp), 99.0 (d, $J = 2.7$, C1), 74.1 (d, $J = 14.2$, C5), 33.1 (C3), 32.0 (d, $J = 3.2$, C4), 12.8 (d, $J = 32.7$, PMe$_3$). ^{31}P NMR (acetone-d_6): −7.57 ($J_{WP} = 273$ Hz). FTIR (HATR glaze): $\nu_{NO} = 1634$ cm^{-1}.

Supporting Information Available: ^{1}H, ^{13}C, and 2D NMR data for complexes **3**, **4**, **7**, **8**, **10**, **13**, **19**, and **20−22** and cif files for crystal structure determinations (**3**, **10**, **11b**, **13b**). This material is available free of charge via the Internet at http://pubs.acs.org.

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