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Paper:

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Cationic and Neutral Cp*M(NO)(κ^2-Ph$_2$PCH$_2$CH$_2$PPh$_2$) Complexes of Molybdenum and Tungsten: Lewis-acid Induced Intramolecular C-H Activation

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ABSTRACT:

Treatment of CH_2Cl_2 solutions of $Cp*M(NO)Cl_2$ ($Cp* = \eta^5-C_5(CH_3)_5$; M = Mo, W) first with 2 equiv of $AgSbF_6$ in the presence of PhCN and then with 1 equiv of $Ph_2PCH_2CH_2PPh_2$ affords the yellow-orange salts $[Cp*M(NO)(PhCN)(\kappa^2-Ph_2PCH_2CH_2PPh_2)](SbF_6)_2$ in good yields (M = Mo, W). Reduction of $[Cp*M(NO)(PhCN)(\kappa^2-Ph_2PCH_2CH_2PPh_2)](SbF_6)_2$ with 2 equiv of Cp_2Co in C_6H_6 at 80 °C produces the corresponding 18e neutral compounds, $Cp*M(NO)(\kappa^2-Ph_2PCH_2CH_2PPh_2)$ which have been isolated as analytically pure orange-red solids. Addition of 1 equiv of the Lewis acid, $Sc(OTf)_3$, to solutions of $Cp*M(NO)(\kappa^2-Ph_2PCH_2CH_2PPh_2)$ at room temperature results in the immediate formation of thermally stable $Cp*M(NO{\rightarrow}Sc(OTf)_3)(H)(\kappa^3-(C_6H_4)PhPCH_2CH_2PPh_2)$ complexes in which one of the phenyl substituents of the $Ph_2PCH_2CH_2PPh_2$ ligands has undergone intramolecular orthometalation. In a similar manner, addition of BF_3 produces the analogous $Cp*M(NO{\rightarrow}BF_3)(H)(\kappa^3-(C_6H_4)PhPCH_2CH_2PPh_2)$ complexes. In contrast, $B(C_6F_5)_3$ forms the 1:1 Lewis acid-base adducts, $Cp*M(NO{\rightarrow}B(C_6F_5)_3)(\kappa^2-Ph_2PCH_2CH_2PPh_2)$ in CH_2Cl_2 at room temperature. Upon warming to 80 °C, $Cp*Mo(NO{\rightarrow}B(C_6F_5)_3)(\kappa^2-Ph_2PCH_2CH_2PPh_2)$ converts cleanly to the orthometalated product $Cp*Mo(NO{\rightarrow}B(C_6F_5)_3)(H)(\kappa^3-(C_6H_4)PhPCH_2CH_2PPh_2)$, but $Cp*W(NO{\rightarrow}B(C_6F_5)_3)(\kappa^2-Ph_2PCH_2CH_2PPh_2)$ generates a mixture of products whose identities remain to be ascertained. Attempts to extend this chemistry to include related $Ph_2PCH_2PPh_2$ compounds have had only limited success. All new complexes have been characterized by conventional spectroscopic and analytical methods, and the solid-state molecular structures of most of them have been established by single-crystal X-ray crystallographic analyses.

INTRODUCTION

Metal-nitrosyl complexes often exhibit chemical properties different than those of their isoelectronic carbonyl analogues. This difference is usually a manifestation of the NO ligand's strong π-accepting ability, in effect allowing it to act as a reservoir of electron density depending on the degree of M→NO backbonding.[1] M-N-O linkages most commonly exist in their linear configurations with the angles at N being in the range of 160-180°. In such linkages the nitrosyl ligands (formally NO^+) function as 3e-donors to the metal centers, and the bonding can be described in terms of varying contributions of the resonance forms $M^--N^+\equiv O \leftrightarrow M=N=O \leftrightarrow M\equiv N^+-O^-$. Alternatively, coordination of NO to a transition-metal center may result in the formation of a bent M-N=O link (M-N-O angles of 110-140°) in which the nitrosyl ligands (formally NO^-) are 1e-donors and much weaker π-acids.[2] In general, bent M-N-O groups have been exhibited by complexes containing Group 7-9 metals[3–5], whereas those of Group 6 display mainly linear M-N-O linkages.[5] For the majority of nitrosyl complexes, bound NO primarily behaves as an ancillary ligand during their chemical transformations, acting to accept or donate electron density to the metal centers as required. Reactions that do involve the NO ligands often result in cleavage or rearrangement of the M-N or N-O bonds.[6–8] As a result, the ability of NO to function as a non-innocent ligand while facilitating transformations at the metal center currently remains a relatively underexplored topic. In that connection though, recent work by Berke and coworkers has demonstrated that for several $ReCl(PR_3)_2(NO)_2$ complexes, NO-aided reactivity at the metal centers can be induced by the addition of Lewis acids such as $B(C_6F_5)_3$ or Et^+ to the O-termini of the apical, linear NO ligands.[9] The resulting adducts are highly active olefin-hydrogenation catalysts, and this enhancement in reactivity as compared to control experiments

without an added Lewis acid has been attributed to the reversible generation of an open coordination site at the rhenium centers through linear/bent configurational changes of the Re-N-O groups.

In recent years, we have developed Cp*M(NO)-containing complexes (Cp* = η^5-$C_5(CH_3)_5$; M = Mo or W) as reagents for the selective activation and functionalization of otherwise unreactive hydrocarbon C-H bonds.[10,11] However, the focus of these investigations has centered on the properties and reactions of the M-C bonds already extant in these complexes rather than on the reactivity at the NO ligands. To address the question of NO-based reactivity, we have recently extended our investigations to complexes that possess electron-rich metal centers that should, in principle, facilitate the oxidative addition of hydrocarbon C-H bonds to them as a result of linear/bent configurational changes of their M-N-O linkages. Specifically, we now wish to report the results of our studies in this regard with new 18e Cp*M(NO)(κ^2-$Ph_2PCH_2CH_2PPh_2$) (M = Mo, W) compounds which have demonstrated that these complexes are rendered prone to effecting C-H activation reactions not by thermolyses, as are some of the other Cp*M(NO)-containing compounds,[10,11] but rather by treatment with an equimolar amount of an appropriate Lewis acid. We begin our narrative by outlining the synthetic methodology that leads to the novel nitrosyl complexes of interest.

RESULTS AND DISCUSSION

Synthesis and Characterization of [Cp*M(NO)(PhCN)(κ^2-$Ph_2PCH_2CH_2PPh_2$)](SbF_6)_2 Complexes. The complexes [Cp*M(NO)(PhCN)(κ^2-

Ph$_2$PCH$_2$CH$_2$PPh$_2$)](SbF$_6$)$_2$ (M = Mo (**1**); W (**2**)) can be conveniently synthesized in the manner summarized in Scheme 1. Treatment of CH$_2$Cl$_2$ solutions of Cp*M(NO)Cl$_2$ (Cp* = η^5-C$_5$(CH$_3$)$_5$) first with 2 equiv of AgSbF$_6$ and then later with PhCN affords red-brown reaction mixtures that contain an AgCl precipitate and solutions of complexes that we presume to be [Cp*M(NO)(PhCN)$_3$](SbF$_6$)$_2$ by analogy to the known [Cp*Mo(NO)(MeCN)$_3$](PF$_6$)$_2$.[12] Filtration of these mixtures and treatment of the filtrates with 1 equiv of Ph$_2$PCH$_2$CH$_2$PPh$_2$ results in an immediate color change to orange-brown. Removal of volatiles in vacuo produces dark-brown oils that afford the desired salts when triturated with Et$_2$O. In this manner **1** and **2** are obtained as yellow-orange powders in good yields.

Scheme 1. Synthesis of [Cp*M(NO)(PhCN)(κ^2-Ph$_2$PCH$_2$CH$_2$PPh$_2$)](SbF$_6$)$_2$ Complexes
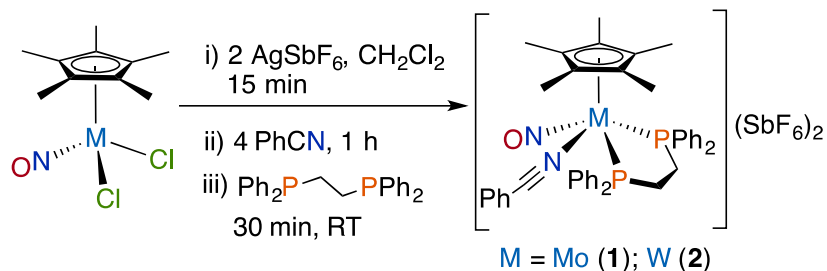
Recrystallization of the molybdenum salt from MeCN/Et$_2$O at -30 °C affords single crystals of [Cp*Mo(NO)(PhCN)(κ^2-Ph$_2$PCH$_2$CH$_2$PPh$_2$)](SbF$_6$)$_2$•MeCN•Et$_2$O suitable for an X-ray crystallographic analysis. The solid-state molecular structure of the dication in these crystals is shown in Figure 1. Its intramolecular metrical parameters are similar to those exhibited by related four-legged, piano-stool molecules containing nitrosyl ligands.[13] The solid-state molecular structure of the [Cp*W(NO)(PhCN)(κ^2-Ph$_2$PCH$_2$CH$_2$PPh$_2$)]$^{2+}$ dication as it occurs in

its OTf$^-$ salt (OTf$^-$ = $^-$OSO$_2$CF$_3$) has metrical parameters very similar to those of its

molybdenum counterpart shown in Figure 1 and it is presented in the Supporting Information.
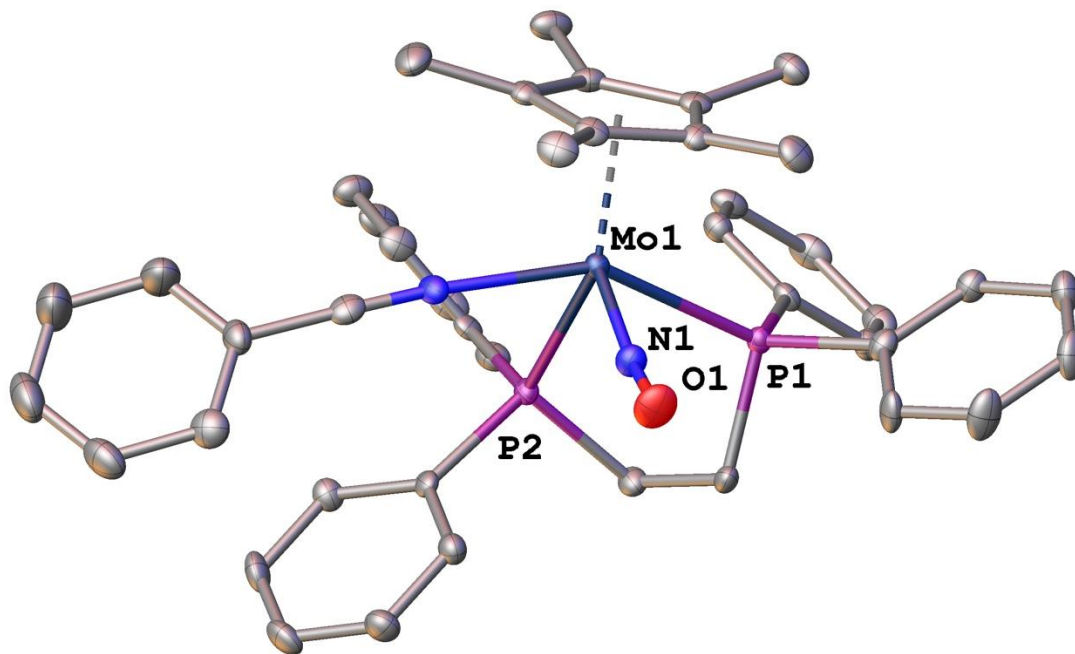
Figure 1. Solid-state molecular structure of the [Cp*Mo(NO)(PhCN)(κ^2-Ph$_2$PCH$_2$CH$_2$PPh$_2$)]$^{2+}$

cation as it occurs in [Cp*Mo(NO)(PhCN)(κ^2-Ph$_2$PCH$_2$CH$_2$PPh$_2$)](SbF$_6$)$_2$•MeCN•Et$_2$O with

50% probability thermal ellipsoids shown. Hydrogen atoms, along with counteranions and

solvent molecules, have been omitted for clarity. Selected bond lengths (Å) and angles (deg):

Mo(1)-P(1) = 2.5421(9), Mo(1)-P(2) = 2.6111(9), P(1)-Mo(1)-P(2) = 73.54(3), Mo(1)-N(1) =

1.796(3), N(1)-O(1) = 1.182(3), Mo(1)-N(1)-O(1) = 167.4(3).

During the preparation of **2**, if the mixture is not stirred following the addition of AgSbF$_6$

for at least 1 h prior to filtration of the Ag salts, a second product can be detected in the reaction

mixture. No analogous product has been detected under similar conditions during the

preparation of **1**. This product is believed to result from a single chloride abstraction from the Cp*W(NO)Cl$_2$ starting material. To confirm this hypothesis, [Cp*W(NO)(Cl)(κ^2-Ph$_2$PCH$_2$CH$_2$PPh$_2$)](OTf) has been prepared independently from Cp*W(NO)Cl$_2$ and AgOTf as summarized in Scheme 2.

Scheme 2. Synthesis of [Cp*W(NO)(Cl)(κ^2-Ph$_2$PCH$_2$CH$_2$PPh$_2$)](OTf)
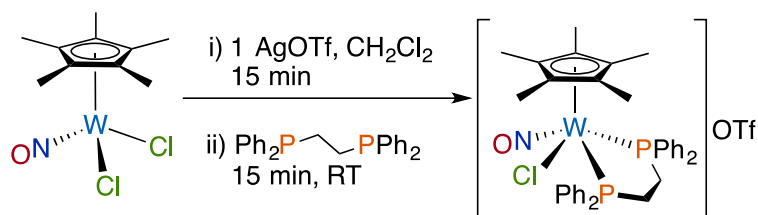
As expected, the ^{1}H- and ^{31}P{^{1}H}-NMR resonances of [Cp*W(NO)(Cl)(κ^2-Ph$_2$PCH$_2$CH$_2$PPh$_2$)](OTf) match those of the byproduct formed during the preparation of **2**. For example, the ^{31}P{^{1}H} NMR spectrum of the monochloro complex clearly indicates the presence of two inequivalent ^{31}P nuclei with resonances possessing unique ^{183}W satellites at δ 30.0 and 40.8 ppm, both of which are doublets ($^2J_{PP}$ = 8.53 Hz).

Synthesis and Characterization of Cp*M(NO)(κ^2-Ph$_2$PCH$_2$CH$_2$PPh$_2$) Complexes. Reductions of **1** and **2** can be effected in C$_6$H$_6$ at 80 °C with 2 equiv of cobaltocene (Cp$_2$Co) as the reducing agent. The 18e neutral Cp*M(NO)(κ^2-Ph$_2$PCH$_2$CH$_2$PPh$_2$) (M = Mo (**3**); M = W (**4**)) product complexes can be isolated as analytically pure orange-red solids by chromatography on alumina with pentane/Et$_2$O as eluant (Scheme 3).

Scheme 3. Synthesis of Cp*M(NO)(κ²-Ph₂PCH₂CH₂PPh₂) Complexes

M = Mo (**1**); W (**2**)   M = Mo (**3**); W (**4**)
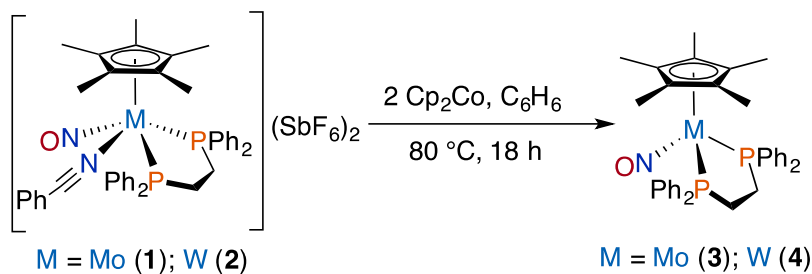
X-ray quality crystals of **3** were deposited along the walls of the reaction flask during the course of its preparation from **1**, and its solid-state molecular structure is shown in Figure 2. The structure is that of a classic three-legged piano-stool molecule containing the Cp*M(NO) scaffold.[10] The NO ligand is linear, with a Mo(1)-N(1)-O(1) bond angle of 176.33(16)º. The Mo(1)-P(1) and Mo(1)-P(2) bond lengths of 2.3940(5) Å and 2.3881(5) Å, respectively, are shorter than the average Mo-P bond lengths found in comparable complexes such as [Cp*Mo(H)(MeCN)₂(κ²-Ph₂PCH₂CH₂PPh₂)](BF₄)₂ (Mo-P = 2.554(2) Å, 2.541(2) Å),[14] and Cp*Mo(H)₂(κ²-Ph₂PCH₂CH₂PPh₂)(OCOCF₃) (Mo-P = 2.5206(5) Å, 2.3962(5) Å).[15] This shortening is best viewed as a consequence of the low oxidation state Mo(0) center in **3**, which can participate in greater backbonding to the phosphorus centers of the Ph₂PCH₂CH₂PPh₂ ligand as compared to the Mo(IV) hydrides listed above.
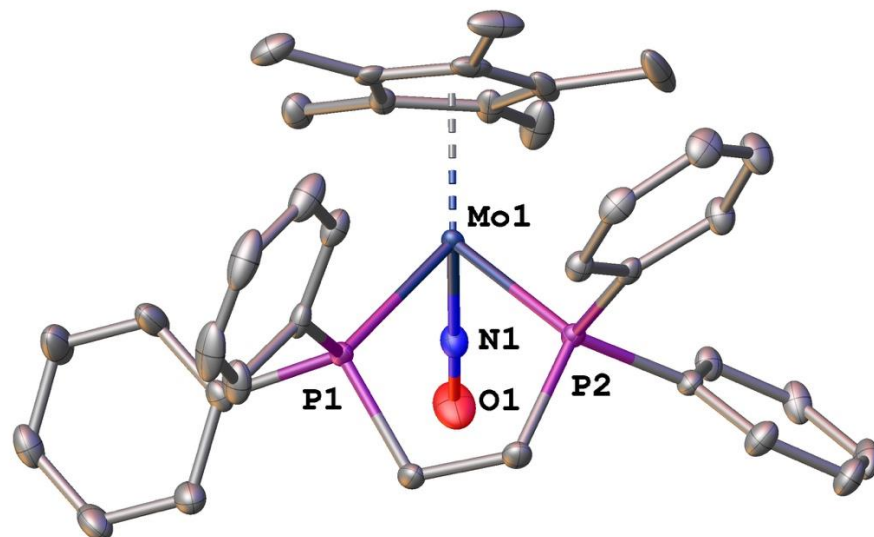
Figure 2. Solid-state molecular structure of **3** with 50% probability thermal ellipsoids shown. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Mo(1)-P(1) = 2.3940(5), Mo(1)-P(2) = 2.3881(5), P(1)-Mo(1)-P(2) = 79.418(17), Mo(1)-N(1) = 1.7878(16), N(1)-O(1) = 1.223(2), Mo(1)-N(1)-O(1) = 176.33(16).

The NMR spectra of the congeneric tungsten complex **4** are particularly informative. Thus, the ^{31}P signal in the 162 MHz $^{31}P\{^1H\}$-NMR spectrum of **4** in C_6D_6 shows a singlet possessing characteristic ^{183}W satellites with $^1J_{PW}$ = 440.0 Hz. This feature is comparable to that exhibited by the related complex, Cp*W(NO)(PMe$_3$)$_2$, which also exhibits a large $^1J_{PW}$ value of 456.8 Hz.[16] For comparison, related W(II) complexes containing either the Cp*W(NO) or TpW(NO) scaffolds consistently display much smaller $^1J_{PW}$ values nearer ~250 Hz.[16–18] Consistent with previous reports, the magnitudes of these coupling constants are functions of the tungstens' oxidation states and their coordination numbers.[19] Larger coupling constants in W(0)

complexes indicate a stronger W-P interaction through increased W→P backbonding than is possible when the same metal exists in a higher oxidation state such as W(II).[20]

IR spectra of the Cp*M(NO)(κ^2-Ph$_2$PCH$_2$CH$_2$PPh$_2$) complexes reveal strong ν_{NO} absorptions at 1557 and 1549 cm^{-1} for **3** and **4**, respectively. These low-wavenumber absorptions are indicative of considerable M→NO backbonding that renders the terminal oxygen atoms of the nitrosyl ligands quite Lewis basic.[16] In other words, a significant contribution to the overall nitrosyl bonding motif present in **3** and **4** involves the resonance structure M≡N$^+$-O$^-$ in which the M-N-O group remains linear. The diminished N-O bond order due to this resonance structure is manifested by the low-wavenumber ν_{NO} absorptions present in the IR spectra of **3** and **4**. In addition, this inference is supported for M = Mo by the increased N-O bond length extant in the solid-state molecular structure of **3** (N-O = 1.223(2) Å) relative to that found in **1** (N-O = 1.182(3) Å).

The chemistry that results from the coordination of these nitrosyl-O termini to various Lewis acids is outlined in the following sections.

Reactions of Cp*M(NO)(κ^2-Ph$_2$PCH$_2$CH$_2$PPh$_2$) with Lewis Acids. The coordinatively saturated 18e Cp*M(NO)(κ^2-Ph$_2$PCH$_2$CH$_2$PPh$_2$) complexes are thermally stable, but are surprisingly air sensitive both in solution and in the solid state. Furthermore, these compounds lack any open coordination sites that would allow for the oxidative addition of various substrates to the metal centers. However, we have now discovered that such reactivity at the metal can be induced by exploiting configurational changes of the NO ligands caused by coordination of various Lewis acids [LA] to form Cp*M(NO→LA)(κ^2-Ph$_2$PCH$_2$CH$_2$PPh$_2$)

adducts possessing non-linear NO ligands. The results of our investigations in this regard are summarized below in terms of the various Lewis acids studied.

LA = Sc(OTf)₃. Addition of $Sc(OTf)_3$ to CD_2Cl_2 or CD_3NO_2 solutions of **3** or **4** at ambient temperatures results in the immediate formation of thermally stable $Cp*M(NO{\rightarrow}Sc(OTf)_3)(H)(\kappa^3\text{-}(C_6H_4)PhPCH_2CH_2PPh_2)$ complexes (M = Mo (**5**); M = W (**6**)) in which one of the phenyl substituents of the $Ph_2PCH_2CH_2PPh_2$ ligands has undergone intramolecular orthometalation (Scheme 4).

**Scheme 4. Synthesis of Cp*M(NO→Sc(OTf)₃)(H)(κ³-(C₆H₄)PhPCH₂CH₂PPh₂) Complexes**

M = Mo (**3**); W (**4**)   M = Mo (**5**); W (**6**)
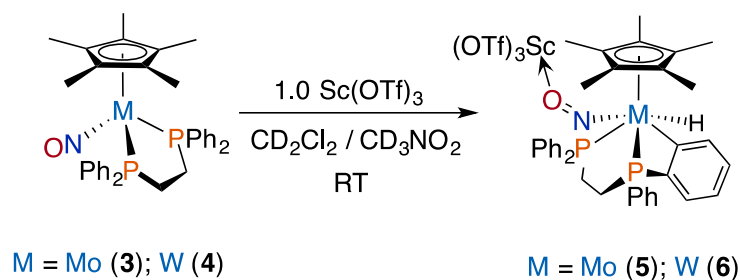
The overall transformations shown in Scheme 4 probably involve initial formation of the 16e $Cp*M(NO{\rightarrow}Sc(OTf)_3)(\kappa^2\text{-}Ph_2PCH_2CH_2PPh_2)$ adducts in which the NO ligands have been converted from linear 3e donors to bent 1e donors by virtue of coordination of their oxygen atoms to the Lewis-acidic Sc^{3+} centers. The electronic unsaturation extant in the 16e $Cp*M(NO{\rightarrow}Sc(OTf)_3)(\kappa^2\text{-}Ph_2PCH_2CH_2PPh_2)$ compounds is then rapidly relieved by one of the phenyl substituents of the $Ph_2PCH_2CH_2PPh_2$ ligands undergoing intramolecular orthometalation

to form the final 18e product complexes. To the best of our knowledge, this is an unprecedented transformation of a $Ph_2PCH_2CH_2PPh_2$ ligand.

Even though both $Sc(OTf)_3$-complexed products have been isolated in excellent yields as analytically pure orange solids, all attempts to obtain single crystals of them suitable for an X-ray crystallographic analysis have been unsuccessful to date. Nevertheless, the spectroscopic properties exhibited by these two compounds are fully consistent with the structures depicted in Scheme 4 and closely resemble those displayed by the related 18e $Cp^*M(NO{\rightarrow}BF_3)(H)(\kappa^3-(C_6H_4)PhPCH_2CH_2PPh_2)$ complexes which are prepared in an identical manner (vide infra). For instance, the 400 MHz ^1H NMR spectrum of **5** in CD_2Cl_2 contains a signal attributable to the hydride ligand at δ -1.23 ppm ($^2J_{HP}$ = 83.9 and 13.1 Hz) which exhibits coupling to two inequivalent phosphorus nuclei. Consistently, the hydride signal in its $^1H\{^{31}P\}$ NMR spectrum is a singlet. The 400 MHz ^1H NMR spectrum of **6** in CD_2Cl_2 exhibits very similar features but with ^{183}W satellites, thereby confirming that the hydride ligand is indeed bound to the metal center. The inequivalent ^{31}P environments in both compounds are manifestations of their differing orientations with respect to the hydride ligands.

Further confirmation of the identities of **5** and **6** is provided by their $\{^1H-^{13}C\}$ HMBC NMR spectra in which a cross-peak is observed between the M-*H* resonance and the metalated carbon nucleus. In the 100 MHz $^{13}C\{^1H\}$ spectrum of **5** in CD_2Cl_2, the signal due to this carbon nucleus shows a significantly more downfield shift as compared to other aromatic resonances, appearing at δ 136.1 ppm. As well, it exhibits characteristic coupling to two inequivalent phosphorus nuclei ($^2J_{CP}$ = 58.7, 3.0 Hz). A portion of the $\{^1H-^{13}C\}$ HMBC NMR spectrum of **5**

in CD$_2$Cl$_2$ is shown in Figure 3. The {^{1}H-^{13}C} HMBC spectrum of complex **6** shows an identical

H-C correlation, and it is presented in the Supporting Information (Figure S6).
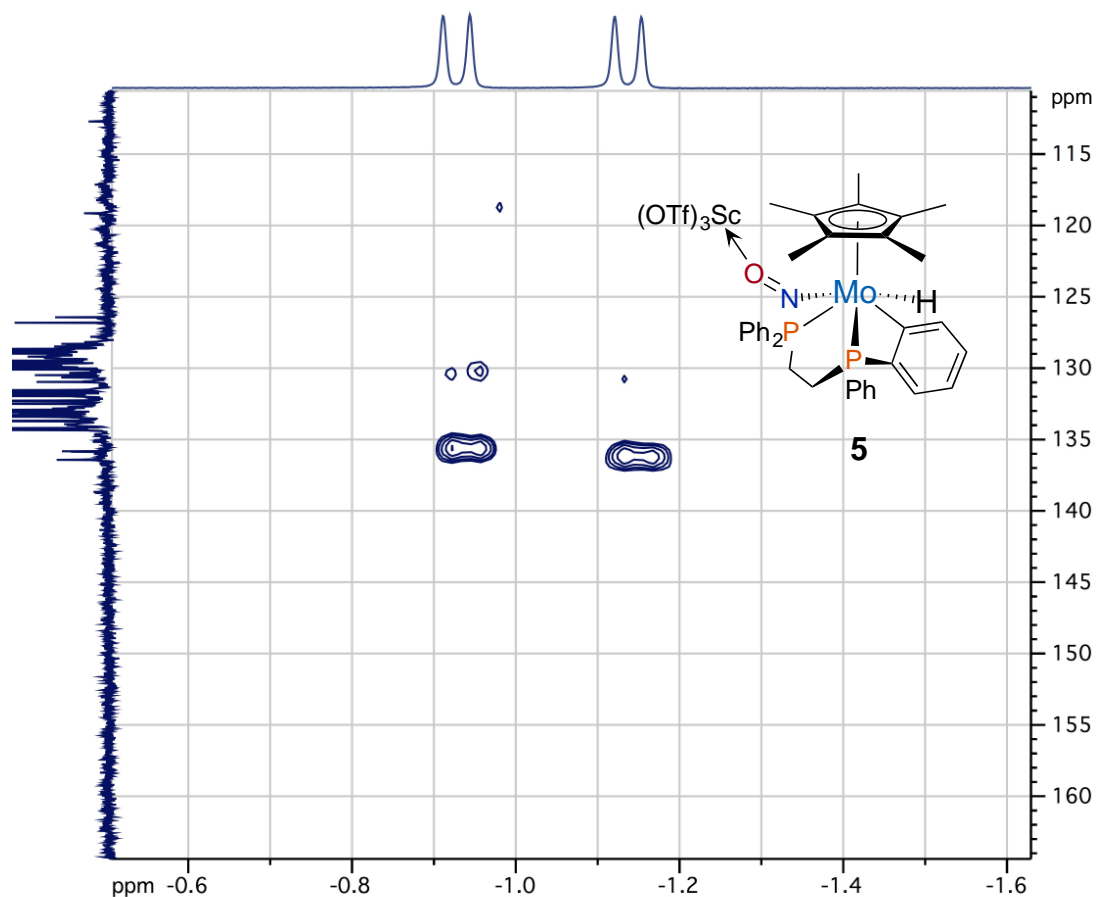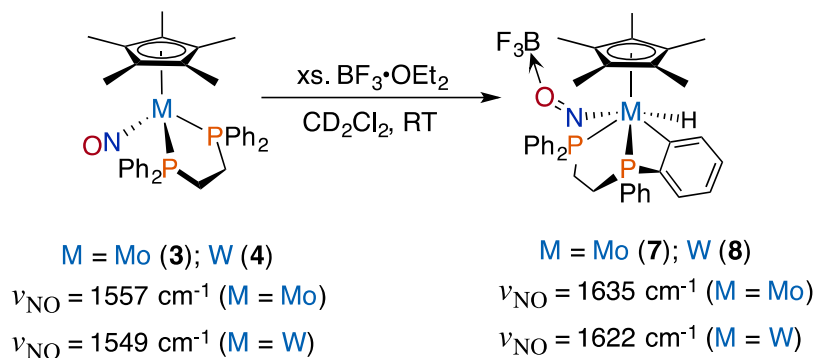

Figure 3. Partial {^{1}H-^{13}C} HMBC NMR spectrum of **5** in CD$_2$Cl$_2$ showing correlation between

the Mo-*H* and Mo-*C* resonances.

Attempts to characterize the nature of the NO ligands in **5** and **6** by using IR spectroscopy

have been unsuccessful because of strong overlapping absorptions due to Sc(OTf)$_3$ in the region

of interest. While it is possible that the Sc(OTf)$_3$ is attached at the nitrogen atoms of the NO

ligands in **5** and **6**,[21,22] this is unlikely given the identical behavior of sterically more demanding

Lewis acids (vide infra).

LA = BF₃•OEt₂. Addition of $BF_3 \cdot OEt_2$ to CD_2Cl_2 solutions of **3** and **4** results in the immediate formation of the Cp*M(NO→BF₃)(H)(κ^3-(C₆H₄)PhPCH₂CH₂PPh₂) complexes (M = Mo (**7**); M = W (**8**)) (Scheme 5). Exact yields of these two compounds could not be obtained due to the retention of $BF_3 \cdot OEt_2$ in the final reaction mixtures despite prolonged exposure to high vacuum. The ^1H and $^{31}P\{^1H\}$ NMR spectra of complexes **7** and **8** are virtually indistinguishable from those of their Sc(OTf)₃ analogues (vide supra). However, their IR spectra do provide NO-stretching frequencies since the presence of BF_3 in the complexes does not obscure the spectral features of interest, unlike Sc(OTf)₃.[23] Thus, as shown in Scheme 5, the formation of **7** and **8** is accompanied by shifts in the v_{NO} stretching frequencies to 1635 cm⁻¹ and 1622 cm⁻¹ for the Mo and W compounds, respectively, thereby confirming the existence of the NO→BF₃ linkages. These higher-wavenumber absorptions are indicative of the stronger N=O double-bond present in the orthometalated complexes relative to the starting materials (**3** and **4**), whose NO ligands possess significant N-O single-bond character (vide supra).

Scheme 5: Synthesis of Cp*M(NO→BF₃)(H)(κ^3-(C₆H₄)PhPCH₂CH₂PPh₂) Complexes

M = Mo (**3**); W (**4**)
v_{NO} = 1557 cm⁻¹ (M = Mo)
v_{NO} = 1549 cm⁻¹ (M = W)

xs. BF₃•OEt₂
CD₂Cl₂, RT

M = Mo (**7**); W (**8**)
v_{NO} = 1635 cm⁻¹ (M = Mo)
v_{NO} = 1622 cm⁻¹ (M = W)

Scheme 6. Synthesis of the Cp*M(NO→B(C₆F₅)₃)(κ²-Ph₂PCH₂CH₂PPh₂) Adducts

M = Mo (**3**); W (**4**)   M = Mo (**9**); W (**10**)
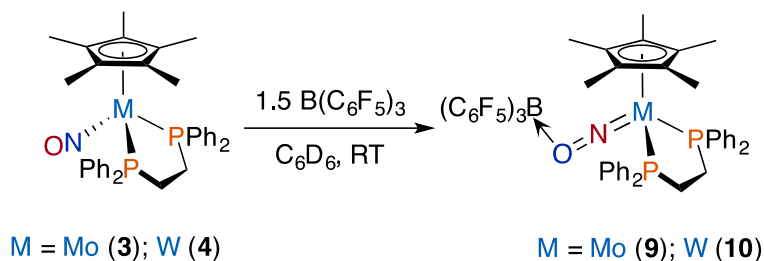
LA = B(C₆F₅)₃. As shown in Scheme 6, addition of 1.5 equiv of B(C₆F₅)₃ to C₆D₆

solutions of either **3** or **4** results in the immediate formation of the Cp*M(NO→B(C₆F₅)₃)(κ²-

Ph₂PCH₂CH₂PPh₂) adducts (M = Mo (**9**); M = W (**10**)). Since these adducts do not undergo

orthometalation at room temperature, it is unlikely that they are 16e complexes possessing fully

bent NO ligands. Rather, they are probably better formulated as 18e entities possessing

M=N=O→B(C₆F₅)₃ groups. In these linkages, the M=N link formally consists of an M-N

covalent bond as well as an N→M dative bond thus making the =N=O→B(C₆F₅)₃ ligand an

overall 3e donor. This interpretation is consistent with the NMR spectra displayed by complexes

9 and **10**, as outlined in the next paragraph.

The ¹H NMR spectrum of **9** in C₆D₆ shows significant upfield shifts of its Cp* and

Ph₂PC*H*₂C*H*₂PPh₂ resonances relative to those exhibited by **3**. Similarly, its ³¹P{¹H} NMR

spectrum shows a lone singlet attributable to **9** at 1.29 ppm, while that of **3** occurs at 1.79 ppm.

The relatively upfield ¹H NMR and ³¹P{¹H} resonances in the NMR spectra of **9** and **10** indicate

stronger shielding about the Cp* and Ph₂PCH₂CH₂PPh₂ environments. These features can be

attributed to the $=N=O \rightarrow B(C_6F_5)_3$ groups which, in contrast to the NO ligands themselves, are

apparently not as efficient at removing electron density from the metal centers. The presence of

a singlet in the $^{31}P\{^1H\}$ NMR spectrum of **9** is also consistent with it possessing C_S symmetry.

Unfortunately, the ν_{NO} absorption in the IR spectrum of **9** is obscured by strong overlapping

absorptions due to $B(C_6F_5)_3$. The spectroscopic properties of the analogous tungsten complex **10**

are comparable. Attempts to purify complex **9** by chromatography on alumina result in the

quantitative recovery of the precursor complex **3**, presumably formed via cleavage of the B-O

bond by the alumina support.

As shown in Scheme 7, heating of **9** in CD_2Cl_2 at 80 ℃ for 1 h results in the quantitative

formation of $Cp*Mo(NO \rightarrow B(C_6F_5)_3)(H)(\kappa^3\text{-}(C_6H_4)PhPCH_2CH_2PPh_2)$ (**11**), whose characteristic

NMR resonances are virtually identical to its $Sc(OTf)_3$ congener **7** (vide supra). The formation

of **11** probably proceeds through a 16e intermediate in which the $M=N=O \rightarrow B(C_6F_5)_3$ group of **9**

becomes a fully bent $M\text{-}N=O \rightarrow B(C_6F_5)_3$ linkage, thereby opening a slot in the metal's

coordination sphere and facilitating the activation of a ligand phenyl substituent's C-H bond. To

satisfy the 18e rule, the M-N=O linkage must also remain fully bent in **11**, as is the case for all

the other complexes of the $Cp*M(NO \rightarrow LA)(H)(\kappa^3\text{-}(C_6H_4)PhPCH_2CH_2PPh_2)$ family.

In contrast to **9**, heating **10** at 80 ℃ in CD_2Cl_2 affords a mixture of products, there being

no evidence for the formation of a W-H bond. The reason for this difference between the Mo and

W complexes is not immediately obvious, but previous studies with other compounds based on

the Cp*M(NO) scaffold have shown that molybdenum complexes tend to react at significantly

greater rates than the corresponding tungsten compounds.[24] Thus, while orthometalation of a phenyl substituent from $Cp*M(NO{\rightarrow}B(C_6F_5)_3)(\kappa^2\text{-}Ph_2PCH_2CH_2PPh_2)$ proceeds rapidly for M = Mo, the same transformation for M = W likely proceeds at a slow enough rate to permit various unwanted side reactions to occur.

Scheme 7. Thermal Synthesis of $Cp*Mo(NO{\rightarrow}B(C_6F_5)_3)(H)(\kappa^2\text{-}(C_6H_4)PhPCH_2CH_2PPh_2)$

9   **11**
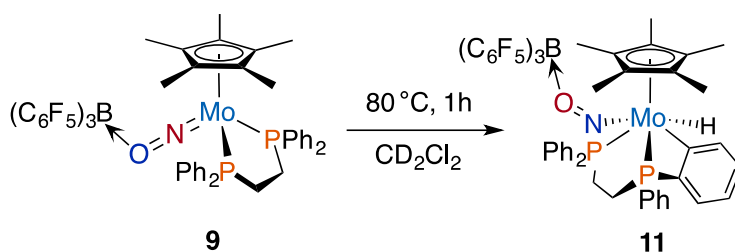
The reaction of $Cp*M(NO)(\kappa^2\text{-}Ph_2PCH_2CH_2PPh_2)$ with $B(C_6F_5)_3$, and the subsequent orthometalation of the Mo-containing adduct **9** clearly illustrates the stepwise nature of the overall transformation. By analogy, this sequence of steps should also apply when describing the reaction pathways involving LA = $Sc(OTf)_3$ or BF_3. For either of these Lewis acids, their reactions with $Cp*M(NO)(\kappa^2\text{-}Ph_2PCH_2CH_2PPh_2)$ instantly produce $Cp*M(NO{\rightarrow}LA)(H)(\kappa^3\text{-}(C_6H_4)PhPCH_2CH_2PPh_2)$ complexes, the putative $Cp*M(NO{\rightarrow}LA)(\kappa^2\text{-}Ph_2PCH_2CH_2PPh_2)$ intermediates possessing M=N=O groups, which are presumably first formed, have not been detected.

Disappointingly, neither **9** nor **10** reacts with pentane or methane in CD_2Cl_2 at 80 ºC or with C_6D_6 under the same conditions. Thus, intermolecular C-H bond activation is outcompeted by the intramolecular process even when a milder Lewis acid which precludes the immediate

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formation of the Cp*M(NO→LA)(H)(κ^3-(C$_6$H$_4$)PhPCH$_2$CH$_2$PPh$_2$) complexes is used. Prolonged heating of pentane solutions of **9** or **10** at 120 ºC results in further reactivity and affords mixtures of intractable products.

LA = BPh₃ or LaCl₃. Addition of 1.5 equiv BPh$_3$ or 1.5 equiv LaCl$_3$ to C$_6$D$_6$ solutions of either **3** or **4** does not result in association of the Lewis acids with the NO ligands. IR spectra of the final product mixtures show that the NO-stretching frequencies have not changed from those of either **3** or **4** alone, indicating that no NO→LA linkages have been formed.

Synthesis and Characterization of [Cp*W(NO)(PhCN)(κ^2-Ph₂PCH₂PPh₂)](OTf)₂. To gain an understanding of the role of bite angle in modulating the properties of the [Cp*M(NO)]$^{2+}$ complexes, Ph$_2$PCH$_2$PPh$_2$ has been investigated as a possible ligand, and the tungsten complex [Cp*W(NO)(PhCN)(κ^2-Ph₂PCH₂PPh₂)](OTf)$_2$ (**12**), has been synthesized in the customary manner (Scheme 8).

**Scheme 8. Synthesis of [Cp*W(NO)(PhCN)(κ^2-Ph₂PCH₂PPh₂)](OTf)₂**

17
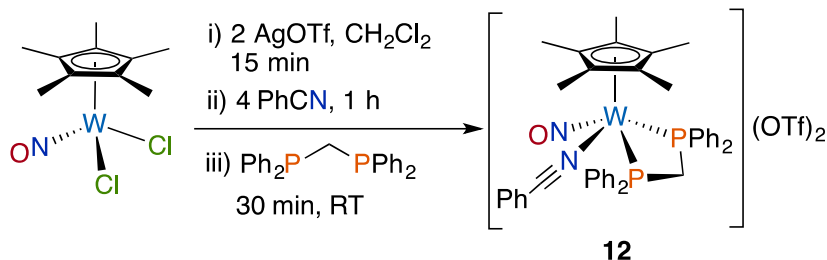
Single crystals of **12** suitable for an X-ray diffraction analysis have been grown by dissolving a solid sample in MeCN-d_3, and then layering the solution with Et$_2$O. The mixture was maintained at -30 ℃ for 14 d to induce the deposition of yellow, star-shaped crystals having the composition [Cp*W(NO)(MeCN-d_3)(κ^2-Ph$_2$PCH$_2$PPh$_2$)](OTf)$_2$. The solid-state molecular structure of the [Cp*W(NO)(MeCN-d_3)(κ^2-Ph$_2$PCH$_2$PPh$_2$)]$^{2+}$ dication is shown in Figure 4; its metrical parameters are similar to those of the related Ph$_2$PCH$_2$CH$_2$PPh$_2$ complexes **1** and **2** (vide supra). Interestingly, this is the only complex of this series to show exchange of the original PhCN ligand for the MeCN-d_3 solvent, despite identical recrystallization conditions being employed for all complexes. Significant strain is evident in the ring formed between the metal center and Ph$_2$PCH$_2$PPh$_2$ ligand in **12** which exhibits a P(1)-W(1)-P(2) angle of 63.63(3)°, which is substantially smaller than the reported bite angle of 72°.[25] This feature is a consequence of the steric interactions between the P(2) phenyl substituents and the MeCN-d_3 ligand that also results in the two W-P bond lengths being inequivalent.
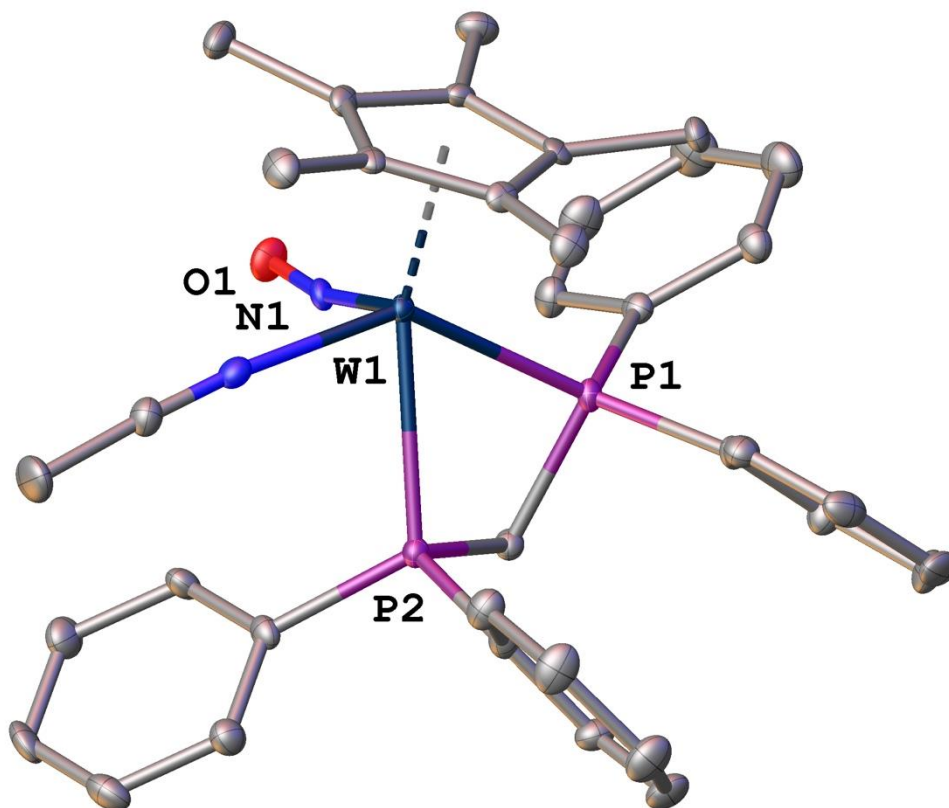
Figure 4. Solid-state molecular structure of the $[Cp*W(NO)(MeCN-d_3)(\kappa^2-Ph_2PCH_2PPh_2)]^{2+}$

cation as it occurs in $[Cp*W(NO)(MeCN-d_3)(\kappa^2-Ph_2PCH_2CH_2PPh_2)](OTf)_2$ with 50% probability

thermal ellipsoids shown. Hydrogen atoms and counteranions have been omitted for clarity.

Selected bond lengths (Å) and angles (deg): W(1)-P(1) = 2.5359(8), W(1)-P(2) = 2.5696(9),

P(1)-W(1)-P(2) = 63.63(3), W(1)-N(1) = 1.794(2), N(1)-O(1) = 1.200(3) W(1)-N(1)-O(1) =

167.2(3).

The $^{31}P\{^1H\}$ NMR spectrum of **12** in CD_2Cl_2 consists of an AB quartet at δ -12.8 ppm for

two strongly-coupled phosphorus nuclei. An expansion of the spectrum is shown in Figure 5.

Due to the low intensity of the tungsten satellites, the full pattern of splittings due to P-P and P-

W couplings has not been identified. In addition, the $^1J_{PW}$ coupling constants could not be reliably measured for either of the ^{31}P resonances in the AB system.
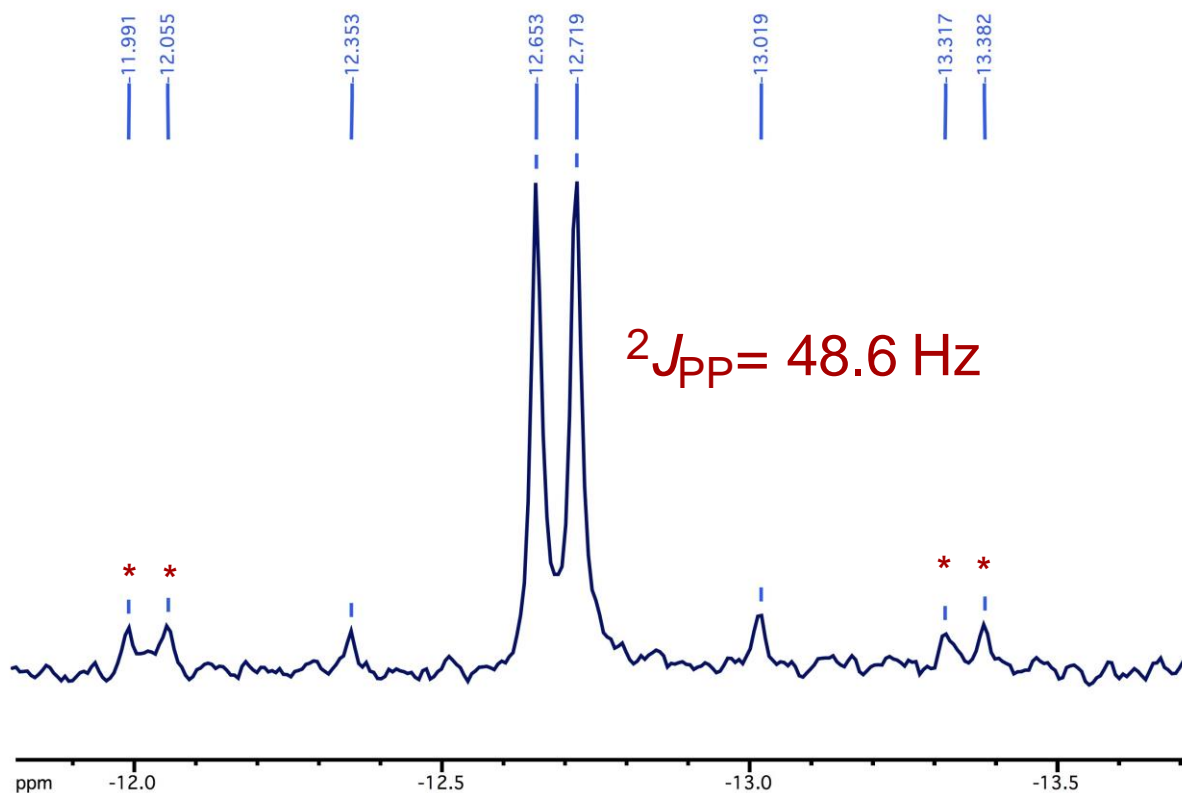
Figure 5. $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2) spectrum of **12** illustrating the AB spin system with the asterisks indicating additional splitting due to coupling with tungsten.

Attempts to prepare and isolate the congeneric molybdenum complex, [Cp*Mo(NO)(PhCN)(κ^2-Ph$_2$PCH$_2$PPh$_2$)](OTf)$_2$ in the manner depicted for the tungsten compound in Scheme 8 have been unsuccessful since the compounds formed in the final reaction mixture decompose rapidly even at -30 ºC before they can be isolated and characterized. In contrast, the thermal robustness of the Ph$_2$PCH$_2$CH$_2$PPh$_2$ analogue **1** is clearly a manifestation of

the stability imparted by the five-membered ring formed by Mo and the $Ph_2PCH_2CH_2PPh_2$

ligand.

Attempted Synthesis of Cp*W(NO)(κ^2-Ph$_2$PCH$_2$PPh$_2$). Attempts to synthesize

Cp*W(NO)(κ^2-Ph$_2$PCH$_2$PPh$_2$) in the manner employed for the preparation of the analogous

Ph$_2$CH$_2$CH$_2$PPh$_2$ complexes **3** and **4** (Scheme 3) have not been successful. Reduction of **12** with

2 equiv of Cp$_2$Co results in the formation of an intractable mixture of products, with the ^{31}P{^{1}H}

NMR spectrum of the final reaction mixture in C_6D_6 exhibiting only signals attributable to the

Ph$_2$PCH$_2$PPh$_2$ proligand. This inability to generate Cp*W(NO)(κ^2-Ph$_2$PCH$_2$PPh$_2$) is again a

result of the smaller bite angle of Ph$_2$PCH$_2$PPh$_2$ in a four-membered ring relative to

Ph$_2$PCH$_2$CH$_2$PPh$_2$ in a five-membered ring (72º vs 83º, respectively) [25] which inhibits the

effective bonding of both phosphorus atoms to the tungsten center.

EPILOGUE

In summary, we have demonstrated that the electron-rich complexes Cp*M(NO)(κ^2-

Ph$_2$PCH$_2$CH$_2$PPh$_2$ react via the Lewis basic O-termini of their NO ligands with Lewis acids (LA)

to form the adducts Cp*M(NO→LA)(κ^2-Ph$_2$PCH$_2$CH$_2$PPh$_2$) that possess NO→LA moieties. In

the case of LA = Sc(OTf)$_3$, this adduct is not detectable since it immediately converts under

ambient conditions to the corresponding 18e complex Cp*M(NO→Sc(OTf)$_3$)(H)(κ^3-

(C_6H_4)PhPCH$_2$CH$_2$PPh$_2$) formed by intramolecular orthometalation of one of the C-H bonds

belonging to a ligand phenyl substituent. For LA = B(C_6F_5)$_3$, the 16e Cp*M(NO→B(C_6F_5)$_3$)(κ^2-

Ph$_2$PCH$_2$CH$_2$PPh$_2$) intermediates can be isolated, and have been characterized by conventional

spectroscopic methods. In contrast to the $Sc(OTf)_3$ complexes, the 16e $B(C_6F_5)_3$ adducts must be thermally converted to the ultimate 18e products. Thus, heating $Cp^*Mo(NO{\rightarrow}B(C_6F_5)_3)(\kappa^2\text{-}Ph_2PCH_2CH_2PPh_2)$ at 80 ºC for 1 h results in the quantitative formation of $Cp^*Mo(NO{\rightarrow}B(C_6F_5)_3)(H)(\kappa^3\text{-}(C_6H_4)PhPCH_2CH_2PPh_2)$, while the congeneric tungsten complex reacts further to form a complex mixture of products. It should be noted that all of the complexes resulting from the oxidative addition reactions formally contain M(IV) centers.

These investigations show that it is unlikely that the current systems will be particularly adept at effecting the intermolecular activation of hydrocarbon substrates. Studies designed to discover and develop related $Cp^*M(NO)$-containing compounds that can be induced to react in such an intermolecular manner by treatment with Lewis acids such as $Sc(OTf)_3$ and $B(C_6F_5)_3$ are currently in progress.

EXPERIMENTAL SECTION

General Methods. All reactions and subsequent manipulations involving organometallic reagents were performed under anhydrous and anaerobic conditions except where noted. Vacuum (50 mtorr) and inert atmosphere techniques were performed either using double-manifold lines or in Innovative Technologies LabMaster 100 and MS-130 BG glove boxes equipped with freezers maintained at −30 °C. Preparative scale reactions were performed with Schlenk or round bottom flasks; reactions were performed in thick-walled glass reaction flasks (larger scale) or J. Young NMR tubes (smaller scale), both of which were sealed with Kontes greaseless stopcocks.

All solvents were dried with an appropriate dessicant and distilled prior to use. *n*-Pentane, dichloromethane, and deutero-dichloromethane (CD_2Cl_2) were distilled from calcium hydride. Diethyl ether (Et_2O) was distilled from sodium benzophenone ketyl. Anhydrous benzonitrile (PhCN; Sigma Aldrich, $\geq$ 99%) was dried over molecular sieves (3 Å) for 24 h and degassed with argon prior to use. Benzene and deutero-benzene was distilled from sodium benzophenone ketyl. All solvents were stored in flasks sealed with Kontes greaseless stopcocks and further dessicated over 3 Å molecular sieves for at least 24 h prior to use. 1,2-*bis*(diphenylphosphino)ethane ($Ph_2PCH_2CH_2PPh_2$, Sigma Aldrich, 97%), *bis*-cyclopentadienyl cobalt (II) (Cp_2Co; Alfa Aesar), boron trifluoride diethyl etherate ($BF_3\bullet OEt_2$; Sigma Aldrich, for synthesis), scandium (III) triflate ($Sc(OTf)_3$; Alfa Aesar, 98%), *tris*-(pentafluorophenyl)borane ($B(C_6F_5)_3$; Alfa Aesar, 97%), silver (I) triflate (AgOTf; Alfa Aesar, 98%), and silver (I) hexafluoroantimonate ($AgSbF_6$; Alfa Aesar, 98%) were used as received. $Cp*M(NO)Cl_2$ (M = Mo, W) were prepared according to the published procedure.[26]

Unless otherwise specified, all IR samples were prepared as Nujol mulls sandwiched between NaCl plates, and their spectra were recorded on a Thermo Nicolet Model 4700 FT-IR spectrometer. Except where noted, all NMR spectra were recorded at room temperature on Bruker Avance 400 instruments, and all chemical shifts are reported in ppm and coupling constants are reported in Hz. For the characterization of most complexes 2-dimensional NMR experiments, {^{1}H–^{1}H} COSY, {^{1}H–^{13}C} HSQC, {^{1}H-^{31}P} HMBC, and {^{1}H–^{13}C} HMBC, were performed to correlate and assign ^{1}H, ^{13}C and ^{31}P NMR signals and establish atom connectivity. Low- and high-resolution mass spectra (EI, 70 eV) spectra were recorded by Mr. Marshall Lapawa of the UBC mass spectrometry facility using a Kratos MS-50 spectrometer. Mr. Marco Yeung recorded ESI mass spectra on a Bruker HCT spectrometer, and elemental analyses were

performed by Mr. Derek Smith of the UBC microanalytical facility. X-ray crystallographic data collection, solution, and refinement were performed at the UBC X-ray crystallography facility.

Synthesis of [Cp*Mo(NO)(PhCN)(κ^2-Ph$_2$PCH$_2$CH$_2$PPh$_2$)](SbF$_6$)$_2$ (1). In a glove box, Cp*Mo(NO)Cl$_2$ (0.501 g, 1.51 mmol), AgSbF$_6$ (1.06 g, 3.08 mmol), and a stir bar were added to a Schlenk flask. On a double-manifold, CH$_2$Cl$_2$ (40 mL) was transferred into the reaction flask while the contents were stirred. After 15 min, PhCN (0.680 mL, 6.59 mmol) was added to the reaction mixture. After 1 h, stirring was stopped to allow the solids to settle. The red-brown mixture was then filtered through Celite (1 x 8 cm) supported above a medium porosity silica frit into a second Schlenk flask. The reaction flask was washed with CH$_2$Cl$_2$ (2 x 10 mL), and these washes were also filtered into the receiving flask. Ph$_2$PCH$_2$CH$_2$PPh$_2$ (0.630 g, 1.58 mmol) was added to the Schlenk flask containing the filtrate. A color change occurred immediately to produce a clear orange-brown solution. After 1 h, the volatile components were removed in vacuo to obtain a dark-brown oil. Successive trituration of the oil with Et$_2$O (3 x 30 mL) produced a solid yellow-orange powder. Residual Et$_2$O was removed under reduced pressure to obtain **1** as a fine yellow-orange powder (0.841 g, 76% yield).

Crystals of **1** suitable for an X-ray diffraction analysis were obtained by dissolving a sample of the compound (0.025 g) in MeCN-d_3 (1 mL), and carefully layering the mixture with Et$_2$O (10 mL). The mixture was cooled to -30 °C for 3 d to induce deposition of yellow-orange, needle-like crystals having the composition [Cp*Mo(NO)(PhCN)(κ^2-Ph$_2$PCH$_2$CH$_2$PPh$_2$)](SbF$_6$)$_2$•MeCN•Et$_2$O.

1
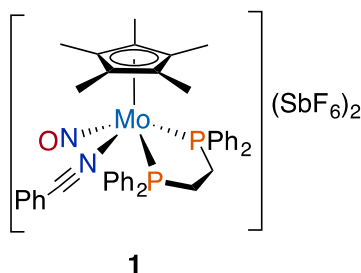
Characterization data for **1**. mp: 134-137 °C. IR (cm^{-1}): 2245 (s, ν_{CN}), 1694 (s, ν_{NO}).

ESI(+)-MS (40 V) *m/z*: 993.0 for C$_{43}$H$_{44}$F$_6$^{92}MoN$_2$OP$_2$^{121}Sb, [[M] – SbF$_6$]$^+$. ^{1}H NMR (400 MHz,

CD$_2$Cl$_2$): δ 1.85 (s, 15H, C$_5$(C*H*$_3$)$_5$), 2.03-2.13 (m, 1H, Ph$_2$PC*H*HCH$_2$PPh$_2$), 2.82-3.04 (m, 1H,

Ph$_2$PCH*H*CH$_2$PPh$_2$), 3.06-3.31 (m, 1H, Ph$_2$PCH$_2$C*H*HPPh$_2$), 3.47-3.56 (m, 1H,

Ph$_2$PCH$_2$CH*H*PPh$_2$), 7.11 (m, 2H, Ar *H*), 7.25-7.41 (m, 11H, Ar *H*), 7.48-7.53 (m, 2H, Ar *H*)

7.67-7.91 (m, 10H, Ar *H*). ^{31}P{^{1}H} NMR (162 MHz, CD$_2$Cl$_2$): δ 56.7 (d, $^2J_{PP}$ = 39.6,

(Ph$_2$*P*CH$_2$CH$_2$PPh$_2$), 68.0 (d, $^2J_{PP}$ = 31.9, Ph$_2$PCH$_2$CH$_2$*P*Ph$_2$). ^{13}C{^{1}H} NMR (100 MHz,

CD$_2$Cl$_2$): Selected resonances δ 10.7 (C$_5$(*C*H$_3$)$_5$), 24.0 (m, Ph$_2$P*C*H$_2$CH$_2$PPh$_2$), 37.2 (m,

Ph$_2$PCH$_2$*C*H$_2$PPh$_2$), 100.5 (*C*$_5$(CH$_3$)$_5$). Anal. Calcd for C$_{43}$H$_{44}$F$_{12}$MoN$_2$OP$_2$Sb$_2$: C, 41.85; H,

3.59; N, 2.27. Found: C, 42.07; H, 3.79; N, 2.11.

Synthesis of [Cp*W(NO)(PhCN)(κ^2-Ph$_2$PCH$_2$CH$_2$PPh$_2$)](SbF$_6$)$_2$ (2). Complex **2** was

prepared from Cp*W(NO)Cl$_2$ (0.500 g, 1.19 mmol), AgSbF$_6$ (0.827 g, 2.41 mmol), PhCN (0.500

mL, 4.95 mmol), and Ph$_2$PCH$_2$CH$_2$PPh$_2$ (0.516 g, 1.30 mmol), and it was subsequently purified

in a manner analogous to the procedure employed for the molybdenum congener (1.57 g, 69%

yield).

2
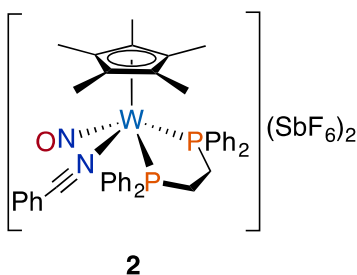
Characterization data for **2**. mp: 114-118 °C. IR (cm^{-1}): 2243 (s, ν_{CN}), 1674 (s, ν_{NO}).

ESI(+)-MS (40 V) *m/z*: 1083.1 for C$_{43}$H$_{44}$F$_6$N$_2$OP$_2$^{121}Sb^{182}W, [[M] – SbF$_6$]$^+$. ^{1}H NMR (400

MHz, CD$_2$Cl$_2$): δ 1.97 (s, 15H, C$_5$(C*H*$_3$)$_5$), 2.10-2.19 (m, 1H, Ph$_2$PC*H*HCH$_2$PPh$_2$), 2.92-3.15 (m,

1H, Ph$_2$PCH*H*CH$_2$PPh$_2$), 3.32-3.43 (m, 1H, Ph$_2$PCH$_2$C*H*HPPh$_2$), 3.52-3.63 (m, 1H,

Ph$_2$PCH$_2$CH*H*PPh$_2$), 7.15-7.23 (m, 2H, Ar *H*), 7.24-7.48 (m, 9H, Ar *H*), 7.53-7.61 (m, 3H, Ar

H), 7.74-7.98 (m, 11H, Ar *H*). ^{31}P{^{1}H} NMR (162 MHz, CD$_2$Cl$_2$): δ 46.2 (d, $^2J_{PP}$ = 12.7, $^1J_{PW}$ =

232.5, Ph$_2$*P*CH$_2$CH$_2$PPh$_2$), 50.0 (d, $^2J_{PP}$ = 12.7, $^1J_{PW}$ = 242.8, Ph$_2$PCH$_2$CH$_2$*P*Ph$_2$). ^{13}C{^{1}H} NMR

(100 MHz, CD$_2$Cl$_2$): Selected resonances δ 10.5 (C$_5$(*C*H$_3$)$_5$), 24.2-24.5 (m, Ph$_2$P*C*H$_2$CH$_2$PPh$_2$),

37.2-37.7 (m, Ph$_2$PCH$_2$*C*H$_2$PPh$_2$), 117.0 (*C*$_5$(CH$_3$)$_5$). Anal. Calcd for C$_{47}$H$_{54}$F$_{12}$N$_2$O$_2$P$_2$Sb$_2$W

([Cp*W(NO)(κ^2-Ph$_2$PCH$_2$CH$_2$PPh$_2$)(PhCN)](SbF$_6$)$_2$•Et$_2$O): C, 40.43; H, 3.90; N, 2.01. Found:

C, 40.52; H, 3.82; N, 2.04. ^{1}H-qNMR (400 MHz, CD$_2$Cl$_2$) analysis of the sample used in

elemental analysis indicates Et$_2$O is present in equimolar amounts to **2**.

The analogous triflate salt, [Cp*W(NO)(κ^2-Ph$_2$PCH$_2$CH$_2$PPh$_2$)(PhCN)](OTf)$_2$, was

prepared from Cp*W(NO)Cl$_2$ (0.200 g, 0.480 mmol), AgOTf (0.257 g, 1.00 mmol), PhCN

(0.206 mL, 0.199 mmol), and Ph$_2$PCH$_2$CH$_2$PPh$_2$ (0.383 g, 0.960 mmol) as per the procedure

detailed for **2** (0.315 g, 57% yield). Crystals of [Cp*W(NO)(PhCN)(κ^2-

Ph$_2$PCH$_2$CH$_2$PPh$_2$)](OTf)$_2$ were grown by dissolving a sample of the compound (0.025 g) in

MeCN-*d*$_3$ (1 mL), and carefully layering the mixture with Et$_2$O (10 mL). The mixture was

maintained at -30 °C for 3 d to induce deposition of orange, needle-like crystals having the composition [Cp*W(NO)(κ^2-Ph$_2$PCH$_2$CH$_2$PPh$_2$)(PhCN)](OTf)$_2$•MeCN•Et$_2$O.

Synthesis of [Cp*W(NO)(Cl)(κ^2-Ph$_2$PCH$_2$CH$_2$PPh$_2$)](OTf). In a glove box, a Schlenk flask was charged with Cp*W(NO)Cl$_2$ (0.200 g, 0.476 mmol), AgOTf (0.122 g, 0.476 mmol), and a stir bar. On a double manifold, CH$_2$Cl$_2$ (40 mL) was cannulated into the reaction flask while the contents were stirred for 15 min, and the solid components were then allowed to settle. The dark-green supernatant solution was filter-cannulated into a second Schlenk flask. The reaction flask was washed with CH$_2$Cl$_2$ (2 x 10 mL), and the washes were combined with the filtrate. Ph$_2$PCH$_2$CH$_2$PPh$_2$ (0.0490 g, 0.476 mmol) was then added to the filtrate, whereupon a color change to red brown occurred immediately. After 15 min, the volatile components were removed in vacuo to obtain [Cp*W(NO)(Cl)(κ^2-Ph$_2$PCH$_2$CH$_2$PPh$_2$)](OTf) as a dark-brown solid (0.447 g, 39% yield).
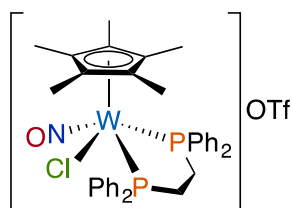
Characterization data for [Cp*W(NO)(Cl)(κ^2-Ph$_2$PCH$_2$CH$_2$PPh$_2$)](OTf). IR (cm^{-1}): 1634 (s, ν_{NO}). ESI(+)-MS (40 V) *m/z*: 780.2 for C$_{36}$H$_{39}$ClNOP$_2$^{182}W, [[M] – OTf]$^+$. TOF-ESI(+)-MS *m/z*: [[M] – OTf]$^+$ Calcd for C$_{36}$H$_{39}$ClNOP$_2$^{182}W, 780.1678; Found, 780.1660. ^{1}H NMR (400 MHz, C$_6$D$_6$): δ 1.41 (s, 15H, C$_5$(C*H*$_3$)$_5$), 1.60-1.71 (m, 1H, Ph$_2$PC*H*HCH$_2$PPh$_2$), 3.33-3.55 (m, 1H, Ph$_2$PC*H*HCH$_2$PPh$_2$), 3.59-3.84 (m, 2H, Ph$_2$PCH$_2$C*HH*PPh$_2$), 6.60-6.67 (m, 1H, Ar *H*), 6.69-6.81 (m, 5H, Ar *H*), 6.94-7.10 (m, 3H, Ar *H*), 7.23-7.30 (m, 3H, Ar *H*), 7.38-7.45 (m, 3H, Ar *H*),

7.52-7.59 (m, 3H, Ar H), 7.96-8.03 (m, 2H, Ar H). ^{31}P{^{1}H} NMR (162 MHz, C$_6$D$_6$): δ 30.0 (d, $^{2}J_{PP}$ = 8.53, $^{1}J_{PW}$ = 205.3, Ph$_2$$PCH_2CH_2PPh_2$), 40.1 (d, $^{2}J_{PP}$ = 8.53, $^{1}J_{PW}$ = 242.5, Ph$_2$PCH$_2$CH$_2$$PPh_2$). ^{13}C{^{1}H} NMR (100 MHz, C$_6$D$_6$): Selected resonances δ 9.7 (s, C$_5$(CH_3)$_5$), 24.4 (m, Ph$_2$PCH_2CH$_2$PPh$_2$, 30.4 (m, Ph$_2$PCH$_2$$CH_2PPh_2$), 114.4 (d, $^{2}J_{CP}$ = 1.13, C_5(CH$_3$)$_5$).

Synthesis of Cp*Mo(NO)(κ^2-Ph$_2$PCH$_2$CH$_2$PPh$_2$) (3). In a glove box, complex **1** (0.350 g, 0.284 mmol), Cp$_2$Co (0.113 g, 0.598 mmol), and a stir bar were added to a Schlenk flask. The vessel was then charged with C$_6$H$_6$ (30 mL), and sealed with a Kontes greaseless stopcock. The vessel containing a dark reddish-brown solution was immersed in an ethylene glycol bath at 80 °C for 18 h. Crystals of **3** suitable for an X-ray diffraction analysis were deposited along the walls of the reaction vessel, and they were removed for analysis prior to further purification of the reaction mixture.

Subsequently, the reaction flask was allowed to cool to room temperature, and the volume of the reaction mixture was reduced in vacuo to *ca*. 10 mL. The dark-brown solution was transferred to the top of a basic alumina column (1 x 10 cm) made up in *n*-pentane. A bright orange fraction was eluted using 0-100% Et$_2$O in *n*-pentane, and the volatiles were removed from the collected eluate under reduced pressure to obtain **3** as an orange-red solid (0.187 g, 81% yield).

3

Characterization data for **3**. IR (cm^{-1}): 1557 (s, ν_{NO}). LREI-MS (150 °C) m/z: 661, [M]$^+$ (^{98}Mo). ^{1}H NMR (400 MHz, C$_6$D$_6$): δ 1.79 (s, 15H, C$_5$(CH_3)$_5$), 2.01-2.15 (m, 2H, Ph$_2$PCHHCHHPPh$_2$), 2.15-2.30 (m, 2H, Ph$_2$PCHHCHHPPh$_2$), 6.93-7.04 (m, 7H, Ar H), 7.04-7.15 (m, 5H, Ar H), 7.25-7.31 (m, 4H, Ar H), 7.85-7.94 (m, 4H, Ar H). ^{31}P{^{1}H} NMR (162 MHz, C$_6$D$_6$): δ 93.6 (s, Ph$_2$$PCH_2CH_2$$PPh_2$). ^{13}C{^{1}H} APT NMR (100 MHz, C$_6$D$_6$): δ 11.4 (C$_5$(CH$_3$)$_5$), 31.6 (dd, $^1J_{CP}$ = 21.0, $^2J_{CP}$ = 17.6, Ph$_2$PCH$_2$$CH_2PPh_2$), 102.0 ($C_5$(CH$_3$)$_5$), 128.0 (Ar C), 128.5 (Ar C), 128.8 (Ar C), 129.5 (Ar C), 132.6 (Ar C), 134.0 (Ar C), 139.4 (Ar C), 140.0 (Ar C). Anal. Calcd for C$_{36}$H$_{39}$MoNOP$_2$: C, 65.55; H, 5.96; N, 2.12. Found: C, 65.75; H, 5.93; N, 1.33.
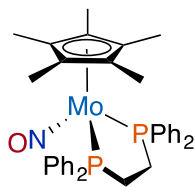
Synthesis of Cp*W(NO)(κ^2-Ph$_2$PCH$_2$CH$_2$PPh$_2$) (4). Complex **4** was prepared from **2** (0.350 g, 0.265 mmol), and Cp$_2$Co (0.106 g, 0.593 mmol) and subsequently purified in a manner analogous to that described for the molybdenum congener (0.0940 g, 47% yield).

4
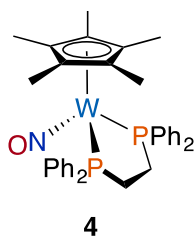
Characterization data for **4**. IR (cm^{-1}): 1549 (s, ν_{NO}). LREI-MS (150-200 °C) m/z: 747, [M]$^+$ (^{184}W). HREI-MS (180 °C) m/z: [M]$^+$ calcd for C$_{36}$H$_{39}$NOP$_2$^{182}W, 745.19892; found, 745.19953. ^{1}H NMR (400 MHz, C$_6$D$_6$): δ 1.82 (s, 15H, C$_5$(CH_3)$_5$), 2.00-2.10 (m, 2H, Ph$_2$PCHHCHHPPh$_2$), 2.19-2.28 (m, 2H, Ph$_2$PCHHCHHPPh$_2$), 6.97-7.03 (m, 7H, Ar H), 7.09-7.13 (m, 5H, Ar H), 7.29-7.33 (m, 4H, Ar H), 7.90-7.95 (m, 4H, Ar H). ^{31}P{^{1}H} NMR (162 MHz, C$_6$D$_6$): δ 71.9 (s, $^1J_{PW}$ = 440.0, Ph$_2$$PCH_2CH_2$$PPh_2$). ^{13}C{^{1}H}-APT NMR (100 MHz, C$_6$D$_6$): δ 11.4 (C$_5$(CH$_3$)$_5$), 35.6 (m, Ph$_2$PCH$_2$$CH_2PPh_2$), 100.2 ($C_5$(CH$_3$)$_5$), 127.3 (Ar C), 127.9 (Ar C),

128.0 (Ar C), 128.2 (Ar C), 128.8 (Ar C), 129.5 (Ar C), 132.7 (m, Ar C), 134.5 (Ar C). Anal.

Calcd for $C_{36}H_{39}NOP_2W$: C, 57.9; H, 5.26; N, 1.87. Found: C, 57.9; H, 4.97; N, 1.67.

Synthesis of Cp*Mo(NO→Sc(OTf)₃)(H)(κ³-(C₆H₄)PhPCH₂CH₂PPh₂) (5). In a glove

box, complex **3** (0.0260 g, 0.0386 mmol), Sc(OTf)₃ (0.0190 g, 0.0386 mmol), and a stir bar were

added to a Schlenk flask. The flask was connected to a double manifold and CH_2Cl_2 (10 mL) was

added. The contents of the Schlenk flask were stirred for 15 min, after which time the volatile

components of the reaction mixture were removed in vacuo to obtain **5** as a light orange powder

(0.0400 g, 91% yield).

5

Characterization data for **5**. IR (cm⁻¹): 1638 (s), 1341 (s), 1266 (s), 1206 (s), 1153 (m),

1101 (m), 1029 (s), 747 (m). ESI(+)-MS (40 V) *m/z*: 662.2 for $C_{37}H_{39}{}^{98}MoNOP_2$, [[M]-

Sc(OTf)₃+H]⁺. ¹H NMR (400 MHz, CD₂Cl₂): δ -1.23 (dd, $^2J_{HP}$ = 83.9, $^2J_{HP}$ = 13.1, 1H, Mo-*H*),

1.65 (s, 15H, C₅(C*H₃*)₅), 2.19-2.33 (m, 1H, (C₆H₄)PhPC*H*HCH₂PPh₂), 2.41-2.54 (m, 1H,

(C₆H₄)PhPCH₂C*H*HPPh₂), 2.60-2.98 (m, 2H, (C₆H₄)PhPCH*H*CH*H*PPh₂), 6.98-7.04 (m, 2H, Ar

H), 7.18-7.22 (m, 1H, Ar *H*) 7.29-7.57 (m, 16H, Ar *H*). ³¹P{¹H} NMR (162 MHz, CD₂Cl₂): δ

63.3 (d, $^2J_{PP}$ = 42.4, (C₆H₄)PhPCH₂CH₂*P*Ph₂), 68.0 (d, $^2J_{PP}$ = 42.4, (C₆H₄)Ph*P*CH₂CH₂PPh₂).

¹³C{¹H} NMR (100 MHz, CD₂Cl₂): Selected resonances δ 10.3 (C₅(*C*H₃)₅), 25.7 (dd, $^1J_{CP}$ = 20.0,

$^2J_{CP}$ = 13.8, (C₆H₄)Ph*P*CH₂CH₂PPh₂), 31.9 (dd, $^1J_{CP}$ = 31.4, $^2J_{CP}$ = 18.2,

(C_6H_4)PhPCH$_2$CH$_2$PPh$_2$), 109.5 (C_5(CH$_3$)$_5$), 136.1 (dd, $^2J_{CP}$ = 58.7, $^2J_{CP}$ = 3.02, Mo-*C*). Anal.

Calcd for C$_{39}$H$_{39}$F$_9$MoNO$_{10}$P$_2$S$_3$Sc: C, 40.67; H, 3.41; N; 1.22. Found: C, 40.92; H, 3.75; N, 1.08.

Synthesis of Cp*W(NO→Sc(OTf)$_3$)(H)(κ^3-(C_6H_4)PhPCH$_2$CH$_2$PPh$_2$) (6). Complex **6**
was prepared from **4** (0.0460 g, 0.0610 mmol) and Sc(OTf)$_3$ (0.0300 g, 0.0610 mmol) in a
manner analogous to that outlined for the molybdenum congener (0.0740 g, 98% yield).

6

Characterization data for **6**. IR (cm^{-1}): 1622 (s), 1341 (s), 1205 (s), 1101 (w), 1019 (s),
880 (w), 857 (w), 817 (w), 745 (m). ESI(+)-MS (40 V) *m/z*: 748.3 for C$_{37}$H$_{39}$NOP$_2$^{184}W, [[M]-

Sc(OTf)$_3$+H]$^+$. ^{1}H NMR (400 MHz, CD$_2$Cl$_2$): δ 0.06 (dd, $^2J_{HP}$ = 80.7, $^2J_{HP}$ = 12.4, $^1J_{HW}$ = 64.1,

1H, W-*H*), 1.74 (s, 15H, C$_5$(C*H*$_3$)$_5$), 2.11-2.26 (m, 1H, (C_6H_4)PhPCH$_2$C*H*HPPh$_2$), 2.50-2.64 (m,

1H, (C_6H_4)PhPC*H*HCH$_2$PPh$_2$), 2.64-2.85 (m, 1H, (C_6H_4)PhPCH$_2$CH*H*PPh$_2$), 2.94-3.17 (m, 1H,

(C_6H_4)PhPCH*H*CH$_2$PPh$_2$), 7.23 (m, 2H, Ar *H*), 7.39 (m, 2H, Ar *H*), 7.51 (m, 3H, Ar *H*), 7.57-

7.66 (m, 11H, Ar *H*), 7.75 (m, 1H, Ar *H*). ^{31}P{^{1}H} NMR (162 MHz, CD$_2$Cl$_2$): δ 49.3 (d, $^2J_{PP}$ =

26.2, $^1J_{PW}$ = 178.6, (C_6H_4)Ph*P*CH$_2$CH$_2$PPh$_2$), 52.2 (d, $^2J_{PP}$ = 26.2, $^1J_{PW}$ = 271.7,

(C_6H_4)PhPCH$_2$CH$_2$*P*Ph$_2$). ^{13}C{^{1}H} NMR (100 MHz, CD$_2$Cl$_2$): Selected resonances δ 10.2

(C$_5$(*C*H$_3$)$_5$), 25.2 (dd, $^1J_{CP}$ = 24.2, $^2J_{CP}$ 11.1, (C_6H_4)PhPCH$_2$*C*H$_2$PPh$_2$), 34.1 (dd, $^1J_{CP}$ = 26.0, $^2J_{CP}$

16.3, (C_6H_4)PhPCH$_2$CH$_2$PPh$_2$), 107.6 (C_5(CH$_3$)$_5$), 137.0 (dd, $^2J_{CP}$ = 61.6, $^2J_{CP}$ = 4.4, W-C). Anal

Calcd for $C_{39}H_{39}F_9NO_{10}P_2S_3ScW$: C, 37.79; H, 3.17; N, 1.13. Found: C, 36.85; H, 3.56; N, 0.97.

Synthesis of Cp*Mo(NO→BF$_3$)(H)(κ^3-(C_6H_4)PhPCH$_2$CH$_2$PPh$_2$) (7). In a glove box a

J. Young NMR tube was charged with **3** (0.00600 g, 9.10×10^{-3} mmol), CD$_2$Cl$_2$ (0.7 mL), and a

large excess of BF$_3$•OEt$_2$, whereupon a red reaction mixture was produced. Volatiles were then

removed in vacuo to produce a burgundy solid. ^{1}H and ^{31}P{^{1}H} NMR spectra indicated the

complete consumption of the starting material, and 100% conversion to **7**. BF$_3$•OEt$_2$ was

strongly retained by the final reaction mixture despite prolonged exposure to reduced pressures,

and so an accurate yield of **7** could not be determined.

7

Characterization data for **7**. IR (cm^{-1}): 1635 (s, ν_{NO}). ESI(+)-MS (40 V) *m/z*: 662.2 for

$C_{37}H_{39}{}^{98}MoNOP_2$, [[M]-BF$_3$+H]$^+$. ^{1}H NMR (400 MHz, CD$_2Cl_2$): δ -1.02 (dd, $^2J_{HP}$ = 82.9, $^2J_{HP}$ =

13.2, 1H, Mo-H), 1.65 (s, 15H, C$_5$(CH_3)$_5$), 2.16-2.31 (m, 1H, (C_6H_4)PhPCHHCH$_2$PPh$_2$), 2.39-

2.55 (m, 1H, (C_6H_4)PhPCH$_2$CHHPPh$_2$), 2.66-3.00 (m, 2H, (C_6H_4)PhPCHHCHHPPh$_2$). ^{31}P{^{1}H}

NMR (162 MHz, CD$_2$Cl$_2$): δ 63.6 (d, $^2J_{PP}$ = 42.2, (C_6H_4)PhPCH$_2$CH$_2$$PPh_2$), 68.6 (d, $^2J_{PP}$ = 42.2,
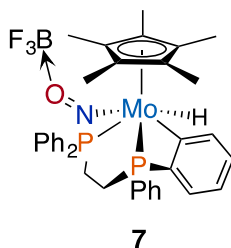
(C_6H_4)PhPCH$_2$CH$_2$PPh$_2$).

Synthesis of Cp*M(NO→BF₃)(H)(κ³-(C₆H₄)PhPCH₂CH₂PPh₂) (8). Complex **8** was prepared from **4** (0.00500 g, 6.67×10^{-3} mmol) and a large excess of BF₃•OEt₂ in a manner analogous to that described for the molybdenum congener. As for **7**, BF₃•OEt₂ was strongly retained by the final reaction mixture, and so an accurate yield for **8** could not be obtained. Nevertheless, ^{1}H and ^{31}P{^{1}H} NMR spectra indicated 100% conversion of the starting material to **8**.

8
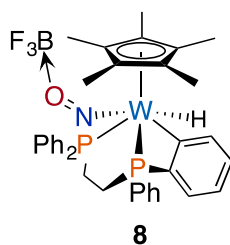
Characterization data for **8**. IR (cm^{-1}): 1622 (s, ν_{NO}). ESI(+)-MS (40 V) *m/z*: 748.2 for C₃₇H₃₉^{184}WNOP₂, [[M]-BF₃+H]$^+$. ^{1}H NMR (400 MHz, CD₂Cl₂): Selected resonances δ 0.08 (dd, 1H, $^2J_{HP}$ = 80.3, $^2J_{HP}$ = 11.2, W-*H*), 1.74 (s, 15H, C₅(C*H₃*)₅), 2.11-2.22 (m, 1H, (C₆H₄)PhPCH₂C*H*HPPh₂), 2.46-2.57 (m, 1H, (C₆H₄)PhPC*H*HCH₂PPh₂), 2.64-2.85 (m, 1H, (C₆H₄)PhPCH₂CH*H*PPh₂), 2.92-3.25 (m, 1H, (C₆H₄)PhPCH*H*CH₂PPh₂). ^{31}P{^{1}H} NMR (162 MHz, CD₂Cl₂): δ 49.3 (d, $^2J_{PP}$ = 26.4, (C₆H₄)Ph*P*CH₂CH₂PPh₂), 52.2 (d, $^2J_{PP}$ = 26.4, (C₆H₄)PhPCH₂CH₂*P*Ph₂).

Synthesis of the Cp*Mo(NO→B(C₆F₅)₃)(κ²-Ph₂PCH₂CH₂PPh₂) Adduct (9). In a glove box, a 4-dram vial was charged with a clear, orange-red C₆H₆ (2 mL) solution of **3** (0.0680 g, 0.103 mmol). To a separate 4-dram vial was added B(C₆F₅)₃ (0.0570 g, 0.108 mmol) and C₆H₆ (6 mL). The solution of B(C₆F₅)₃ was transferred to the solution containing **3** to

immediately form a dark brown solution that turned deep purple after 2 min. The volatile

components were then removed in vacuo to obtain **9** as a deep purple solid, which was then

washed with pentane (3 x 2 mL) (0.0950 g, 79% yield). Attempts to purify the solid by

chromatography on alumina resulted in the quantitative recovery of **3**.


9
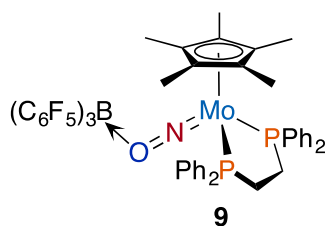
Characterization data for **9**. IR (cm^{-1}): 1644 (s), 1515 (s), 1289 (s), 1273 (s), 1286 (s),

1027 (s), 981 (s), 856 (m), 763 (m), 745 (m), 699 (m). ESI(+)-MS (40V) m/z: 662.3 for

$C_{36}H_{40}{}^{98}MoNOP_2$, [[M]-B(C$_6F_5$)$_3$+H]$^+$. ESI(-)-MS (-40V) m/z: 529.0 for $C_{18}HBF_{15}O$,

[B(C$_6$F$_5$)$_3$+OH]$^-$. TOF-ESI(+)-MS m/z: [[M]-B(C$_6$F$_5$)$_3$+H]$^+$ calcd for $C_{36}H_{40}{}^{92}MoNOP_2$,

656.1653; found, 656.1658. ^{1}H NMR (400 MHz, C$_6$D$_6$): δ 1.29 (s, 15H, C$_5$(CH_3)$_5$), 2.32-2.50 (m,

2H, Ph$_2$PCHHCHHPPh$_2$), 2.59-2.77 (m, 2H, Ph$_2$PCHHCHHPPh$_2$), 6.70-6.78 (m, 4H, Ar H),

6.80-6.86 (m, 4H, Ar H), 6.86-6.93 (m, 2H, Ar H), 7.07-7.14 (m, 3H, Ar H), 7.18-7.24 (m, 3H,

Ar H), 7.49-7.59 (m, 4H, Ar H). ^{31}P{^{1}H} NMR (162 MHz, C$_6$D$_6$): δ 87.6 (s, Ph$_2$$PCH_2CH_2$$PPh_2$).

^{13}C{^{1}H} NMR (100 MHz, C$_6$D$_6$): Selected resonances δ 10.0 (s, C$_5$(CH_3)$_5$), 31.8 (m,

Ph$_2$PCH_2CH_2PPh$_2$), 106.7 (s, C_5(CH$_3$)$_5$). ^{19}F NMR (377 MHz, C$_6$D$_6$): δ -164.8 (t, $^3J_{FF}$ = 22.6,

$^3J_{FF}$ = 20.9, 6F, Ar F_{meta}), -159.4 (t, $^3J_{FF}$ = 20.9, 3F, Ar F_{para}), -131.1 (d, $^3J_{FF}$ = 22.6, 6F, Ar

F_{ortho}). ESI(+)-MS (40 V) m/z: 662.3 for $C_{36}H_{40}{}^{98}MoNOP_2$, [[M]-B(C$_6F_5$)$_3$+H]$^+$.

Synthesis of the Cp*W(NO→B(C₆F₅)₃)(κ²-Ph₂PCH₂CH₂PPh₂) Adduct (10).

Complex **10** (0.0380 g, 94% yield) was prepared from **4** (0.0240 g, 0.0321 mmol) and B(C₆F₅)₃

(0.0180 g, 0.0352 mmol) by following the procedure outlined for the molybdenum congener.

Maintenance of a CH₂Cl₂ solution of **10** (0.0380 g, 0.0302 mmol) at 80 °C for extended

periods results in further reactivity of the starting material to produce a mixture of unidentified

products.

10
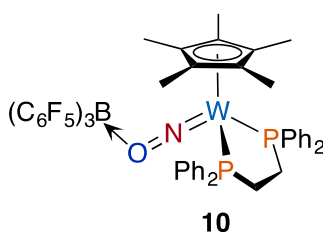
Characterization data for **10**. IR (cm⁻¹): 1645 (s), 1519 (s), 1316 (m), 1290 (s), 1102 (s),

984 (s), 873 (m), 843 (m), 748 (m), 675 (s). ESI(+)-MS (40 V) m/z: 748.3 for C₃₇H₃₉¹⁸⁴WNOP₂,

[[M]-B(C₆F₅)₃+H]⁺. ESI(-)-MS (-40 V) m/z: 529.0 for [B(C₆F₅)₃+OH]⁻. TOF-ESI(+)-MS m/z:

[[M]-B(C₆F₅)₃+H]⁺ calcd for C₃₆H₄₀NOP₂¹⁸²W, 746.2067; found, 746.2068. ¹H NMR (400 MHz,

C₆D₆): δ 1.38 (s, 15H, C₅(CH₃)₅), 2.28-2.39 (m, 2H, Ph₂PCHHCHHPPh₂), 2.56-2.59 (m, 2H,

Ph₂PCHHCHHPPh₂), 6.75-6.92 (m, 10H, Ar H), 7.10-7.16 (m, 3H, Ar H), 7.19-7.24 (m, 3H, Ar

H), 7.55-7.62 (m, 4H, Ar H). ³¹P{¹H} NMR (162 MHz, C₆D₆): δ 62.9 (s, ¹J_{PW} = 411.6,

Ph₂PCH₂CH₂PPh₂). ¹³C{¹H} NMR (100 MHz, C₆D₆): δ 10.8 (s, C₅(CH₃)₅), 37.2 (m,

Ph₂PCH₂CH₂PPh₂), 103.7 (s, C₅(CH₃)₅). ¹⁹F NMR (377 MHz, C₆D₆): δ -164.9 (t, ³J_{FF} = 23.1,

³J_{FF} = 21.0, 6F, Ar F_{meta}), -159.7 (t, ³J_{FF} = 21.0, 3F, Ar F_{para}), -131.1 (d, ³J_{FF} = 23.1, 6F, Ar

F_{ortho}).

**Thermal Synthesis of Cp*Mo(NO→B(C₆F₅)₃)(H)(κ²-(C₆H₄)PhPCH₂CH₂PPh₂) (11).**

Complex **11** was prepared by maintaining a CH_2Cl_2 solution of **9** (0.0430 g, 0.0367 mmol) at 80 °C for 1 h in a glass vessel sealed with a Kontes greaseless stopcock. The volatile components were then removed under reduced pressure to obtain **11** as a shiny dark-red solid (0.0430 g, 100% yield).

11
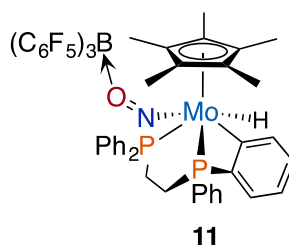
Characterization data for **11**. IR (cm^{-1}): 1664 (s), 1515 (s), 1278 (s), 1093 (s), 978 (s), 744 (m), 694 (m), 669 (m). ESI(+)-MS (40 V) *m/z*: 664.3 for $C_{36}H_{40}{}^{100}MoNOP_2$, [[M]-B(C₆F₅)₃+H]$^+$. ESI(-)-MS (-40V) *m/z*: 529.0 for $C_{18}HBF_{15}O$, [B(C₆F₅)₃+OH]$^-$. TOF-ESI(+)-MS *m/z*: [[M]-B(C₆F₅)₃+H]$^+$ calcd for $C_{36}H_{40}{}^{100}MoNOP_2$, 664.1660; found, 664.1671. ^1H NMR (400 MHz, CD₂Cl₂): δ -1.02 (dd, $^2J_{HP}$ = 84.2, $^2J_{HP}$ = 13.1, 1H, Mo-*H*), 1.65 (s, 15H, C₅(C*H*₃)₅), 2.11-2.24 (m, 1H, (C₆H₄)PhPC*H*HCH₂PPh₂), 2.38-2.51 (m, 1H, (C₆H₄)PhPCH₂C*H*HPPh₂), 2.60-2.96 (m, 2H, (C₆H₄)PhPCH*H*CH*H*PPh₂), 7.15-7.22 (m, 3H, Ar *H*), 7.29-7.38 (m, 6H, Ar *H*) 7.46-7.70 (m, 10H, Ar *H*). $^{31}P\{^1H\}$ NMR (162 MHz, CD₂Cl₂): δ 62.9 (d, $^2J_{PP}$ = 42.0, (C₆H₄)PhPCH₂CH₂*P*Ph₂), 68.5 (d, $^2J_{PP}$ = 42.0, (C₆H₄)Ph*P*CH₂CH₂PPh₂). $^{13}C\{^1H\}$ NMR (100 MHz, CD₂Cl₂): Selected resonances δ 10.2 (s, C₅(*C*H₃)₅), 114.2 (s, *C*₅(CH₃)₅). ^{19}F NMR (377 MHz, CD₂Cl₂): -167.2- -167.1 (m, 6F, Ar *F*$_{meta}$), -162.5- -162.3 (m, 3F, Ar *F*$_{para}$), -136.1 (d, $^3J_{FF}$ = 23.0, 6F, Ar *F*$_{ortho}$).

Synthesis of [Cp*W(NO)(PhCN)(κ²-Ph₂PCH₂PPh₂)](OTf)₂ (12). Complex **12** (0.110

g, 20% yield) was prepared from Cp*W(NO)Cl₂ (0.200 g, 0.480 mmol), AgOTf (0.257 g, 1.00

mmol), PhCN (0.210 mL, 2.04 mmol), and Ph₂PCH₂PPh₂ (0.369 g, 0.960 mmol) in a manner

analogous to that described for the synthesis of **1**.

Crystals suitable for an X-ray diffraction analysis were obtained by dissolving a sample

of **12** (0.025 g) in MeCN-d_3 (1 mL), and carefully layering the mixture with Et₂O (10 mL). The

mixture was cooled to -30 °C for 14 d to induce deposition of yellow-orange, needle-like crystals

having the composition [Cp*W(NO)(MeCN-d_3)(κ²-Ph₂PCH₂PPh₂)](OTf)₂.

12
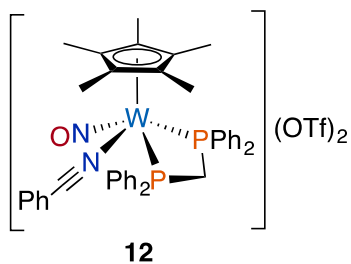
Characterization data for **12**. IR (cm⁻¹): 2228 (s, ν_{CN}), 1667 (s, ν_{NO}). ESI(+)-MS (40 V):

no peaks could be definitively assigned to a reasonable formula. ¹H NMR (400 MHz, CD₂Cl₂): δ

2.17 (s, 15H, C₅(CH_3)₅), 4.57-4.70 (m, 1H, Ph₂PCHHPPh₂), 4.95-5.01 (m, 1H, Ph₂PCHHPPh₂),

6.78-6.88 (m, 2H, Ar H), 7.37-7.44 (m, 4H, Ar H), 7.51-7.47 (m, 4H, Ar H), 7.57-7.54 (m, 4H,

Ar H), 7.68-7.63 (m, 3H, Ar H), 7.75-7.71 (m, 1H, Ar H), 7.84-7.78 (m, 4H, Ar H), 7.97-7.88

(m, 3H, Ar H). ³¹P{¹H} NMR (162 MHz, CD₂Cl₂): δ -12.6, -12.8 (ABq, ²J_{PP} = 48.6,

Ph₂PCH₂PPh₂). ¹³C{¹H} NMR (100 MHz, CD₂Cl₂): Selected resonances δ 10.8 (s, C₅(CH_3)₅),

39.4 (pseudo-t, ¹J_{PC} = 32.0 Hz, Ph₂PCH_2PPh₂), 117.1 (s, C_5(CH₃)₅). Anal. Calcd for

C₃₉H₃₇D₃F₆N₂O₇P₂S₂W ([Cp*W(NO) (MeCN-d_3)(κ²-Ph₂PCH₂PPh₂)](OTf)₂]): C, 43.55; H, 4.03;

N, 2.60; S, 5.96. Found: C, 43.88; H, 3.89; N, 2.47; S, 5.80.

X-Ray Crystallography. Full details of all single-crystal X-ray diffraction analyses are presented in the Supporting Information.

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Notes

The authors declare no competing financial interest.

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For Table of Contents Use Only:

Chloride abstraction from Cp*M(NO)Cl$_2$ (M = Mo, W) with AgSbF$_6$, followed by

trapping with PhCN and Ph$_2$PCH$_2$CH$_2$PPh$_2$ affords [Cp*M(NO)(PhCN)(κ^2-

Ph$_2$PCH$_2$CH$_2$PPh$_2$)](SbF$_6$)$_2$ complexes. Reduction of these complexes in C$_6$H$_6$ with 2 equiv of

Cp$_2$Co produces the 18e compounds Cp*M(NO)(κ^2-Ph$_2$PCH$_2$CH$_2$PPh$_2$). Coordinative

unsaturation is induced in these compounds by coordination of a Lewis acid (LA) to the O-

termini of the NO ligands. The open coordination slot is rapidly filled by intramolecular C-H

activation of a ligand phenyl substituent to form the hydrido complexes, Cp*M(NO→LA)(H)(κ^3-

(C$_6$H$_4$)PhPCH$_2$CH$_2$PPh$_2$). The progress of these orthometalation reactions is markedly

dependent on the nature of the Lewis acid employed.

M = Mo, W   LA = Sc(OTf)$_3$, BF$_3$·OEt$_2$, B(C$_6$F$_5$)$_3$