Dihapto-Coordination of Electron-Deficient Arenes with Group 6 Dearomatization Agents

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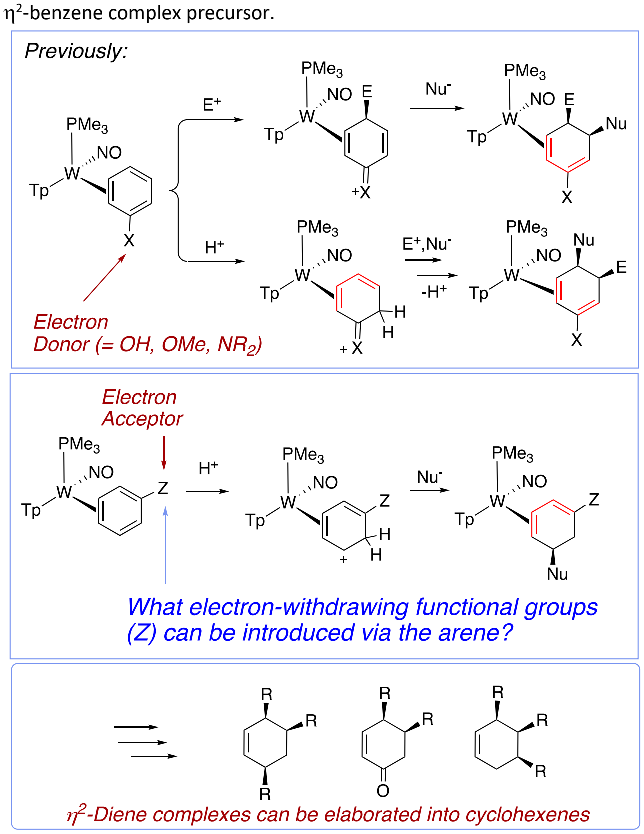
Abstract: The exceptionally π-basic metal fragments {MoTp(NO)(DMAP)} and {WTp(NO)(PMe_3)} (Tp = tris(pyrazolyl)borate; DMAP = 4-(N,N-dimethylamino)pyridine) form thermally stable dihapto-coordinate complexes with a variety of electron-deficient arenes. The tolerance of substituted-arenes with fluorine-containing electron withdrawing groups (EWG; -F, -CF_3, -SF_5) is examined for both the molybdenum and tungsten systems. When the EWG contains a π-bond (nitriles, aldehydes, ketones, ester), η^2-coordination occurs predominantly on the non-aromatic functional group. However, complexation of the tungsten complex with trimethyl orthobenzoate ($PhC(OMe)_3$) followed by hydrolysis allows access to a dihapto-coordinate arene with an ester substituent. In general, the tungsten system tolerates sulfur-based withdrawing groups well (e.g., $PhSO_2Ph$, $MeSO_2Ph$), and the integration of multiple electron-withdrawing groups on a benzene ring further enhances the π-backbonding interaction between the metal and aromatic ligand. While the molybdenum system did not form stable η^2-arene complexes with the sulfones or ortho esters, it was capable of forming rare examples of stable dihapto-coordinated arene complexes with a range of fluorinated benzenes (e.g., fluorobenzene, difluorobenzenes). In contrast to what has been observed for the tungsten system, these complexes formed without interference of C-H or C-F insertion.

Introduction

The binding of aromatic molecules to a transition-metal can enable a wide array of chemical transformations, often inaccessible by other means. Over the past several decades, our research group has endeavored to explore how transition-metal complexes can activate aromatic molecules toward new organic transformations through coordination to just two carbons (η^2).[1-3] Most of these studies have focused on anisoles,[4-6] phenols,[7-9] anilines,[7, 10-11] and other arenes bearing a single π-donor group. In this situation, the metal and heteroatom substituent act together as π-electron donors and render the arene susceptible to protonation and electrophilic addition (Scheme 1). Until recently, it was thought that although arenes with electron-withdrawing groups are better π-acids, they would be inferior as η^2-aromatic substrates for organic reactions since this type of substituent and the electron-donating metal assert opposite electronic effects. Despite this, we recently demonstrated that the addition of a CF_3 group to WTp(NO)(PMe_3)(η^2-benzene) significantly stabilized the π-complex, and yet did not preclude protonation of the ring by strong acid.[12] Furthermore, the electron-withdrawing group was found to polarize the arene in such a way that protonation occurs ortho to the CF_3 group, and nucleophilic additions can then occur adjacent to the sp^3 carbon of the corresponding η^2-arenium complex. The resulting η^2-diene complexes are electronically complementary to η^2-diene complexes prepared from electron-rich arenes, and can be elaborated further into novel trisubstituted cyclohexenes (Scheme 1).[12] Significantly, even though the diastereoselectivity for the neutral α,α,α,-trifluorotoluene (TFT) complex is poor, protonation and subsequent nucleophilic additions were found to be highly regio- and stereoselective.[12] Similar results were obtained from the analogous MoTp(NO)(DMAP)(η^2-TFT) system.[13]

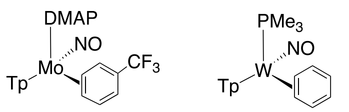
Scheme 1. The incorporation of functional groups into cyclohexenes via a η^2-benzene complex precursor.



Of note, η^2-arene complexes are exceedingly rare, owing to the loss of aromatic stability upon such coordination. Besides the trifluorotoluene complex of these systems,[12,14] the only other examples of thermally stable η^2-benzene complexes bearing a single EWG are pentaammineosmium(II) complexes of TFT, benzophenone, and pivalophenone.[15] The potential for novel organic transformations of η^2-arene complexes has prompted us to evaluate the scope and binding selectivity for other electron-deficient arenes with the {WTp(NO)(PMe$_3$)} and {MoTp(NO)(DMAP)} systems, particularly where the substituent is relevant to pharmaceutical design (e.g., nitriles,[16] esters,[17] sulfones,[18] fluorines[19]).

Results and Discussion

Various benzenes bearing a single EWG were surveyed for their potential coordination to either {MoTp(DMAP)(NO)} or {WTp(PMe$_3$)(NO)} fragments. The complexes MoTp(DMAP)(NO)(TFT) (**1**) and WTp(PMe$_3$)(NO)(benzene) (**2**) serve as synthons to these fragments.[14, 20]

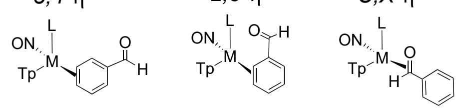


1 **2**

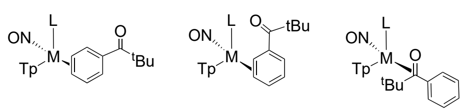
In many of these cases, the EWG itself often proved to be a superior position for coordination, and DFT results (M06; hybrid LANL2DZ, 6-31G(d,p) basis set; in vacuum) supporting this notion are summarized in Table 1.

Table 1. DFT calculations of bond dissociation enthalpies (BDE) for electron-deficient benzenes calculated at 298 K in vacuum; kcal/mol). For reference, the κ-N isomer BDEs are **11N**: 36.6 and **12N**: 45.2 kcal/mol. Only the most stable structure for Mo is shown, but enthalpy values are given for the most stable diastereomer for either metal.

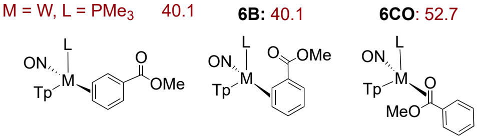
3,4-η²	*2,3-η²*	*C,X-η²*



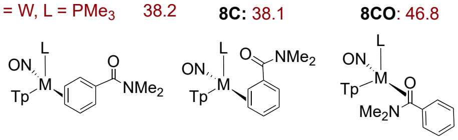
3A: M = Mo, L = DMAP 32.4 **4A**: M = W, L = PMe$_3$ 38.9	**3B**: 33.6 **4B**: 37.4	**3CO**: 52.0 **4CO**: 61.4



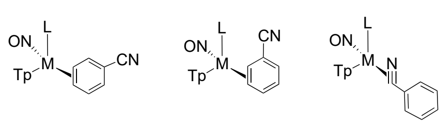
5A: M = Mo, L = DMAP 33.8 **6A**: M = W, L = PMe$_3$ 40.1	**5B**: 36.0 **6B**: 40.1	**5CO**: 43.1 **6CO**: 52.7



7A: M = Mo, L = DMAP 32.0 **8A**: M = W, L = PMe$_3$ 38.2	**7B**: 34.2 **8C**: 38.1	**7CO**: 35.3 **8CO**: 46.8



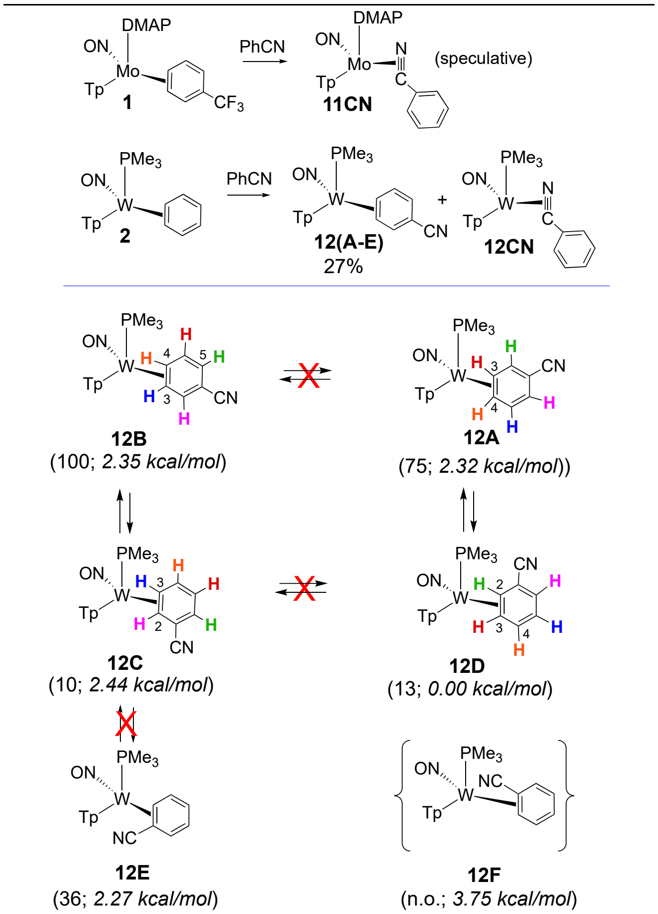
9A: M = Mo, L = DMAP 32.8 **10A**: M = W, L = PMe$_3$ 38.7	**9B**: 36.1 **10B**: 39.2	**10CO**: 34.0 **10CO**: 43.3



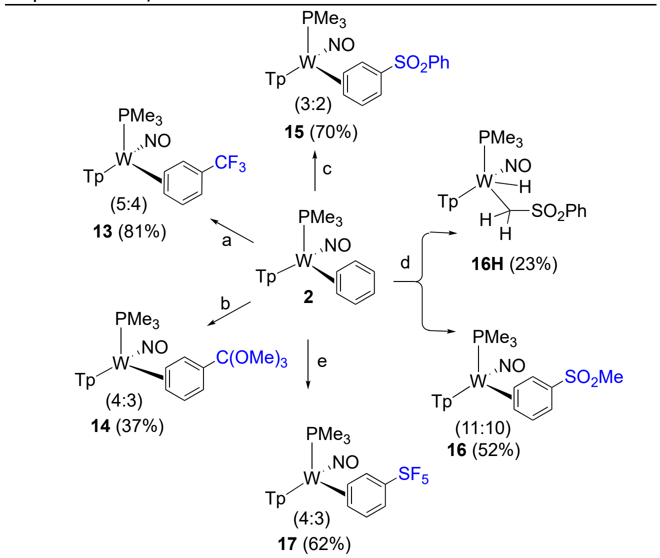
11A: M = Mo, L = DMAP 32.8 **12A**: M = W, L = PMe$_3$ 38.5	**11B**: 35.3 **12D**: 41.2	**11CN**: 43.9 **12CN**: 54.9

For benzaldehyde, benzonitrile, methyl benzoate and even the bulky ketone pivalophenone, these calculations indicate that binding at the substituent is heavily favored over coordination to the arene ring for both the molybdenum and tungsten systems. Thus, formation of a purported ring-bound complex for these arenes relies on kinetic trapping of such an isomer. As a case in point, benzonitrile appears to form a complex with {MoTp(NO)(DMAP)} in which only the nitrile is coordinated (**11CN**).[13,21] Yet, when benzonitrile was allowed to react with the more substitution-inert tungsten precursor **2**, at least seven tungsten complexes were present in the crude reaction mixture, judging from ^{31}P NMR data. Of these, the major (-9.39 ppm, **12CN**), has a chemical shift and ^{183}W-^{31}P coupling constant (313 Hz), outside the ranges expected for a κ-N species or an η^2-arene,[22] and this species is tentatively ascribed to a *C,N*-η^2 nitrile complex.[21] The two most downfield (-9.39 ppm, -13.05 ppm) signals, accounting for roughly 60% of the reaction mixture, are absent after silica chromatography. Recovered from the separation process was an analytically pure compound of the form WTp(NO)(PMe$_3$)(PhCN) (yield 27%). In solution this compound exists as an equilibrium mixture of five η^2-arene isomers (**12A**-**12E**; Scheme 2). The two major isomers are coordination diastereomers bound across the C3 and C4 carbons (**12A** and **12B**). Three other isomers of **12** can be conclusively identified, including two 2,3-η^2-bound diastereomers (**12C** and **12D**) and a fifth η^2-arene isomer (**12E**), thought to be a rare example of a 1,2-η^2-benzonitrile complex (Scheme 2). While the low equilibrium concentrations and extensive overlap of ^{1}H NMR signals for some of these η^2-arene complexes make their conclusive identification challenging, NOESY data reveals a complex set of chemical exchange processes that occur under ambient conditions (SI). This NOESY data thus allows for characterization of the minor isomers (**12C** and **12D**) through their relationship to the major isomers (**12A** and **12B**; *vide infra*). For example, as shown in Scheme 2, the H5 proton of the 3,4-η^2-isomer **12A** (*green H*) undergoes chemical exchange exclusively with that same position of the minor 2,3-η^2 isomer **12D**. Likewise, H3 (*blue H*) of **12A** undergoes chemical exchange exclusively with H3 of **12D**. Similar correlations are present for the other ring hydrogens. Meanwhile, all five hydrogens for the 3,4-η^2 isomer **12B** undergo spin saturation exchange with their counterparts in the minor 2,3-η^2 isomer **12C**. Taken together, these observations indicate that the 2,3-η^2 ⇔ 3,4-η^2 isomerization is not only facile, but that it occurs via a ring-slip mechanism, to the exclusion of any other mechanism (i.e., a face-flip, or oxidative addition).[23] In contrast, the anticipated isomerization between the two major isomers **12A** and **12B** is not detected through either an interfacial (face-flip) or intrafacial (ring-slip) mechanism (red X in Scheme 2). The fifth isomer, in which the metal is bound across the ipso carbon and an ortho carbon, does not undergo chemical exchange with any of the other species at ambient temperature. All five nitrile isomers (**12A**-**12E**) are considerably more stable in acetone solution than their η^2-benzene counterpart, and no dissociation of the benzonitrile ligand, nor isomerization to the purported CN isomer (**12CN**), was observed over a period of four days.

Scheme 2. Synthesis of multiple isomers of the dihapto-coordinated benzonitrile complex **12.** arrows: chemical exchange observed. Red X: no chemical exchange observed; (**12A**-**12D** are equilibrated, but for **12E** equilibration is uncertain; (ratio; calculated Gibbs free energy)). Colored hydrogens indicate where chemical exchange was observed.

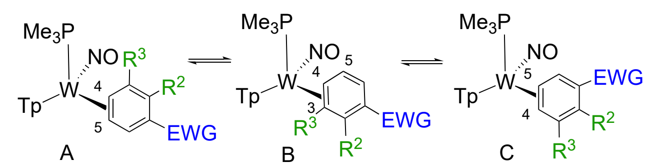


Scheme 3. Benzene complexes with a single EWG. a) Neat $PhCF_3$, 20 h, ambient temperature b) Neat $PhC(OMe)_3$, 16 h, ambient temperatures c) $PhSO_2Ph$ dissolved in dimethoxyethane (DME), 48 h, ambient temperature d) $PhSO_2Me$ dissolved in THF, 16 h, ambient temperature e) Neat $PhSF_5$, 24 h, ambient temperature. Only one of the two coordination diastereomers shown, with ratio in parenthesis).



Given the large energetic preferences for coordination to the nitrile or carbonyl group (**4**, **6**, **8**, **10**, **12**; 10-20 kcal/mol, Table 1), we decided to explore benzenes that had an EWG without covalent π-bonds (Scheme 3). Stirring a solution of benzene complex **2** and an excess of the target arene resulted in formation of several new dihapto-coordinate arene complexes of the form $WTp(NO)(PMe_3)(\eta^2\text{-arene})$, where arene = trimethyl o-benzoate (**14**), methyl phenyl sulfone (**16**), diphenyl sulfone (**15**), and pentafluorosulfanyl benzene (**17**). Despite the strongly electron-withdrawing substituents, these complexes were formed with minimal oxidative decomposition. In most cases the metal complex was isolated as a ~1:1 mixture of two coordination diastereomers in which the metal was bound 3,4-η^2 analogous to **12A** and **12B**. The reaction mixture resulting from methyl phenyl sulfone contained a third species, which we tentatively assign as the sulfonylmethyl hydride **16H**. Key features in the ^1H NMR spectrum include a diastereotopic methylene group at 3.14 and 1.88 ppm, and a matching hydride signal at 9.03 ppm with a large J_{PH} = 114.9 Hz and tungsten-183 satellites (J_{WH} = 9.3 Hz). While DFT calculations (Table 1) suggested that in some cases the 2,3-η^2 arene isomers were energetically competitive, only in **12** were they conclusively identified.

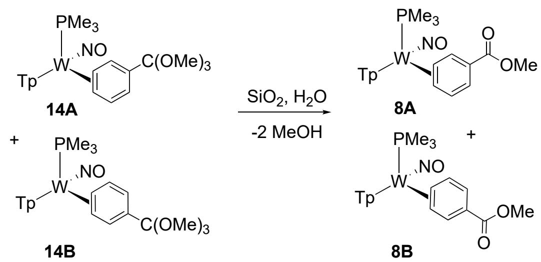
Table 2. Coordination diastereomer ratios, infrared and electrochemical data for **2**, **13** - **21**.



Cpd	EWG	R^2	R^3	cdr A:B:C	IR (νNO) (cm^{-1})	CV ($E_{p,a}$) (V, NHE)
2	H	H	H	NA : NA : NA	1564	-0.13
13	CF_3	H	H	NA : 5 : 4	1575	0.06
14	$C(OMe)_3$	H	H	NA : 4 : 3	1580	-0.08
15	SO_2Ph	H	H	NA : 3 : 2	1564	0.07
16	SO_2Me	H	H	NA : 11 : 10	1568	0.07
17	SF_5	H	H	NA : 4 : 3	1573	0.14
18	CF_3	H	OMe	10 : NA : 1	1573	0.07
19	CF_3	H	NMe_2	1 : NA : >20	1570	-0.16
20	CF_3	CF_3	H	20 : 1 : 1	1592	0.45
21	CF_3	H	CF_3	1 : NA : 7	1582	0.42

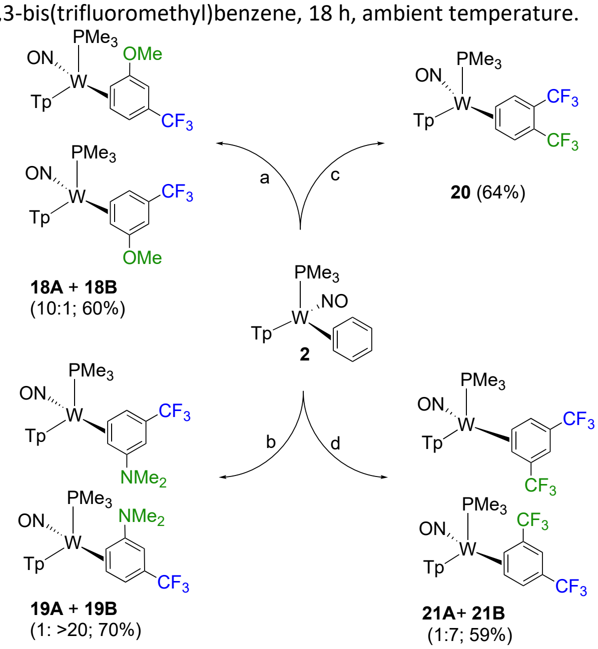
During our attempts to purify the ortho-benzoate complex **14**, hydrolysis occurred on silica, and the resulting *C,C*-η^2-benzoate ester, (**8A** + **8B**), was recovered. This provided a rare example of a dihapto-coordinated arene with a carbonyl group (Scheme 4). Even though DFT calculations predict that ester coordination is thermodynamically favored by roughly 8 kcal/mol, relative to the dihapto-coordination of the arene, the rate of arene-to-ester isomerization is sufficiently slow that a purported carbonyl-bound complex is not observed in solution after several hours (further time points were not investigated).

Scheme 4. The formation of an arene-bound benzoate complex (**22**).



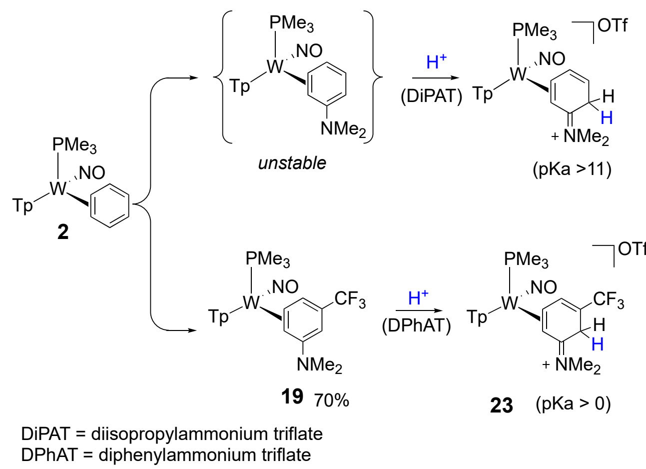
We next considered how an η^2- benzene complex bearing an EWG would be influenced by an additional benzene substituent (Scheme 5). Thus, we examined a family of trifluorotoluene derivatives with a methoxy- (**18**), dimethylamino- (**19**), or trifluoromethyl -(**21**), group at the 3 position. In addition, we examined one case of a 1,2-disubstituted arene (**20**; Figure 1). For examples where the second substituent was a π-donor (**18**, **19**), the metal was directed exclusively to the 5,6 position. For both **18** and **19**, the complex was isolated as a mixture of two different coordination diastereomers.

Scheme 5. Regioselective formation of substituted trifluorotoluene complexes a) 3-trifluoromethyl-anisole and DME co-solvent, 48 h, ambient temperature b) Neat 3-trifluoromethyl-N,N-dimethylaniline, 16 h, ambient temperature c) Neat 1,2-bis(trifluoromethyl)benzene, 16 h, ambient temperature d) Neat 1,3-bis(trifluoromethyl)benzene, 18 h, ambient temperature.



As an example, combining **2** and 3-(trifluoromethyl)-N,N-dimethylaniline,[24] resulted in the synthesis of **19**. The robust nature of this compound stands in contrast to that observed for the *N,N*-dimethylaniline analog, which is too thermally sensitive to isolate. In the latter case, the aniline ligand must be stabilized as an η^2-2H-anilinium complex (Scheme 6) by the action of a weak acid.[11] The ability to isolate **19** in its neutral form demonstrates the ability of a single -CF_3 group to stabilize arenes functionalized with π-donor groups. The trifluoromethylated aniline complex **19** can be still be selectively protonated at the C2 ring carbon but stronger acid is required (e.g., diphenylammonium triflate (DPhAT); pKa ~ 0). The resulting 2H-anilinium compound has spectroscopic features similar to those reported for [W(PMe_3)(NO)(η^2-N,N-dimethyl-2H-anilinium)]OTf (Scheme 6).[11]

Scheme 6. Preparation of 3-(trifluoromethyl)-N,N-dimethylaniline complex **19** and its protonation to give an anilinium **23** as a single isomer.



When the {WTp(NO)(PMe_3)} synthon **2** was dissolved in a DME solution of nitrobenzene, oxidation of the metal rapidly occurred, resulting in free benzene and uncharacterized paramagnetic materials. Cationic benzene derivatives such as N,N,N-trimethylanilinium iodide or trityl triflate, when combined with **2**, resulted in reaction mixtures that showed encouraging signs of dihapto-coordination, with resonances in their ^{1}H NMR spectra resembling those associated with the previously reported tungsten-$PhCF_3$ complex **13**. However, difficulties in purification and low yields of the desired products dissuaded us from pursuing these complexes further, as dihapto-coordination of these cationic complexes was accompanied by large amounts of decomposition. Other arenes bearing electron-withdrawing groups that did not give promising indications of complex formation included $PhOCF_3$, $PhCCl_3$, and $PhSCF_3$. A summary of all new η^2-arene complexes for the {WTp(NO)(PMe_3)} system appears in Table 2.

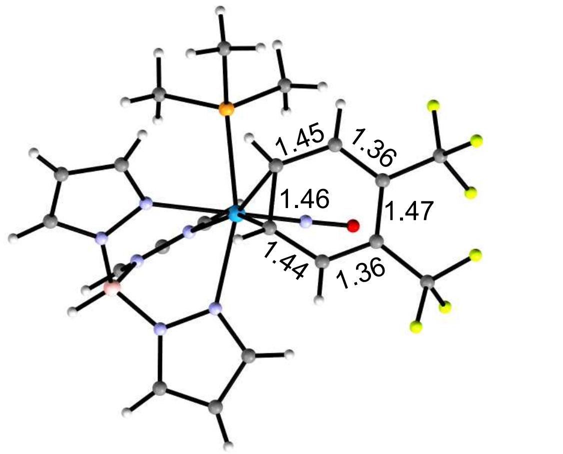
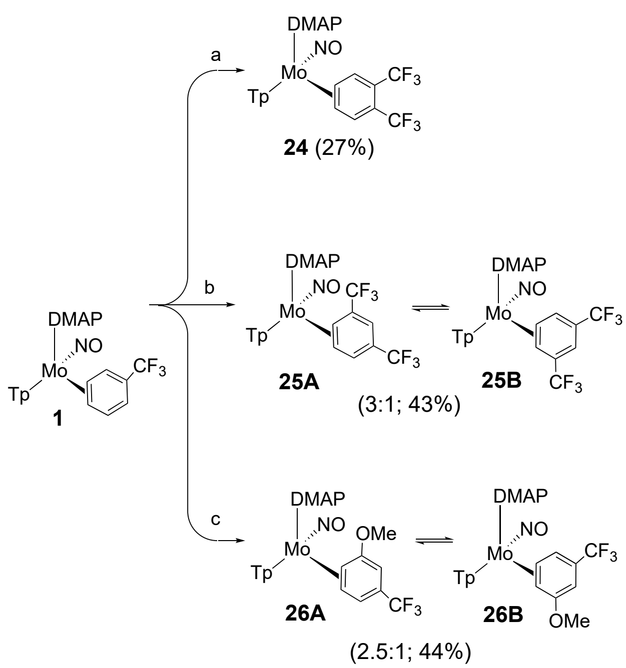


Figure 1. SC-XRD molecular structure determination for the 1,2-bis(trifluoromethyl)benzene complexes **20.**

Turning our attention to the weaker π-base {MoTp(NO)(DMAP)}, the complex MoTp(NO)(DMAP)(η^2-α,α,α,-trifluorotoluene) (**1**) can be prepared from the precursor MoTp(NO)(DMAP)(I) on a 37 g scale at a 70 % yield without the need for chromatography, as an analytically pure red powder.[14] We found this complex to be an efficient precursor to several trifluoromethylated aromatic ligands (**24**-**26**, Scheme 7; Figure 2), analogous to those of the tungsten analog.

Scheme 7. Preparation of several derivatives of a molybdenum trifluorotoluene complex. a) 1,2-bis-trifluoromethylbenzene, DME. b) 1,2-bis(trifluoromethyl)benzene, DME c) 3-(Trifluoromethyl)anisole, DME.



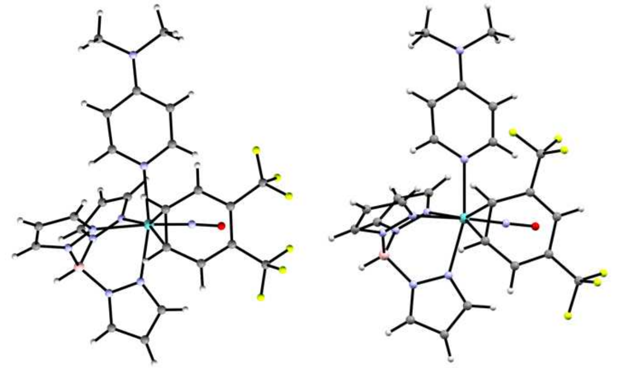


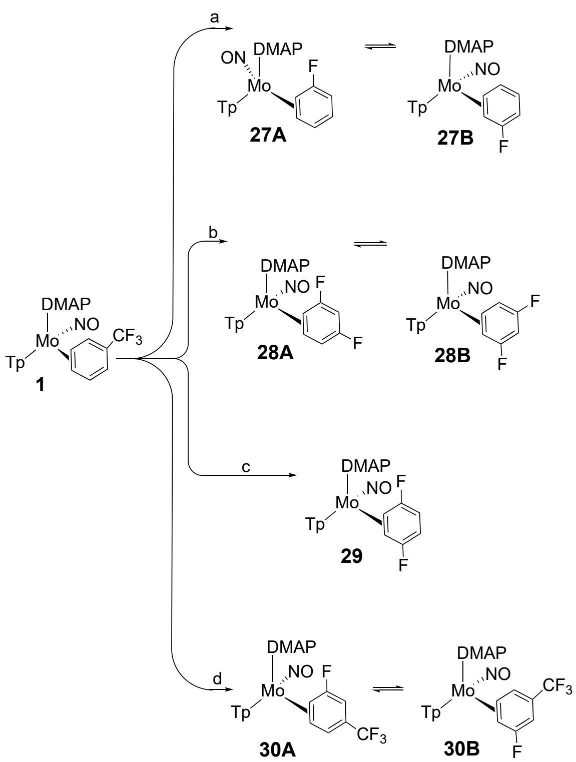
Figure 2. SC-XRD molecular structure determination for the bis(trifluoromethyl)benzene complexes **24 and 25A.**

Compared to their heavy metal counterparts (**18**, **20**, **21**), the molybdenum complexes **24**-**26** have NO stretching features consistently 3-5 cm^{-1} higher and anodic peak currents ($E_{p,a}$) roughly 400 mV more negative. Reactions of **1** with $Ph(OMe)_3$, $PhSF_5$, and 3-trifluoromethyl-N,N-dimethylaniline were all unsuccessful.

Aryl fluorides. Fluorine is widely recognized as a unique substituent for arenes. While it acts inductively as an electron-withdrawing group, it has the ability to act as a significant π-donor (and hence is ortho/para directing). Fluorine is also of interest for its role in the efficacy of drugs.[25] The ability of the tungsten complex {WTp(NO)(PMe_3)} to form complexes with aryl halides of any type has been largely unsuccessful. Reactions with iodobenzene, bromobenzene, and chlorobenzene all result in intractable mixtures of paramagnetic materials. Only in the case of fluorinated arenes have well-defined reactions been observed. For fluorobenzene itself, a clean oxidative addition product, WTp(NO)(PMe_3)(F)(Ph), was produced from **2** in neat PhF with a ligand exchange half-life of 3.3 h at 298 K.[26] Even in the presence of a CF_3- group, C-F insertion occurs with 3-fluoro-trifluorotoluene at ambient temperature. In contrast, stable η^2-arene complexes were realized for tungsten with 1-fluoronaphthalene, as well as hexafluorobenzene.[26] We questioned if the molybdenum fragment, {MoTp(NO)(DMAP)}, which is more tempered in its π-basicity than its tungsten analog,[27] might allow for a stable dihapto-coordinated arene complex. We hoped that the addition of fluorine substituents would lower the energy of the π* orbitals of the arene enough to significantly strengthen the Mo-arene backbonding interaction. Gratifyingly, in contrast to its heavy metal cousin, the {MoTp(DMAP)(NO)} fragment successfully binds fluorobenzene, o-, m-, and p- difluorobenzene, and various tetrafluorotoluenes in a dihapto fashion (**Scheme 8**).[26] These compounds constitute exceedingly rare examples of thermally stable dihapto-coordinated fluorobenzenes,[28-30] where the arene is not exhaustively fluorinated, and where C-H or C-F insertion does not pre-empt formation of the η^2-arene complexes.[29-34] In no case were there any spectroscopic indications of either aryl hydride or aryl fluoride formation in the analysis of complexes **27**-**29**.

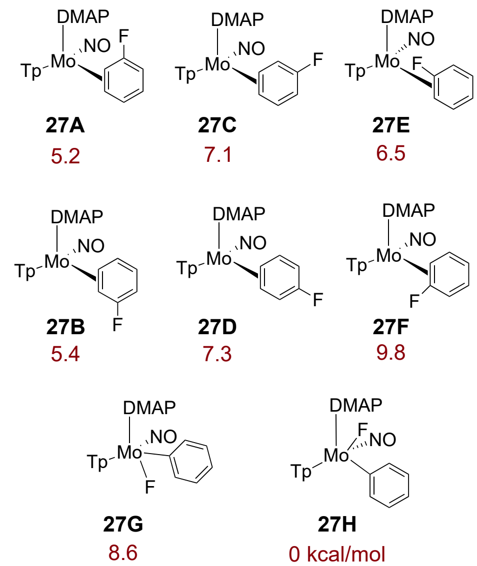
Fluorobenzene reacts with the TFT complex **1** to provide two isomers of the fluorobenzene complex, **27A** and **27B** in a 1:1 ratio, and this compound can be isolated by precipitation into cold pentane (-60 °C). Cyclic voltammetry ($E_{p,a}$= -0.36 V @ 100 mV/s), IR (ν_{NO}= 1573 cm^{-1}), and NMR data (^{13}C, ^1H, ^{19}F) support the presence of dihapto-coordinated arene complexes.[35] Predictably, the fluorinated benzene complex has a higher energy stretching feature and less negative $E_{p,a}$ than the parent (cf. 1563 cm^{-1}, -0.55 V @ 100 mV/sec), indicating the F is predominantly inductively withdrawing. But like that predicted for $ReCp(CO)_2$ from DFT calculations,[32] the π-donating F directs the metal exclusively to the C2 and C3 carbons. Despite its proximity to the fluorine, π-donation from both the halogen and the molybdenum cause the ortho proton for both isomers to be relatively shielded: well resolved resonances in the ^{1}H NMR spectrum for the arene protons (-20 °C) include signals near 5.7 ppm, corresponding to the unbound ortho-proton (H6; cf. H4, ~ 6.7 ppm). In acetone solution at 25 °C, this complex has a substitution half-life of 8 min, which is slightly longer than the parent benzene complex (cf. **33** has a half-life estimated to be 20 s at 25 °C), but substantially longer than any other example reported to date for an η^2-fluorobenzene complex.

Scheme 8. Preparation of several molybdenum fluorobenzene, difluorobenzene, and tetrafluorotoluene complexes.



A DFT study was carried out for the six possible isomers of the fluorobenzene complex (**27A**-**E**) along with two isomers of the purported C-F insertion product (**27G**,**H**). These calculations support the experimental observation that the metal favors binding across C2 and C3, similar to experimentally determined preferences for anisole complexes of W, Re, and Os.[1] Coordination diastereomers (**27A**, **27B**) of the 2,3-η^2 form are roughly 2 kcal/mol more stable than **27C** and **27D**, the corresponding 3,4-η^2 isomers. Not surprisingly, DFT calculations indicate that these ring-bound isomers are not as stable as the aryl fluoride isomer **27H** (5.2 kcal/mol lower in energy; Table 3). This suggests that the lack of observed C-F activation in the reaction of molybdenum with fluorobenzene is a result of a large kinetic barrier for this pathway, which is preempted by arene dissociation followed by decomposition. Even if the arene complex (**27**) is allowed to stand in neat fluorobenzene for longer reaction times (48 h) or at higher temperatures (50 °C), no discernable C-F insertion occurs. Similar conclusions were reached by Caulton, Eisenstein, and Perutz whose DFT calculations predicted high kinetic barriers of C-F addition for osmium and rhodium systems.[30] In contrast, as mentioned above, the tungsten system inserts into the C-F bond within minutes at room temperature.[27]

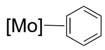
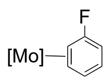
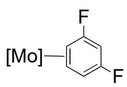
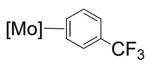
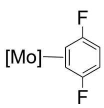
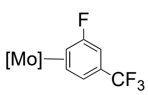
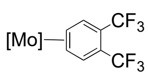
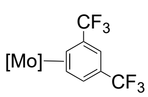
Table 3. DFT calculations for relative stabilities (Gibbs free energies, vacuum) for various isomers of MoTp(NO)(DMAP)(fluorobenzene).



As anticipated, the incorporation of F or CF_3 as substituents on the benzene ring stabilizes the complex toward dissociation and oxidation. Calculated BDEs, approximate half-lives, and anodic peak potentials are given in Table 4 along with the observed diastereomer ratios. The addition of a second fluorine atom increases the BDE by roughly 4 kcal/mol and renders the arene over 300 mV more resistant to oxidation. Meanwhile, substitution half-lives in acetone increase from seconds to hours. In Table 4, the effects of CF_3 substituents are also highlighted, where again these substituents act to raise both the BDE and anodic peak potential ($E_{p,a}$ (NHE), 100 mV/s).

From the observed coordination diastereomers in Table 4, we recognize several trends regarding the ability of -CF_3 and -F groups to direct the location of metal coordination. As observed for tungsten, trifluoromethyl groups direct the metal to the 3,4-η^2 position, whereas a fluorine substituent directs the metal to the 2,3-position. We speculate that, as with anisole,[4, 36] the preference of fluorobenzene to be coordinated at C2 and C3 is due to the π-donor fluorine substituent being in linear conjugation with the *uncoordinated* portion of the arene π-system. These trends are consistent for all fluorinated arene complexes shown in Table 4. We note that in contrast to that calculated for $CpRe(CO)_2$,[32] the bond dissociation energy for difluorobenzene complexes is *increased* by several kcal/mol compared to the benzene complex **32.** This is manifest in the increased stability in solution (relative to ligand exchange) for these complexes (e.g., for the 1,3-difluorobenzene complex **28**, $t_{1/2}$ = 80 min at 298 K cf. $t_{1/2}$ = 0.4 min at 298 K for **32**). A plot of BDE vs ln(1/t) shows good correlation indicating a linear free energy relationship between activation free energy and bond dissociation energy.[37]

Table 4. Compilation of DFT (BDE, 298 K, kcal/mol); ligand exchange in acetone, and electrochemical data for fluorinated molybdenum benzene complexes.

Complex	(#)	BDE (kcal/mol)	$t_{1/2}$ (min)	$E_{p,a}$ (V)
	(**32**)	28.3	0.4	-0.55
	(**27**)	31.1	8	-0.36
	(**28**)	31.6	80	-0.35
	(**1**)	31.7	40	-0.28
	(**29**)	33.8	280	-0.21
	(**30**)	34.1	1390	-0.05
	(**24**)	36.1	2880	-0.06
	(**25**)	37.1	3040	-0.10

Finally, we briefly explored the solution dynamics for the molybdenum and tungsten complexes of trifluorotoluene, **1** and **13** respectively, along with the molybdenum fluorobenzene complex **27** (Scheme 9). Interestingly, both of the molybdenum complexes show spin saturation exchange, even at reduced temperatures (0 °C) that is consistent with an intramolecular ring-walk isomerization. In contrast, a NOESY experiment for the tungsten analog **13** at 50 ºC in MeCN-d_3 reveals an exchange process that passes through an aryl hydride intermediate.[23] While this tungsten-hydride species exists as only a minor isomer (~4 % of population) and full characterization is thwarted by its low concentration, exchange-correlations clearly demonstrate that isomerization occurs through the C-H of the arene ring at the and para position (Figure 4; Scheme 9).

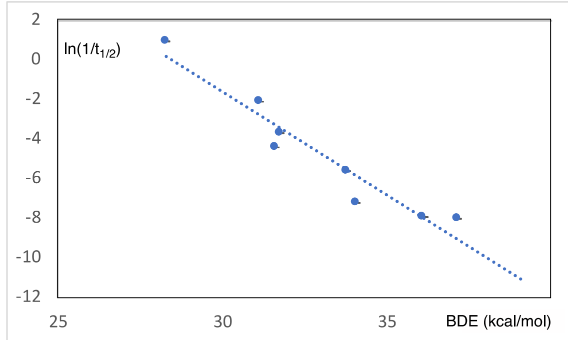


Figure 3. Plot of calculated BDE vs $\ln(1/t_{1/2})$ for dissociation in acetone at 298K for comounds in Table 4.

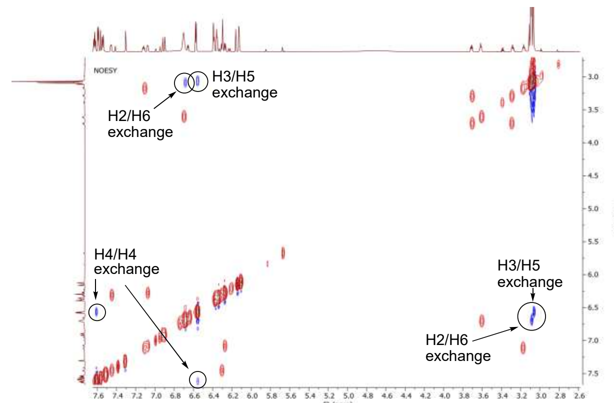
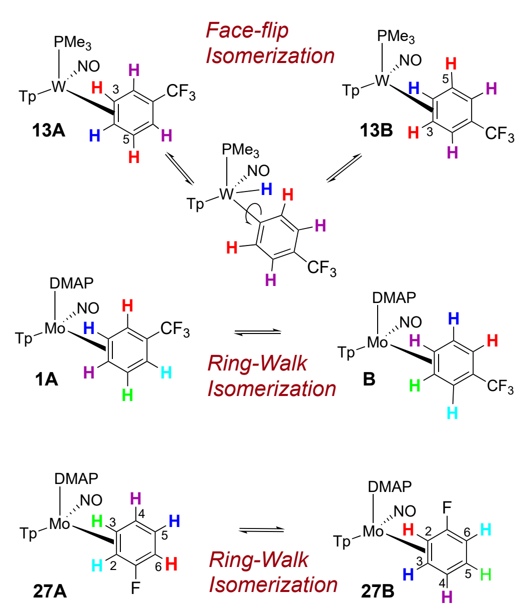


Figure 4. NOESY data for fluorobenzene complex **27** at 0 °C showing chemical exchange (blue cross peaks) between **27A** and **27B**.

Scheme 9. Comparison of isomerization pathways for **1**, **13**, and **27**. Colored hydrogens indicate chemical exchange observed.



A detailed study of the activation of electron-deficient arenes by the molybdenum or tungsten systems described above is beyond the scope of this study. Yet we felt it was important to establish that, like the complex $WTp(NO)(PMe_3)(TFT)$,[12] a ~1:1 mixture of coordination diastereomers does not preclude obtaining the η^2-diene products derived from them as single stereoisomers. Hence, we briefly explored the ability of the sulfone complex **16** to undergo protonation followed by nucleophilic addition. Gratifyingly, treatment of **16** with HOTf at 0 °C in acetonitrile solvent followed by addition of the ester enolate ((1-methoxy-2-methylprop-1-en-1-yl)oxy)trimethylsilane (MMTP) results in a single diastereomer of the diene **33** (54%, dr >20:1). This result indicates that both isomers of **16** (**16A** and **16B**) are capable of leading to a single common η^2-arenium species in which the "cationic carbon" is favored distal to the PMe_3.[12] A single crystal X-ray structure determination provides confirmation of the proposed stereochemistry (Figure 5).

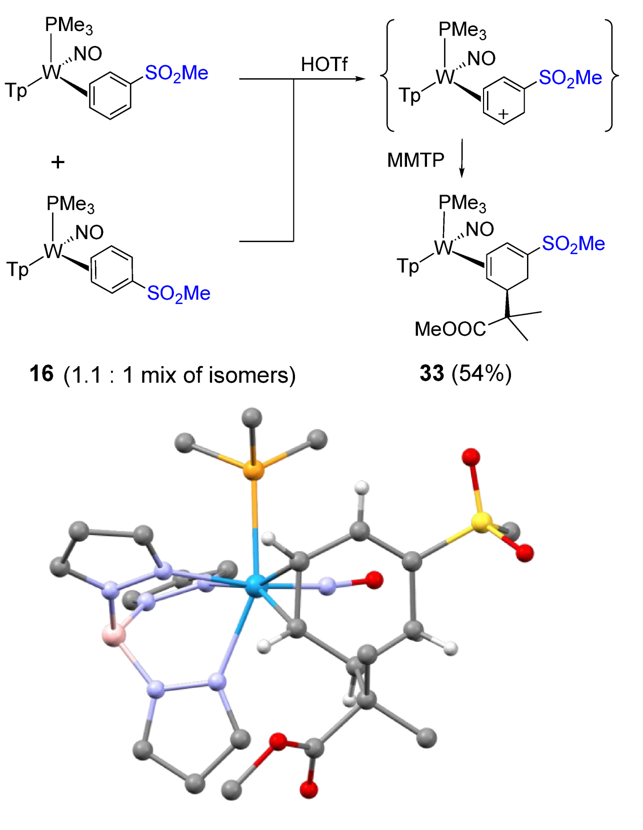


Figure 5. Preliminary test of dearomatization: protonation of phenyl sulfone ring followed by addition of ester enolate to stereoselectively form η^2-diene complex **33** (dr >20:1). Solid state structure generated from SC-XRD data.

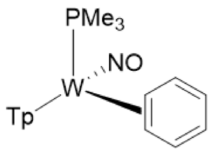
Conclusions

We have prepared a series of tungsten and molybdenum complexes of dihapto-coordinated benzenes bearing electron-deficient substituents. In general, arenes with electron-withdrawing groups direct the metal to C3 and C4, whereas π donor substituents (F, OMe, NMe_2) direct the metal to C2 and C3. While tungsten readily inserts into C-F bonds of fluorinated benzenes, the molybdenum system the {MoTp(NO)(DMAP)} is able to form stable dihapto-coordinate complexes. The addition of fluorine atoms stabilizes the complex toward ligand substitution. The isomerization dynamics of trifluorotoluene complexes were examined for both molybdenum and tungsten, and there appears to be mechanistic divergence for these Group 6 metals. Whereas the tungsten system undergoes isomerization of coordination diastereomers preferentially through an oxidative addition mechanism that results in interfacial isomerization, the molybdenum system undergoes isomerization through a ring-slip mechanism. A comparison of C-F activated and dihapto-coordinate molybdenum-fluorobenzene isomers has been evaluated by DFT calculations and we conclude that lack of an observed C-F activated product is the result of a high kinetic barrier for C-F addition as opposed to any fundamental thermodynamic argument. Although many of the η^2-arene complexes described herein exist in solution as a mixture of diastereomers, preliminary experiments with the methyl phenyl sulfone complex **16** indicate that upon protonation, a single η^2-arenium complex is formed that can be regio- and stereoselectively elaborated into an η^2-diene complex. Efforts to further develop these η^2-arene complexes into novel functionalized dienes and cyclohexenes are currently under way.

Experimental Section.

General Methods. NMR spectra were obtained on 500, 600 or 800 MHz spectrometers. Chemical shifts are referenced to tetramethylsilane (TMS) utilizing residual ^1H signals of the deuterated solvents as internal standards. Chemical shifts are reported in ppm and coupling constants (J) are reported in hertz (Hz). Chemical shifts for ^{19}F and ^{31}P spectra were reported relative to standards of hexafluorobenzene (164.9 ppm) and triphenylphosphine (-6.00 ppm) or triphenyl phosphate (-16.58 ppm). Infrared Spectra (IR) were recorded on a spectrometer as a solid with an ATR crystal accessory, and peaks are reported in cm^{-1}. Electrochemical experiments were performed under a nitrogen atmosphere. Most cyclic voltammetric data were recorded at ambient temperature at 100 mV/s, unless otherwise noted, with a standard three electrode cell from +1.8 V to -1.8 V with a platinum working electrode, acetonitrile or dimethylacetamide (DMA) solvent, and tetrabutylammonium (TBAH) electrolyte (~1.0 M). All potentials are reported versus the normal hydrogen electrode (NHE) using cobaltocenium hexafluorophosphate ($E_{1/2}$ = -0.78 V, -1.75 V) or ferrocene ($E_{1/2}$ = 0.55 V) as an internal standard. Peak separation of all reversible couples was less than 100 mV. All synthetic reactions were performed in a glovebox under a dry nitrogen atmosphere unless otherwise noted. All solvents were purged with nitrogen prior to use. Deuterated solvents were used as received from Cambridge Isotopes and were purged with nitrogen under an inert atmosphere. When possible, pyrazole protons of the trispyrazolylborate (Tp) ligand were uniquely assigned (e.g., "Tp3B") using two-dimensional NMR data (see Fig. S1). If unambiguous assignments were not possible, Tp protons were labeled as "Tp3/5 or Tp4". All J values for Tp protons are 2 (±0.4) Hz. Compounds **1**[14] and **2**[22] have previously been reported.

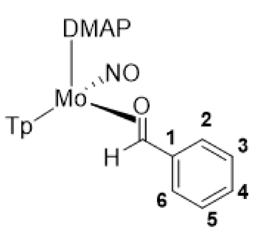
$WTp(NO)(PMe_3)(\eta^2$-benzene) (2) (large scale procedure)



2

Anhydrous benzene (4.0 L) was added to a 4 L Erlenmeyer flask containing a stir bar. $WTp(NO)(PMe_3)(Br)$ (50.0 g, 85.8 mmol) followed by an excess of 35 wt % sodium dispersion in toluene (48.0 g, 731 mmol) were then added to the flask. The resulting heterogeneous green reaction mixture was allowed to stir rapidly for 14 h. Subsequently, the dark golden-brown reaction mixture was filtered through a slurry of Celite (200 mL) and anhydrous benzene (100 mL) in a 600 mL medium porosity fritted funnel. The filtrate was collected and set aside. A slurry of silica (450 mL) and Et2O (1.5 L) was prepared and transferred to a 2 L large capacity pressure filter funnel. The Et2O was allowed to drain until the solvent surface was 4 cm from the top of the silica, and then benzene (500 mL) was carefully added. The solvent was allowed to drain until the surface was 4 cm from the top of the silica, and then the reaction mixture filtrate was added until the funnel was full. Using nitrogen pressure, the filtrate was loaded onto the column. The funnel was refilled with filtrate as necessary, until all of the filtrate had been loaded. At this point, a green band was ~1 cm from the bottom of the column. The green band was eluted with 4:1 benzene/Et2O (600 mL) using nitrogen pressure. When the green band had eluted and the solvent level was within 2 cm of the top of the silica, Et2O was added to fill the funnel. Nitrogen pressure was used to elute a vivid yellow band, which was collected. Additional Et2O was added to the funnel, and the elution was continued until the filtrate became colorless (after ~2 L total Et2O). The golden yellow eluent was evaporated under vacuum until the volume was approximately 500 mL. Hexanes (400 mL) was added to the concentrated solution, and the resulting solution was evaporated under vacuum to a final volume of 400 mL. The solid which had precipitated was isolated on a 150 mL medium porosity fritted funnel, washed with hexanes (3 x 75 mL), and desiccated under dynamic vacuum to yield 2, as a vivid yellow solid (22.7 g, 45.5%). Complex has been previously reported.[20]

MoTp(NO)(DMAP)(C,O-η^2-benzaldehyde) (3C)

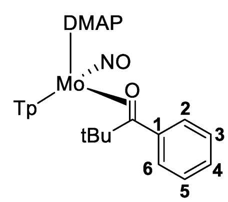


3C

A 15 mL vial was charged with **1** (1.05 g, 1.72 mmol) and benzaldehyde 10.4 g (98.0 mmol). This homogeneous light green mixture was capped and stirred at room temperature for 10 minutes. This substitution reaction is believed to be catalyzed by the presence of trace acid that forms from benzaldehyde over time; and this phenomenon has been reported elsewhere.[37] This reaction mixture was then loaded onto a 60 mL coarse porosity fritted disc 2/3 full with silica gel. This column was washed with diethyl ether (50 mL) and the product was isolated using THF (100 mL). The green solution was evaporated *in vacuo* to an approximate volume of 20 mL and added to chilled pentane (100 mL) yielding a white precipitate. This reaction mixture was then decanted to collect a white solid on a fine 15 mL fritted disc. Some product had oiled out on the bottom of the filter flask, and this was re-dissolved in a minimal amount of DCM (~3 mL) and then re-precipitated into stirring pentane (50 mL) that had been chilled to -30 ^oC. A white precipitate was again isolated on a 15mL fine porosity fritted disc. The white products obtained but both precipitation steps were combined and then washed with chilled pentane (2 x 10 mL) and dried under static vacuum for 2 h to yield **3C**. An off-white solid was obtained (0.518 g, 55.0 %).

CV (DMA) $E_{p,a}$ = + 0.40 V (NHE). IR: ν(BH) = 2484 cm^{-1}, ν(NO) = 1580 cm^{-1}. ^1H-NMR (acetone-d_6, δ, 25 ^oC): 7.95 (1H, d, Tp3/5), 7.92 (1H, d, Tp3/5), 7.88 (1H, d, Tp3), 7.78 (2H, m, DMAP-2/6), 7.56 (1H, d, Tp3/5), 7.48 (1H, d, Tp3/5), 7.32 (1H, d, Tp3), 7.28 (2H, t, J =7.84, H3 and H5), 7.19 (2H, d, J =7.31, H2 and H6), 7.02 (1H, t of t, J = 7.25, 1.25, H4), 6.65 (2H, m, DMAP-3/5), 6.29 (1H, t, Tp4), 6.24 (1H, t, Tp4), 6.23 (1H, t, Tp4), 4.45 (1H, s, aldehyde H), 3.10 (6H, s, NMe_2). ^{13}C {^1H} NMR (acetone-d_6, δ, 25 ^oC). 155.7 (DMAP-C4), 151.63 (DMAP-C2/C6), 149.13 (C1), 143.5 (Tp3/5), 143.5 (Tp3/5), 141.9 (Tp3/5), 136.8 (Tp3/5), 136.6 (Tp3/5), 136.3 (Tp3/5), 127.7 (C3 and C5), 126.30 (C2 and C6), 125.4 (C4), 107.6 (DMAP-C3/C5), 106.8 (Tp4), 106.3 (Tp4), 106.0 (Tp4), 98.1 (aldehyde carbonyl C), 39.2 (NMe_2 Cs). This compound is a simple derivative of the complex $WTp(NO)(PMe_3)$(C,O-η^2-acetaldehyde) with closely matching spectra and its characterization was not further pursued.[37, 38]

MoTp(NO)(DMAP)(C,O-η^2-2,2,2-trimethyl-acetophenone) (5C)

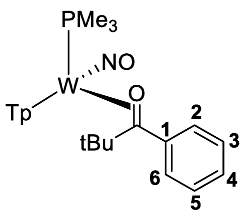


5C

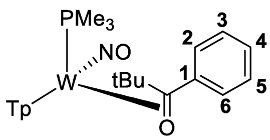
An oven-dried 15 mL vial was charged with **1** (0.198 g, 0.326 mmol), 2,2,2-trimethylacetophenone (0.440 g, 2.71 mmol) and DME (2 mL) and the heterogeneous orange mixture was allowed to stir. After 5 h the reaction mixture had turned to a light homogenous brown solution and the reaction mixture was added to a solution of stirring pentane (30 mL). Upon addition to the pentane solution, an off-white precipitate forms in the solution. The solid was then filtered through a 15 mL fine porosity fritted disc and washed with pentane (3 x 10 mL). The off-white powder was allowed to desiccate under dynamic vacuum for 8 h before a mass was taken of the off-white solid (0.109 g, 53.7 % yield).

CV (DMA): $E_{p,a}$= + 0.32 V (NHE). IR: ν(BH) = 2481 cm^{-1}, ν(NO) = 1574 cm^{-1}. ^1H NMR (acetone-d_6, δ, 25 ^oC): 8.49 (1H, d, Tp3/5C), 7.83 (1H, d, Tp3/5), 7.71 (1H, d, Tp3/5), 7.57 (2H, m, DMAP-2/6), 7.43 (2H, d, overlapping Tp3/5), 7.21 (1H, d, Tp3/5), 7.13 (1H, d, J = 7.84, H3/5), 6.70 (1H, t, J = 7.53, H2/H4), 6.58 (2H, m, DMAP-3/5), 6.51 (1H, t, J = 7.84, H3/H5), 6.42 (1H, t, Tp4), 6.39 (1H, t, J = 7.53, H2/H4), 6.22 (1H, d, J = 7.53, H4/H5), 6.15 (1H, t, Tp4), 5.79 (1H, t, Tp4), 3.09 (6H, s, NMe_2), 1.29 (9H, s, -tBu). $^{13}C\ \{^1H\}$ NMR (acetone-d_6, δ, 25 °C): 155.6 (DMAP-C4), 151.8 (DMAP-C2/6), 147.1 (Tp3/5), 144.7 (Tp3/5), 142.6 (Tp3/5), 138.0 (Tp3/5), 135.4 (Tp3/5), 135.2 (Tp3/5), 130.0 (C1/C5), 127.5 (C1/6), 126.3 (C2/4), 125.3 (C2/4), 124.3 (C3), 112.1 (C=O), 107.2 (DMAP-3/5), 106.3 (Tp4), 106.5 (Tp4), 104.9 (Tp4), 39.2 (DMAP-NMe_2), 31.8 (-tBu). This compound is a simple derivative of the complex MoTp(NO)(DMAP)(C,O-η^2-acetone) with closely matching spectra and its characterization was not further pursued.[13]

WTp(NO)(PMe_3)(C,O-η^2-2,2,2-trimethyl-acetophenone) (6C)



6C



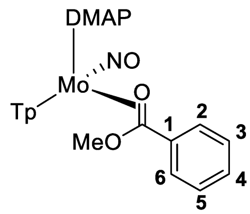
6C'

An oven-dried 15 mL vial was charged with **2** (0.201 g, 0.346 mmol) and trimethylacetophenone (0.505 g, 3.11 mmol) and DME (1 mL) and the heterogeneous orange mixture was allowed to stir. After 24 h, the reaction mixture had turned to a light homogenous brown solution and the reaction mixture was added to a solution of stirring pentane (30 mL). Upon addition to the stirring pentane solution, a light pink precipitate forms in the solution. The solid was then filtered through a 15 mL fine porosity fritted disc and washed with pentane (3 x 10 mL) before the yellow powder was allowed to desiccate under dynamic vacuum for 3 h and a mass was taken of the light pink solid (0.162 g, 70.0 % yield). The ratio of the major isomer (**6C**) to minor (**6C'**) is approximately 9:1.

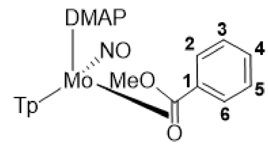
CV (DMA): $E_{p,a}$= + 0.55 V (NHE). Characterization of **6C** ^1H NMR (acetone-d_6, δ, 25 °C): 8.57 (1H, d, Tp3/5C), 8.17 (1H, d, Tp3/5), 7.89 (1H, d, Tp3/5), 7.76 (1H, d, Tp3/5), 7.74 (1H, d, Tp3/5), 7.73 (1H, d, Tp3/5), 7.47 (1H, d, Tp3/5), 7.29 (1H, dt, J = 1.39, 7.89, H2), 6.80 (1H, td, J = 1.39, 7.45, H3), 6.51 (1H, tt, J = 1.27, 7.33, H4), 6.42 (1H, td, J = 1.27, 8.01, H5), 6.35 (1H, roofing m, H6), 6.38 (1H, t, Tp4), 6.28 (1H, t, Tp4), 5.91 (1H, t, Tp4), 1.37 (9H, d, J_{PH} = 9.32, PMe_3), 1.16 (9H, s, -tBu). $^{13}C\ \{^1H\}$ NMR (acetone-d_6, δ, 25 °C): 149.7 (C1), 147.0 (Tp3/5), 145.5 (Tp3/5), 143.7 (Tp3/5), 136.3 (Tp3/5), 135.9 (Tp3/5), 130.8 (C2), 128.1 (C6), 126.2 (C3), 125.2 (C5), 124.1 (C4), 106.6 (Tp4), 106.5 (Tp4), 105.1 (Tp4), 95.3 (C=O), 31.7 (-tBu), 10.7 (d, J_{PC} = 27.2, PMe_3). $^{31}P\ \{^1H\}$ NMR (acetone-d_6, δ, 25 °C): -14.46 (J_{WP} = 278). This compound is a simple derivative of the complex WTp(NO)(PMe_3)(C,O-η^2-acetone) with closely matching spectra and its characterization was not further pursued.[38]

Characterization of **6C'** ^1H NMR (acetone-d_6, δ, 25 °C): 8.65 (1H, d, Tp3/5), 8.07 (1H, d, Tp3/5), 8.05 (1H, d, Tp3/5), 7.93 (1H, d, Tp3/5), 7.92 (1H, d, Tp3/5), 7.85 (1H, d, Tp3/5), 7.72 (1H, buried, -Ph ring), 7.50 (1H, tt, J = 1.40, 7.38, -Ph ring), 7.31 (1H, dt, J = 1.49, 7.76, -Ph ring), 7.17 (1H, buried, Ph-ring), 6.85 (1H, m, -Ph ring), 6.38 (1H, buried, Tp4), 6.35 (1H, t, Tp4), 6.28 (1H, buried, Tp4), 1.26 (9H, d, J_{PH} = 9.16, PMe_3), 0.61 (9H, s, -tBu).

MoTp(NO)(DMAP)(C,O-η^2-(methyl benzoate) (7)



7C



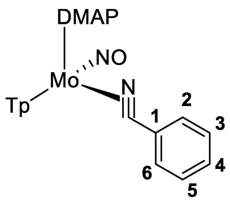
7C'

An oven-dried 15 mL vial was charged with **1** (0.200 g, 0.330 mmol) and methyl benzoate (1 mL, ~7.34 mmol) and DME (1 mL). The heterogeneous orange mixture was allowed to stir. After 20 h the reaction mixture had turned to a dark homogenous brown solution and to the reaction vessel was added pentane (10 mL) to induce precipitation. The resulting heterogeneous brown reaction mixture was then allowed to sit at reduced temperature (- 30 °C) to further induce precipitation over the course of an hour. The organic layer of the reaction mixture was subsequently discarded and the solid contents were dissolved in a minimal amount of THF (~ 2 mL) before it was added to a solution of stirring pentane (15 mL) to induce precipitation of an off-white solid. The solid was then isolated on a fine porosity 15 mL fritted disc and washed with pentane (3 x 10 mL). The off-white powder was allowed to desiccate under dynamic vacuum for 8 h before a mass was taken of the off-white solid (0.148 g**,** 75.5 % yield). The isolated product shows a 2.5:1 ratio of **7C** to **7C'**.

CV (DMA): $E_{p,a}$= + 0.26 V (NHE). IR: ν(BH) = 2483 cm^{-1}, ν(NO) = 1599 cm^{-1}. Characterization of **7C** ^1H NMR (acetone-d_6, δ, 25 °C): 7.91 (1H, d, Tp3/5), 7.83 (1H, d, Tp3/5), 7.82 (1H, d, Tp3/5), 7.75 (2H, m, DMAP-2/6), 7.51 (1H, d, Tp3/5), 7.50 (1H, d, Tp3/5), 7.45 (1H, d, Tp3/5), 7.42 (2H, m, H2/6), 7.37 (2H, m, H3/H5), 7.12 (1H, tt, J = 1.22, 7.24, H4), 6.68 (2H, m, DMAP-3/5), 6.27 (1H, t, Tp4), 6.20 (1H, t, Tp4), 6.19 (1H, t, Tp4), 3.12 (6H, s, NMe_2), 2.92 (3H, s, -OMe). $^{13}C\ \{^1H\}$ NMR (acetone-d_6, δ, 25 °C) of **7C**: 155.7 (DMAP-C4), 151.6 (DMAP-C2/6), 143.6 (Tp3/5), 143.2 (Tp3/5), 142.4 (Tp3/5), 136.6 (Tp3/5), 135.9 (Tp3/5), 135.7 (Tp3/5), 128.0 (Ph-ring), 127.8 (Ph-ring), 126.1 (Ph-ring), 107.5 (DMAP-C3/5), 106.7 (Tp4), 105.6 (Tp4), 105.3 (Tp4), 54.4 (OMe), 39.2 (-NMe_2). This compound is a simple derivative of the complex MoTp(NO)(DMAP)(C,O-η^2-ethyl acetate) with closely matching spectra and its characterization was not further pursued.[13]

Characterization of **7C'** ^1H NMR (acetone-d_6, δ, 25 °C): 8.05 (1H, d, Tp3/5), 8.00 (1H, d, Tp3/5), 7.93 (1H, d, Tp3/5), 7.90 (1H, d, Tp3/5), 7.87 (1H, d, Tp3/5), 7.56 (2H, m, DMAP-2/6), 7.29 (2H, m, H3/5), 7.21 (2H, m, H2/H6), 6.91 (2H, overlapping, H4 and Tp3/5), 6.53 (2H, m, DMAP-3/5), 6.41 (1H, t, Tp4), 6.25 (1H, t, Tp4), 6.18 (1H, t, Tp4), , 3.30 (3H, s, -OMe), 3.07 (6H, s, NMe_2). $^{13}C\ \{^1H\}$ NMR (acetone-d_6, δ, 25 °C) of **7C'**: 155.2 (DMAP-C4), 151.1 (DMAP-C2/6), 144.1 (Tp3/5), 143.4 (Tp3/5), 142.1 (Tp3/5), 136.7 (Tp3/5), 136.4 (Tp3/5), 136.2 (Tp3/5), 127.7 (Ph-ring), 127.6 (Ph-ring), 126.3 (Ph-ring), 107.7 (DMAP-C3/5), 106.6 (Tp4), 106.5 (Tp4), 105.7 (Tp4), 55.2 (-OMe), 39.2 (overlapping with **7C**, -NMe_2).

MoTp(NO)(DMAP)(η²-CN-benzonitrile) (11C)

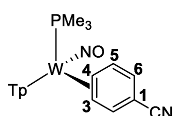


11C

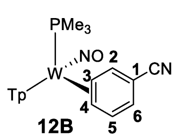
An oven-dried 15 mL vial was charged with **1** (0.201 g, 0.331 mmol), benzonitrile (0.750 g, 7.28 mmol), and DME (1.5 mL). The heterogeneous red mixture was allowed to stir overnight. After 20 h, the reaction mixture had turned to a dark homogenous brown solution and to the reaction vessel was added pentane (12 mL) to induce precipitation. Upon addition of pentane the reaction mixture becomes a gummy, oily substance. The organic layer was decanted and the resulting brown film was dissolved in THF (2 mL) and added to a solution of stirring pentane (15 mL) in a 15 mL vial. Upon addition, a pink solid precipitates from solution. This solid was isolated on a fine 15 mL porosity fritted disc. Washed with pentane (2x 10 mL) and the resulting solid was dried under dynamic vacuum for 3 h before a mass was taken of the light pink solid (0.117 g, 62.3 %). A second isomer of was observed in solution in an approximate 1:4 ratio with the major species **11** but overlapping resonances precluded unambiguous characterization. ^{1}H NMR data show uncoordinated phenyl rings for both isomers so the compound characterization was not further pursued. We note that based on the acetonitrile derivative, MoTp(NO)(DMAP)(η²-NCMe) we suspect the nitrile is dihapto-coordinated.[13]

^{1}H NMR (acetone-d_6, δ, 25° C) : 7.92 (1H, d, Tp3/5), 7.89 (1H, d, Tp3/5), 7.88 (1H, d, Tp3/5), 7.85 (2H, m, DMAP-2/6), 7.47 (2H, overlapping resonances), 7.31 (1H, broad s), 7.18 (3H, overlapping resonances), 6.62 (2H, m, DMAP-3/5), 6.28 (1H, t, Tp4), 6.15 (1H, t, Tp4), 6.13 (1H, t, Tp4), 3.09 (6H, s, NMe_2).

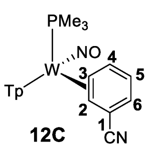
WTp(NO)(PMe_3)(η²-benzonitrile) (12A-E)



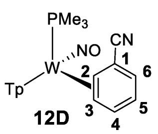
12A



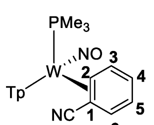
12B



12C



12D

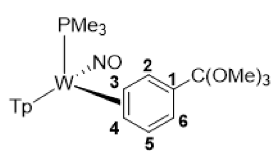


12E

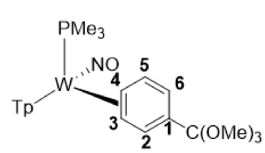
A 15 mL vial was charged with WTp(NO)(PMe_3)(η²-2,3-anisole) complex (1.00 g, 1.64 mmol) and a stir pea. To this vial was added benzonitrile (7.00 mL, 67.9 mmol).[22] This yellow heterogenous solution was allowed to stir at room temperature. After 48 h, the reaction had turned to a black homogenous mixture. A 60 mL course porosity fritted disc was filled 2/3 full of silica and set in diethyl ether. The reaction mixture was added to the column and hexanes (200 mL) were eluted through the column. An orange band could be seen beginning eluting down the column. Next diethyl ether (500 mL) was used to elute the orange band. The resulting orange filtrate was evaporated to dryness under vacuum, pick up in a minimal amount of DCM, and added to a solution of stirring pentane (50 mL). An orange solid was isolated on a 15 mL fine porosity fritted disc. The resulting solid was desiccated overnight yielding **12** (0.271 g, 27.0 % yield).

CV (DMA) $E_{p,a}$= + 0.09, IR: ν(BH) = 2493 cm^{-1}, ν(CN) = 2189 cm^{-1}, ν(NO) = 1550 cm^{-1}. ^{1}H NMR (MeCN-d_3, δ, 25 °C): 8.20 (1H, Tp3/5**E**), 8.11 (1H, Tp3/5**B**), 8.10 (1H, Tp3/5**C**), 8.06 (1H, Tp/5**A**), 8.05 (1H, Tp3/5**D**), 7.93 (6H, Tp3/5**A** 2**B** 2**D E**), 7.91 (7H, Tp3/5 2**A B** 2**C** 2**E**), 7.89 (1H, Tp3/5**E**), 7.87 (3H, Tp3/5 2**C D**), 7.84 (1H, Tp3/5**D**), 7.82 (1H, Tp3/5**B**), 7.81 (1H, Tp3/5**A**), 7.74 (1H, d, *J* = 6.26, H2**A**), 7.62 (1H, d, *J* = 5.73, H2**B**), 7.55 (1H, Tp3/5**E**), 7.38 (1H, dd *J* = 8.57, 6.34, H4**D**), 7.33 (1H, Tp3/5**A**), 7.29 (1H, Tp3/5**B**), 7.25 (1H, Tp3/5**C**), 7.23 (1H, Tp3/5**D**), 7.19 (1H, dd, *J*= 9.04, 5.64, H4**C**), 7.01 (1H, dd, *J* = 9.17, 6.03, H5**B**), 6.88 (1H, dd, *J* = 8.08, 5.40, H5**A**), 6.84 (1H, dd, *J* = 9.28, 5.57, H3**E**), 6.55 (1H, d, *J* = 9.12, H6**E**), 6.54 (1H, d *J* = 7.40, H6**D**), 6.45 (1H, d, *J* = 6.34, H6**C**), 6.33 (15H, Tp3**A B C D E**), 5.77 (2H, m, H5**C** H5**E**), 5.74 (1H, dd, *J* = 8.41, 6.38, H5**D**), 5.69 (1H, dd, *J* = 9.04, 6.05, H4**E**), 5.67 (1H, dd, *J* = 9.19, 1.38, H6**A**), 5.60 (1H, dd, *J*= 9.17, 1.21, H6**B**), 4.16 (1H, dd, *J* = 13.26, 9.89, H2**D**), 3.85 (2H, m, H4**A** H2**E**), 3.82 (1H, dd, *J* = 8.79, 5.42, H3**C**), 3.75 (1H, m, H3**B**), 2.17 (2H, m, H4**B** H2**C**), 2.14 (1H, m, H3**A**), 2.06 (1H, ddd, *J* = 9.96, 6.25, 1.55, H3**D**), 1.29 (9H, d, *J* = 8.70, PMe_3**C**), 1.23 (18H, d, J= 8.69, PMe_3**B E**), 1.22 (18H, d, *J* = 8.70, PMe_3**A D**). ^{13}C {^{1}H} NMR (MeCN-d_3, δ, 25 °C): 150.7 (1C, C2**A**), 147.6 (1C, d, J_{PC} = 3.71, C2**B**), 145.5 (1C, Tp3/5**A**), 145.2 (2C, Tp3/5**B E**), 143.3 (1C, Tp3/5**A**), 143.2 (1C, Tp3/5**E**), 142.2 (1C, Tp3/5**B**), 142.0 (1C, Tp3/5**A**), 142.0 (1C, Tp3/5**B**), 141.9 (1C, Tp3/5**E**), 138.2 (2C, Tp3/5**A E**), 138.1 (1C, Tp3/5**B**), 137.6 (1C, Tp3/5**E**), 137.6 (1C, Tp3/5**A**), 137.5 (1C, Tp3/5**B**), 137.4 (1C, Tp3/5**E**), 137.1 (1C, Tp3/5**A**), 137.1 (1C, Tp3/5**B**), 136.5 (1C, C4**B**), 134.6 (1C, d, J_{PC} = 3.17, C4**A**), 133.6 (1C, d, J_{PC} = 3.48, C3**E**), 128.4 (1C, C6**E**), 126.0 (1C, CN**E**), 121.8 (1C, CN**A**), 121.7 (1C, CN**B**), 117.3 (1C, C4**E**), 116.9 (1C, C5**E**), 114.8 (1C, C6**A**), 113.1 (1C, C6**B**), 107.7 (1C, Tp4**E**), 107.6 (1C, Tp4**A**), 107.6 (1C, Tp4**B**), 107.3 (2C, Tp4**A B**), 107.3 (1C, Tp4**E**), 107.1 (1C, Tp4**A**), 107.1 (1C, Tp4**E**), 106.8 (1C, Tp4**B**), 100.3 (1C, C1**B**), 98.4 (1C, C1**A**), 67.0 (1C, d, J_{PC} = 10.13, C2**E**), 64.9 (1C, d, J_{PC} = 9.05, C4**A**), 63.5 (1C, d, J_{PC} = 7.53, C3**B**), 63.1 (1C, C4**B**), 61.9 (1C, C3**A**), 13.2 (3C, d, J_{PC} = 28.3, PMe_3**B**), 13.2 (3C, d, J_{PC} = 29.15, PMe_3**A**), 13.0 (3C, d, J_{PC} = 30.1, PMe_3**E**). Anal. Calcd for $C_{19}H_{24}BN_8OPW$ · 1/2 (DCM): C, 36.11; H, 3.89; N, 17.28. Found: C, 36.44; H, 3.90; N, 17.19.

WTp(NO)(PMe_3)(3,4-η²-(trimethylorthobenzoate)) (14)



14A



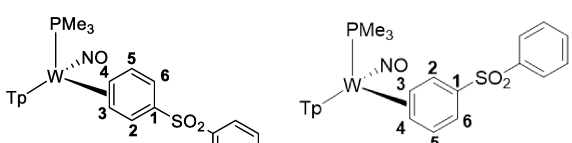
14B

An oven-dried 15 mL vial was charged with **2** (0.092 g, 0.158 mmol) and trimethyl orthobenzoate (1.00 g, 5.49 mmol). The heterogeneous yellow reaction mixture was allowed to stir with a small stir bar. Over time the reaction mixture turns to a homogeneous brown reaction mixture and after 16 h the reaction mixture was added to 15 mL of stirring pentane that had been chilled to -30 °C. Upon addition, a light-yellow solid precipitates from solution. The solid was then filtered through a 15 mL medium porosity fritted disc and washed with pentane (2 x 5 mL) before the light tan powder was allowed to desiccate under active vacuum for 2 h and a mass taken (0.040 g, 37.0 % yield).

CV (DMA): $E_{p,a}$ = - 0.08 V (NHE). IR: ν(BH) = 2496 cm^{-1}, ν(NO) = 1580 cm^{-1}. Characterization of **14A** ^{1}H NMR (acetone-d_6, δ, 0° C): 8.35 (1H, d, Tp3A), 8.00 (1H, d, Tp3/5), 7.95 (1H, d, Tp3B), 7.87 (1H, d, Tp5), 7.49 (1H, d, Tp3C), 7.31 (1H, d, J = 5.94, H2), 7.05 (1H, dd, J = 5.60, 9.09, H5), 6.36 (2H, t, overlapping Tp4), 6.35 (1H, t, Tp4A), 6.32 (2H, t, overlapping Tp4), 6.31 (1H, t, Tp4C), 5.74 (1H, d, J = 9.22, H6), 3.90 (1H, m, H3), 3.14 (9H, overlapping s, (OMe)), 2.28 (1H, m, H4), 1.37 (9H, d, J_{PH} = 8.22, PMe_3). ^{31}P NMR (acetone-d_6, δ, 25 °C): -12.15 (J_{WP} = 310.3). ^{13}C {^{1}H} NMR (acetone-d_6, δ, 25 °C): 137.7/136.3 (C1 for **A** or **B**), 136.4 (C2), 134.9 (C5), 114.9 (C6), 115.8 (overlapping with **A**, ipso C-$(OR)_3$), 63.5 (C3, d, J_{PC} = 7.00), 62.3 (C4), 49.7/49.6 (OMe groups for **A** or **B**), 13.6 (PMe_3, d, J_{PC} = 28.3). ^{13}C {^{1}H} NMR (acetone-d_6, δ, 25 °C): Tp resonances for **A** and **B**. 145.0 (Tp3/5), 144.4 (Tp3/5), 142.4 (Tp3/5), 142.4 (Tp3/5), 141.8 (Tp3/5), 141.5 (Tp3/5), 137.7 (Tp3/5), 137.7 (Tp3/5), 137.6 (Tp3/5), 136.8 (Tp3/5), 136.7 (Tp3/5), 136.5 (Tp3/5), 136.3 (Tp3/5), 107.0 (Tp4), 106.9 (Tp4), 106.8 (Tp4), 106.7 (Tp4), 106.5 (Tp4), 106.4 (Tp4).

Characterization of **14B** ^{1}H NMR (acetone-d_6, δ, 0° C): 8.25 (1H, d, Tp3A), 8.01 (1H, d, Tp5C), 7.93 (1H, d, Tp3B), 7.89 (1H, d, Tp3/5), 7.40 (1H, d, Tp3C), 7.39 (1H, buried, H2), 6.84 (1H, dd, J = 4.91, 9.40, H5), 6.36 (1H, t, overlapping Tp4), 6.35 (1H, t, Tp4A), 6.32 (2H, t, overlapping Tp4), 6.31 (1H, t, Tp4C), 5.84 (1H, d, J = 9.74, H6), 4.13 (1H, m, H4), 3.14 (9H, overlapping s, (OMe)), 2.17 (1H, t, J = 7.89, H3), 1.37 (9H, d, J_{PH} = 8.22, PMe_3). ^{31}P NMR (acetone-d_6, δ, 25° C): -12.79 (J_{WP} = 310). 137.7/136.3 (C1 for **A** or **B**), 137.5 (C2), 133.4 (C5), 116.4 (C6), 115.8 (overlapping with **A**, ipso C-$(OR)_3$), 63.9 (C4, d, J_{PC} = 7.68), 62.3 (C3), 49.7/49.6 (OMe groups for **A** or **B**), 12.9 (PMe_3, d, J_{PC} = 27.7). Attempts to purify **14** for elemental analysis by chromatography led to the generation of **22**.

WTp(NO)(PMe$_3$)(3,4-η^2-diphenyl sulfone) (15)

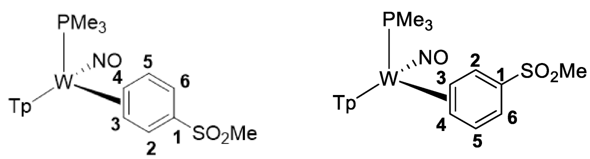


15A **15B**

A 15 mL bottle was charged with WTp(NO)(PMe$_3$)(η^2-2,3-anisole) complex (5.00 g, 8.18 mmol), diphenyl sulfone (5.35 g, 24.5 mmol), and a stir pea.[22] To this vial was added 1,2-dimethoxyethane (20 mL) along with a stir bar. The yellow heterogeneous mixture was stirred for 48 hours, until the reaction became a bright orange heterogenous mixture. The orange precipitate was collected on a 30 mL fine porosity fritted disc. The product was washed with diethyl ether (2 x 20 mL) then hexanes (4 x 20 mL). The product was desiccated overnight, yielding **15A** and **B** (4.13 g, 5.73 mmol, 70.0 % yield).

CV (DMA) $E_{p,a}$= + 0.07, (NHE). IR: v(BH) = 2482, v(NO)= 1564 cm^{-1}, v (SO)= 1407 cm^{-1}. ^{1}H NMR (MeCN-d_3, δ, 25 °C): 8.13 (1H, d, Tp3/5**B**), 8.00 (1H, dd J = 6.54, 1.41, H2**A**), 7.95 (4H, m, H8/12**A B**), 7.90 (6H, m, 3Tp3/5**A**, H2**B**, 2Tp3/5**B**), 7.85 (1H, d, Tp3/5**B**), 7.82 (2H, d, 2Tp3/5**A**), 7.80 (1H, d, Tp3/5**B**), 7.56 (1H, m, H10**B**), 7.52 (3H, m, H10**A**, H11/9**B**), 7.48 (2H, m, H11/9**A**), 7.30 (1H, d, Tp3/5**B**), 7.27 (1H, d, Tp3/5**A**), 7.07 (1H, dd, J = 9.46, 5.90, H5**B**), 6.91 (1H, dd, J = 9.32, 5.20, H5**A**), 6.36 (1H, t, Tp4**A**), 6.33 (2H, t, Tp4**A B**), 6.29 (1H, t, Tp4**B**), 6.28 (2H, t, Tp4**A B**), 5.93 (1H, dd, J = 9.55, 1.78, H6**A**), 5.82 (1H, dd, J = 9.28, 1.55, H6**B**), 3.85 (1H, m, H4**A**), 3.70 (1H, m, H3**B**), 2.10 (2H, m, H3**A**, H4**B**), 1.27 (9H, d, J_{PH} = 8.37, PMe_3**B**), 1.20 (9H, d J_{PH}= 8.45, PMe_3**A**). ^{13}C {^{1}H} NMR (MeCN-d_3, δ, 25 °C): 147.3 (1C, C2**A**), 145.3 (1C, Tp3/5**B**), 144.8 (1C, C7**A**), 144.6 (1C, C7**B**), 143.7 (1C, d, J_{PC} = 3.19, C2**B**), 143.2 (2C, Tp3/5**B**), 142.4 (1C, Tp3/5**B**), 142.1 (1C, Tp3/5**B**), 141.9 (1C, Tp3/5**A**), 138.2 (1C, Tp3/5**B**), 138.1 (1C, Tp3/5**A**), 137.6 (1C, Tp3/5**A**), 137.4 (1C, Tp3/5**B**), 137.4 (1C, Tp3/5**A**), 137.1 (1C, C5**B**), 137.0 (1C, Tp3/5**B**), 135.2 (1C, d, J_{PC} = 3.93, C5**A**), 133.4 (1C, C10**B**), 133.2 (1C, C10**A**), 129.9 (1C, C1**B**), 129.8 (4C, C11/9**A B**), 128.3 (1C, C1**A**), 128.2 (4C, C12/8**A B**), 111.9 (1C, C6**A**), 110.2 (1C, C6**B**), 107.6 (1C, Tp4**A**), 107.5 (1C, Tp4**B**), 107.3 (1C, Tp4**A**), 107.2 (1C, Tp4**B**), 107.2 (1C, Tp4**A**), 106.9 (1C, Tp4**B**), 65.4 (1C, d, J_{PC} = 9.06, H4**A**), 63.4 (1C, C4**B**), 63.1 (1C, d, J_{PC} = 7.52, H3**B**), 61.6 (1C, C3**A**), 13.4 (3C, d, J_{PC} = 29.04, PMe_3**B**), 13.2 (3C, d, J_{PC} = 28.84, PMe_3**A**) Anal. Calcd for $C_{24}H_{29}BN_7O_3PSW$: C, 39.97; H, 4.05; N, 13.59. Found: C, 40.13; H, 4.03; N, 13.42.

WTp(NO)(PMe$_3$)(3,4-η^2-methyl phenyl sulfone) (16)



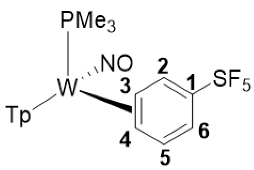
16A **16B**

A 15 mL vial was charged with **2** (5.00 g, 8.60 mmol) and methyl phenyl sulfone (2.42 g, 15.5 mmol) along with THF (8 mL). This heterogenous mixture was stirred at room temperature for 16 h. During this time, an orange solid precipitates out of solution. The orange product was collected on a 30 mL fine porosity fritted disc, washed with diethyl ether (4 x 20 ml) and desiccated under static vacuum overnight to yield **16** (2.95 g, 52.0% yield).

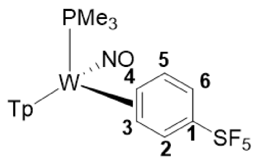
CV (DMA): $E_{p,a}$= + 0.07 V (NHE). IR: v(BH) = 2487 cm^{-1}, v(NO) = 1568 cm^{-1}, v(SO) = 1407 cm^{-1}. ^{1}H-NMR (acetone-d_6, δ, 25 °C): 8.23 (1H, d, Tp3A, **B**), 8.10 (1H, d, Tp3A, **A**), 8.03 (4H, overlapping d, Tp3/5, **A B**), 7.99 (1H, d, Tp3B, **B**), 7.96 (1H, d, Tp3B, **A**), 7.92 (1H, d, J = 6.22 , H2, **A**), 7.90 (1H, d, Tp5, **A**), 7.89 (1H, d, Tp5, **B**), 7.77 (1H, d, J = 5.53, H2, **B**), 7.53 (1H, d, Tp3C, **A**), 7.51 (1H, d, Tp3C, **B**), 7.13 (1H, dd, J = 9.47, 5.89, H5, **B**), 6.98 (1H, dd, J = 9.27, 5.32, H5, **A**), 6.39 (3H, overlapping t, Tp4A, **A,** Tp4B **B,** Tp4**B**), 6.35 (3H, overlapping t, Tp4B **A,** Tp4C **A,** Tp4**B**), 6.01 (1H, dd, J = 9.17, 1.62, H6, **A**), 5.95 (1H, dd, J = 9.15, 1.61, H6, **B**), 4.00 (1H, m, H4, **A**), 3.83 (1H, m, H3, **B**), 2.97 (3H, s, S-CH3, **A**), 2.93 (3H, s, S-CH3, **B**), 2.26 (1H, m, H4, **B**), 2.17 (1H, m, H3, **A**), 1.36 (9H, d, J = 8.42, **B**), 1.33 (9H, d, J_{PH} = 8.45, PMe_3, **A**). ^{13}C {^{1}H} NMR (acetone-d_6, δ, 25 °C): 145.4 (Tp 3/5), 145.4 (Tp 3/5), 145.0 (C2 **A**), 143.1 (Tp 3/5), 142.3 (C2, **B**), 142.1 (Tp 3/5), 142.0 (Tp 3/5), 138.2 (Tp 3/5), 137.6 (Tp 3/5), 137.5 (Tp 3/5), 137.2 (Tp 3/5), 137.1 (Tp 3/5), 137.0 (C5, **B**), 135.0 (C5, **A**), 135.0 (Tp 3/5), 129.5 (C1, **B**), 129.3 (Tp 3/5), 127.3 (C1, **A**), 110.3 (C6, **B**), 112.0 (C6, **A**), 107.6 (Tp 4), 107.6 (Tp 4), 107.3 (Tp 4), 107.3 (Tp 4), 107.2 (Tp 4), 106.9 (Tp 4), 63.6 (C4, **B**), 65.4 (C4, **A**), 62.3 (C5, **B**), 60.5 (C3, **A**), 46.7 (S-Me, **B**), 46.6 (S-Me, **A**), 13.3 (d, J_{PC} = 29.0, PMe_3). ^{31}P {^{1}H} NMR (MeCN-d_3, δ, 25 °C): -13.2 (J_{WP} = 308, PMe_3, **A**), -13.9 (J_{WP}= 302, PMe_3, **B**) Anal. Calcd for

$C_{19}H_{27}BN_7O_3PSW·THF$: C, 37.78; H, 4.82; N, 13.41. Found: C, 37.70; H, 4.62; N, 13.60. A SC-XRD study confirms the identify of this compound (SI). Approximately 23% of the total mass recovery corresponds to the C-H activation of the methyl group (**16H**), though full characterization of this complex was not pursued.

WTp(NO)(PMe$_3$)(3,4-η^2-pentafluorosulfanyl benzene) (17)



17A



17B

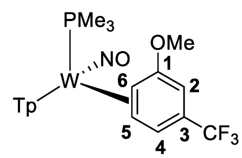
An oven-dried 15 mL vial was charged with **2** (0.411 g, 0.707 mmol), pentafluorosulfanyl benzene (2.21 g, 10.8 mmol), and the heterogeneous yellow reaction mixture was allowed to stir. Over time, the reaction mixture turns to a homogeneous red solution and after 24 h the reaction mixture was added to stirring pentane (50 mL) and upon addition a light tan solid precipitates from solution. The solid was then filtered through a fine porosity 15 mL fritted disc and washed with pentane (3 x 10 mL) before the light tan powder was allowed to desiccate under active vacuum for 3 h and a mass was taken (0.311 g, 62.2 %). The filtrate was collected and the pentane was distilled to re-collect the excess pentafluorosulfanyl benzene. The recovered aromatic ligand was used in similar reaction procedures without noticeable inhibition of yield.

Characterization of **17A**: CV (DMA): $E_{p,a}$ = + 0.14 V (NHE). IR: ν(BH) = 2496 cm^{-1}, ν(NO) = 1573 cm^{-1}. ^{1}H NMR (acetone-d_6, δ, 25 °C): 8.22 (1H, d, Tp3A), 8.08 (1H, d, Tp3/5), 7.98 (1H, d, Tp3/5), 7.87 (1H, d, Tp3/5), 7.51 (1H, d, J = 5.9, H2), 7.02 (1H, m, H5), 6.48 (1H, t, Tp4), 6.37 (2H, t, overlapping Tp4), 6.34 (2H, t, overlapping Tp4), 5.89 (1H, dd, J = 2.2, 9.6, H6), 3.83 (1H, m, H3), 2.15 (1H, t, J = 7.78, H4), 1.34 (9H, d, J_{PH} = 8.56, PMe$_3$). ^{19}F NMR (acetone-d_6, δ, 25 °C): 91.53 (-SF$_5$ (1F), overlapping diastereomers q, J_{FF} = 148.6), 64.12 (SF$_5$ (4F), J_{FF} = 148.6). ^{31}P NMR {^{1}H} (acetone-d_6, δ, 25 °C): -13.54 (buried J_{WP}). Characterization of **17B**: ^{1}H NMR (acetone-d_6, δ, 25 °C): 8.21 (1H, d, Tp3A), 8.08 (1H, d, Tp3/5), 7.98 (1H, d, Tp3/5), 7.96 (1H, d, Tp3/5), 7.89 (1H, d, Tp3/5), 7.60 (1H, d, J = 6.90, H2), 7.47 (1H, t, Tp3A), 6.86 (1H, m, H5), 6.48 (2H, t, overlapping Tp4), 6.37 (1H, t, Tp4) 6.34 (2H, t, overlapping Tp4), 5.96 (1H, dd, J = 2.21, 5.89, H6), 3.93 (1H, m, H4), 2.11 (1H, buried, H4), 1.32 (9H, d, J_{PH} = 8.20, PMe$_3$). ^{19}F NMR (acetone-d_6, δ, 25 °C): 85.10 (-SF$_5$ (1F), overlapping diastereomers q, J_{FF} = 147.3), 64.52 (-SF$_5$ (4F), J_{FF} = 147.3).^{31}P {^{1}H} NMR (acetone- d_6, δ, 25 °C): -12.88 (buried J_{WP}).

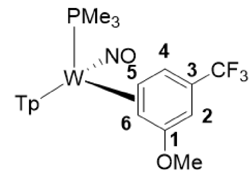
Combined ^{13}C {^{1}H} data for Diastereomers **A** and **B**. When possible, distinction between the isomers is made.

^{13}C NMR (acetone-d_6, δ, 25 °C): 146.0 (C-SF5, identified by HMBC interactions, **A**), 145.2 (overlapping 2C, Tp3/5s), 146.0 (C-SF5, identified by HMBC interactions, **B**), 142.6 (Tp3/5), 142.2 (Tp3/5), 142.6 (Tp3/5), 141.9 (Tp3/5), 141.8 (Tp3/5), 139.1 (C2 for **B**), 137.9 (Tp3/5), 137.9 (Tp3/5), 137.8 (Tp3/5), 137.2 (Tp3/5), 137.1 (Tp3/5), 136.8 (C2 for **A**), 136.7 (Tp3/5), 136.6 (Tp3/5), 135.9 (C2 for **A**), 134.0 (C5 for **B**), 113.3 (C6 for **B**), 111.6 (C6 for **A**), 107.3 (Tp4), 107.2 (2C, overlapping Tp4s), 107.1 (Tp4), 106.8 (Tp4), 106.5 (Tp4), 63.5 (C4 for **B**, d, J_{PC} = 9.5), 62.0 (C4 for **A**), 61.2 (C3 for **A**, d, J_{PC} = 8.5), 59.8 (C3 for **B**), 13.4 (PMe$_3$ for **A**, d, J_{PC} = 28.0), 13.3 (PMe$_3$ for **B**, d, J_{PC} = 28.5).

WTp(NO)(PMe$_3$)(5,6-η^2-(3-trifluoromethylanisole)) (18)



18A



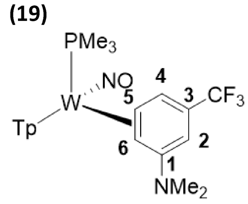
18B

A 15 mL vial was charged with WTp(NO)(PMe$_3$)(η^2-2,3-anisole) (0.519 g, 0.404 mmol), 3-(trifluoromethyl)anisole (2.15 g, 23.8 mmol), DME (2 mL) and a stir pea.[22] This yellow, heterogeneous mixture was stirred over 48 hours. Over this period, the mixture became dark brown and homogenous. Next a medium 30 mL fritted disc was filled with silica (~ 3 cm) and set in diethyl ether. The reaction mixture was loaded onto the column and subsequently eluted with diethyl ether. Upon elution a golden yellow band developed and was eluted with diethyl ether (100 mL). The resulting homogeneous, yellow solution was evaporated in vacuo until product began to precipitate from solution. Next pentane (50 mL) was added to induce further precipitation. The resulting gold precipitate was collected on a fine porosity 15 mL fritted disc (0.154 g, 59.5%). The product is initially isolated as an 8:1 ratio of **18A** : **18B**.

CV (DMA): $E_{p,a}$= +0.07, IR: ν(NO) = 1573 cm^{-1}. Characterization of **18A:** ^{1}H NMR (MeCN-d_3, δ, 0 °C): 7.98 (1H, d, Tp3/5), 7.91 (1H, d, Tp3/5), 7.90 (1H, d, Tp3/5), 7.86 (1H, d, Tp3/5), 7.80 (1H, d, Tp3/5), 7.26 (1H, d, Tp3/5), 7.09 (1H, d, J = 5.57, H4), 6.34 (1H, t, Tp4), 6.30 (1H, t, Tp4), 6.27 (1H, t, 1H), 5.18 (1H, s, H2), 3.88 (1H, dd, J = 13.7, 12.8, H5), 3.75 (3H, s, -OMe), 2.05 (1H, m, H6), 1.20 (9H, d, J_{PH} = 8.73, PMe$_3$). ^{13}C {^{1}H} NMR (MeCN-d_3, δ, 25 °C): 165.9 (C2), 145.0 (Tp3/5), 142.4 (Tp3/5), 141.7 (Tp3/5), 137.9 (Tp3/5), 137.3 (Tp3/5), 137.0 (Tp3/5), 129.2 (d, J_{PC} = 6.03, C4), 126.1 (q, J_{CF} =270, C8), 118.2 (buried, C3), 107.5 (Tp4), 107.0 (Tp4), 106.8 (Tp4), 85.6 (C2), 60.7 (C6), 58.7 (d, J_{PC} = 10.3, C5), 54.9 (-OMe), 13.6 (d, J_{PC} =29.7, PMe$_3$). ^{31}P NMR (MeCN-d_3, δ, 25 °C): -1.51 (J_{WP} =304, PMe$_3$). ^{19}F {^{1}H} NMR (MeCN-d_3, δ, 25 °C): -64.58 (CF$_3$). A SC-XRD study confirms the identify of this compound (SI).

For the minor isomer (**18B**), unambiguous assignment of the carbon resonances was precluded by the low intensity of signals (~ 12% of major isomer) and significant overlap with Tp resonances of **18A**. Partial Characterization of **18B** ^{1}H-NMR (MeCN-d_3, δ, 0 °C): 6.86 (1H, broad d, H4), 4.94 (1H, broad s, H2), 3.83 (1H, m, H6), 3.66 (3H, s, -OMe), 1.21 (9H, buried, PMe$_3$).

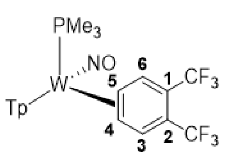
WTp(NO)(PMe$_3$)(η^2-5,6-(3-trifluoromethyl-N,N-dimethylaniline)) (19)



An oven-dried 15 mL vial was charged with **2** (0.817 g, 1.41 mmol) and 3-trifluoromethyl-N,N-dimethylaniline (3.89 g, 20.6 mmol), and the heterogeneous yellow reaction mixture was allowed to stir. After 16 h the reaction mixture had retained its heterogeneous golden-colored consistency but analysis by ^{31}P NMR confirmed the absence of **1** and the generation of a new species. The heterogeneous yellow reaction mixture was added to a solution of stirring pentane (50 mL) to precipitate out a light yellow solid. The solid was then filtered through a 30 mL fine porosity fritted disc and washed with pentane (3 x 20 mL) before the light tan powder was allowed to desiccate under active vacuum and a mass taken of the vibrant yellow solid (0.680 g**,** 70.0 %). The filtrate was collected and the pentane was distilled to re-collect the excess 3-trifluoromethyl-N,N-dimethylaniline and the recovered aromatic ligand was used in similar reaction procedures without noticeable inhibition of yield.

CV (DMA): $E_{p,a}$= - 0.16 V (NHE). IR: ν(BH) = 2483 cm^{-1}, ν(NO) = 1570 cm^{-1}. ^{1}H NMR (acetone-d_6, δ, 25 ^{o}C): 8.03 (1H, d, Tp5C), 7.96 (1H, d, Tp3/5), 7.92 (1H, d, Tp3B), 7.90 (1H, d, Tp3A), 7.88 (1H, d, Tp3/5), 7.48 (1H, d, Tp3C), 6.50 (1H, d, *J* = 5.22, H4), 6.38 (1H, t, Tp4C), 6.33 (1H, t, Tp4), 6.23 (1H, t, Tp4), 4.54 (1H, s, H2), 4.07 (1H, m, H5), 2.47 (6H, broad s, NMe_2), 2.23 (1H, d, *J* = 10.94, H6), 1.33 (9H, d, J_{PH} = 8.18, PMe_3). ^{13}C {^{1}H} NMR (acetone-d_6, δ, 25 ^{o}C): 157.8 (C1), 144.5 (Tp3/5), 142.4 (Tp3/5), 142.1 (Tp3/5), 140.8 (Tp3/5), 136.7 (Tp3/5), 136.5 (Tp3/5), 126.5 (-CF_3, q, J_{CF} = 270.6), 121.5 (C3, q, J_{CF} = 28.9), 118.2 (C4), 105.8 (overlap 2Cs, Tp4), 105.3 (Tp4), 82.6 (C2), 61.0 (C5, d, J_{PC} = 8.51), 56.3 (C6), 39.1 (NMe_2), 13.2 (d, J_{CP} = 28.7, PMe_3). ^{19}F {^{1}H} NMR (acetone-d_6, δ, 25 ^{o}C): -61.68 (s, -CF_3). ^{31}P {^{1}H} NMR (acetone-d_6, δ, 25 ^{o}C): -12.43 (J_{WP} = 308). HRMS ESI-MS (m/z, calculated (rel. intensity, %), observed (rel. intensity, %), ppm, (M + H)+: 691.1812 (84.71), 691.1819 (87.15), 692.1837 (80.03), 692.1844 (83.95), 693. 1835 (100), 693.1845 (100), 694.1877 (42.5), 694.1880 (46.17), 695.1868 (84.18), 695.1875 (87.58).

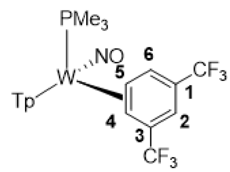
WTp(NO)(PMe$_3$)(4,5-η^2-(1,2-bistrifluoromethylbenzene)) (20)



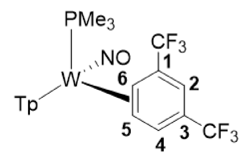
An oven-dried 15 mL vial was charged with **2** (0.608 g, 1.05 mmol) and 1,2-bis-trifluoromethylbenzene (3.02 g, 14.1 mmol), and the heterogeneous yellow reaction mixture was allowed to stir. After 16 h the reaction mixture had retained its heterogeneous golden-colored consistency but analysis by 31P NMR confirmed the absence of **1** and the generation of a new species. The heterogeneous yellow reaction mixture was added to 50 mL of stirring pentane to precipitate out a vibrant yellow solid. The solid was then filtered through a 30 mL fine porosity fritted disc and washed with pentane (3 x 20 mL) before the yellow powder was allowed to desiccate under active vacuum and a mass taken of the vibrant yellow solid (0.477 g**,** 64.0 % yield).

CV (DMA): $E_{p,a}$ = +0.45 V (NHE). IR: *ν*(BH) = 2482 cm^{-1}, *ν*(NO) = 1592 cm^{-1}. ^{1}H NMR (acetone-d_6, δ, 25 ^{o}C): 8.04 (3H, d, overlapping Tp3/5), 8.00 (1H, d, Tp3/5), 7.90 (1H, d, Tp3/5), 7.68 (1H, d, *J* = 6.87, H3), 7.55 (1H, d, *J* = 5.50, H6), 7.53 (1H, d, Tp3C), 6.40 (1H, t, Tp4A), 6.38 (1H, t, Tp4B), 6.37 (1H, t, Tp4C), 3.80 (1H, m, H5), 2.15 (1H, t, *J* = 7.60, H4), 1.71 (9H, d, J_{PC} = 8.48, PMe_3). ^{31}P {^{1}H} NMR (acetone-d_6, δ, 25^{o}C): -13.57 (J_{WP} = 302).^{19}F {^{1}H} NMR (acetone-d_6, δ, 25^{o}C): -56.6 (3F, q, $^{5}J_{FF}$ = 12.5, CF_3), -56.7 (3F, q, $^{5}J_{FF}$ = 12.5, CF_3). ^{13}C {^{1}H} NMR (acetone-d_6, δ, 25 ^{o}C): 144.5 (Tp3/5), 141.7 (Tp3/5), 141.3 (C3), 141.0 (Tp3/5), 138.5 (C6), 137.2 (Tp3/5), 136.5 (Tp3/5), 136.0 (Tp3/5), 124.1 (overlapping CF_3, q, J_{CF} = 273.4), 113.3 (C1/C2, q, J_{CF} = 30.1), 111.0 (C1/C2, q, J_{CF} = 31.2), 106.5 (Tp4), 106.4 (Tp4), 106.0 (Tp4), 60.7 (C5, d, J_{PC} = 9.5), 58.2 (C4), 13.6 (PMe_3, d, J_{PC} = 28.7). A SC-XRD study confirms the identify of this compound (SI).

WTp(NO)(PMe$_3$)(4,5-η^2-(1,3-bistrifluoromethylbenzene)) (21)



21A



21B

A 15 mL vial was charged with **2** (0.097 g, 0.167 mmol) and neat 1,3-bis(trifluoromethyl)benzene (3.17 g, 14.8 mmol) and the initially heterogeneous yellow reaction mixture was allowed to stir. After 18 h the reaction mixture was still a heterogeneous yellow but no starting material was detected by cyclic voltammetry. This mixture was then slowly added a solution of stirring hexanes (20 mL) that had been cooled to – 30 ^{o}C to generate a yellow precipitate. The precipitate was then isolated on a 15mL fine porosity fritted disc, washed with hexanes (3x 10 mL) and desiccated to yield **5**. A yellow solid was obtained (0.041 g, 34%). The filtrate was collected and the pentane was distilled to re-collect the excess aromatic ligand which was used in similar reaction procedures without noticeable inhibition of yield. This complex is isolated in an approximate 7:1 ratio of A:B.

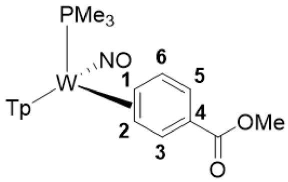
CV (DMA): $E_{p,a}$= + 0.42 V (NHE). IR: ν(BH) = 2493 cm^{-1}, ν(NO) = 1582 cm^{-1}. Characterization for **21A** ^{1}H NMR (acetone-d_6, δ, 25 ^{o}C): 8.06 (1H, d, Tp5C), 8.00 (1H, d, Tp5B), 7.95 (1H, d, Tp3B), 7.88 (1H, d, Tp3/5A), 7.71 (1H, d, Tp3/5A), 7.57 (1H, d, *J* = 4.96, H6), 7.50 (1H, d, Tp3C), 6.39 (1H, t, Tp4C), 6.36 (1H, t, Tp4B), 6.27 (1H, t, Tp4A), 6.25 (1H, broad s, H2), 3.91 (1H, m, H5), 2.30 (1H, d, *J* = 9.32, H4), 1.36 (9H, d, *J* = 8.44, PMe_3). ^{13}C {^{1}H} NMR (acetone-d_6, δ, 25 ^{o}C): 145.3 (Tp3/5A), 142.5 (Tp3/5A), 141.7 (Tp3C), 138.5 (C6), 138.0 (Tp3/5), 137.5 (Tp5B), 137.2 (Tp3/5), 128.8 (C1/C3, q, J_{CF} = 31.5), 126.3 (CF_3, q, J_{CF} = 272.1), 125.7 (CF_3, q, J_{CF} = 272.7), 116.8 (C1/C3, q, J_{CF} = 32.1), 107.5 (Tp4), 107.3 (Tp4), 106.2 (Tp4), 106.5 (H2), 62.1 (H5), 60.7 (H4, *J* = 25.0), 12.95 (d, J_{PC} = 28.7, PMe_3). ^{31}P {^{1}H} NMR (acetone-d_6, δ, 25 ^{o}C): -14.46 (J_{WP} = 289).

Partial characterization for **21B** 7.70 (1H, buried, H4), 6.49 (1H, broad s, H2), 4.33 (1H, dd, *J* = 9.3, 12.4, H4), 2.19 (1H, broad t, *J* = 9.3, H5), 1.14 (9H, d, J_{PH} = 8.50, PMe_3) . ^{31}P NMR (acetone-d_6, δ, 25 ^{o}C): -12.17.

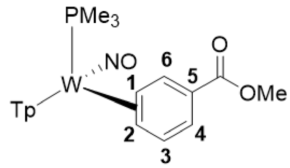
Partial characterization for **21H**: ^{1}H NMR (acetone-d_6, δ, 25 ^{o}C): 9.23 (1H, m, J_{PH} =102.1 J_{WH} = 30.8, W-H resonance), 6.01 (1H, t, Tp4). ^{31}P {^{1}H} NMR (acetone-d_6, δ, 25 ^{o}C): -2.84 (J_{WP} = 172).

^{19}F {^{1}H} NMR resonances for all isomers (acetone-d_6, δ, 25 ^{o}C): -56.9, -59.7 for **21A**, -60.0 for **21A**, -60.8 , -61.8, -62.4. Elemental Analysis for $C_{20}H_{23}BF_6N_7OPW$: Calculated: C, 33.50; H, 3.23; N, 13.67. Found: C, 33.50; H, 3.09; N, 13.54.

WTp(NO)(PMe$_3$)(η^2-1,2-methyl benzoate) (22)



22A

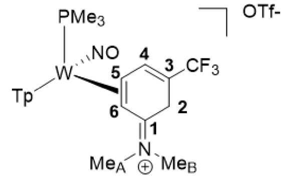


22B

A 15 mL vial was charged with **2** (1.00 g, 1.72 mmol) and trimethyl orthobenzoate (0.94 g, 5.16 mmol) followed by THF (3 mL). This homogenous mixture was stirred at room temperature for 16 h. The resulting solution had turned black over the course of the reaction. A 150 mL coarse porosity fritted disc was filled 2/3 full with silica and set in diethyl ether. The reaction solution was then loaded onto this silica column. Upon eluting with diethyl ether a green band develops on the column followed by a yellow colored band. Upon continued elution with diethyl ether (~ 700 mL total) the initial green filtrate was discarded and with continued elution the original yellow-colored band undergoes a color change to an orange colored band while on the silica column. This orange band was collected in a filter flask and all of the solvent was removed in vacuo. The resulting orange film was dissolved in a minimal amount of DCM (~ 3 mL) and added to a solution of stirring pentane (100 mL). Upon addition of the reaction mixture to the pentane solution an orange solid precipitates from solution. The resulting orange precipitant was collected on a 30 mL fine porosity fritted disc and washed with hexanes (4 x 15mL). The resulting solid was desiccated overnight, yielding **22** (0.495 g, 45% yield).

CV (DMA) $E_{p,a}$= -0.03 (NHE). IR: ν(BH)= 2480 cm^{-1}, ν(CO)= 1688 cm^{-1}, ν(NO)= 1568 cm^{-1}. ^{1}H NMR (MeCN-d_3, δ, 25 °C): 8.18 (1H, d, Tp5A, **B**), 8.13 (1H, d, J = 6.3, H3, **A**), 8.06 (1H, d, Tp5A, **A**), 7.99 (1H, d, J = 5.5, H6, **B**), 7.92 (1H, d Tp5B, **A**), 7.91 (2H, overlapping d, Tp5C for **A** and Tp5B for **B**), 7.90 (1H, d, Tp5C, **B**), 7.87 (1H, d, Tp3B, **A**), 7.86 (1H, d, Tp3B, **B**), 7.82 (2H, overlapping d, TpA3 for **A** and TpA3 for **B**), 7.35 (1H, d, TpC3, **A**), 7.34 (1H, d, TpC3, **B**), 6.96 (1H, dd, J = 9.8, 5.9, H3, **B**), 6.82 (1H, dd, J = 9.6, 4.97, H6, **A**), 6.35 (1H, t, Tp4A, **A**), 6.34 (1H, t, Tp4B, **A**), 6.33 (1H, t, Tp4A, **B**), 6.31 (1H, t, Tp4B, **B**), 6.29 (1H, t, Tp4C, **A**), 6.28 (1H, t, Tp4C, **B**), 6.14 (1H, dd, J = 9.6, 1.5, H5, **A**), 6.07 (1H, dd, J = 9.3, 1.3, H4, **B**), 4.02 (1H, m, H1, **A**), 3.87 (1H, m, H1, **B**), 3.76 (3H, s, -OMe, **A**), 3.75 (3H, s, -OMe, **B**), 2.29 (1H, m, H2, **B**), 2.23 (1H, m, H2, **A**), 1.26 (9H, d, J_{PH} = 8.53, PMe$_3$, **B**), 1.24 (9H, d, J_{PH}= 8.51, PMe$_3$, **A**). ^{13}C {^{1}H} NMR (MeCN-d_3, δ, 25 °C): 167.9 (C7**B**), 167.7 (C7**A**), 147.7 (2C, overlapping, Tp3/5**A**,**B**), 145.4 (Tp3/5**A**), 145.2 (Tp3/5**B**), 144.4 (d, J_{PC} = 2.76, C6**B**), 143.3 (2C, overlapping Tp3/5**A**,**B**), 142.1 (Tp3/5**A**), 142.1 (Tp3/5**B**), 142.0 (C3**A**), 138.1 (Tp3/5**A**), 137.4 (Tp3/5**B**), 137.0 (Tp3/5**A**), 136.9 (Tp3/5**B**), 134.4 (C3**B**), 132.9 (d , J_{PC} = 2.62, C6**A**), 129.3 (C4**A**), 129.2 (C5**B**), 115.5 (C5**A**), 113.9 (C4**B**), 107.5 (Tp4**A**), 107.4 (Tp4**B**), 107.3 (Tp4**A**), 107.2 (Tp4**B**), 107.0 (Tp4**A**), 106.7 (Tp4**B**), 66.3 (d, J_{PC} = 8.54, C1**A**), 64.6 (C2**B**), 64.0 (d, J_{PC} = 7.03, C1**B**), 62.4 (C2**A**), 51.5 (-OMe**B**), 51.5 (-OMe**A**), 13.4 (3C, d, J_{PC} = 28.89, PMe$_3$**B**), 13.32 (3C, d, J_{PC} = 28.71, PMe$_3$**B**).

WTp(NO)(PMe$_3$)(5,6-η^2-(3-trifluoromethyl-N,N-dimethyl-anilinium)]OTf (23)

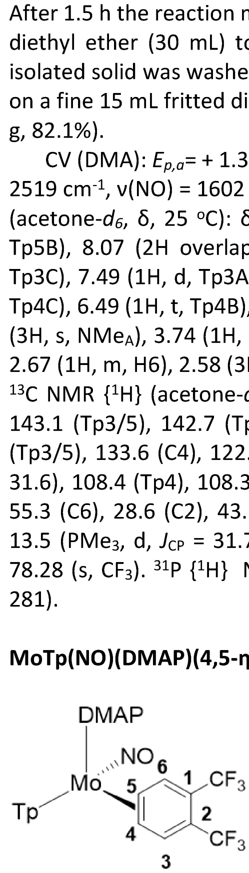


23

To an oven dried 15 mL vials added **19** (0.096 g, 0.139 mmol) and along with MeOH (~ 2 mL) to generate a heterogeneous yellow reaction mixture. This solution was allowed to cool in a -30 °C freezer over a course of 30 min before DPhAT (0.072 g, 0.225 mmol) was added to the reaction mixture at reduced temperature. After 1.5 h the reaction mixture was added to a stirring solution of diethyl ether (30 mL) to precipitate out a yellow solid and the isolated solid was washed with pentane (3 x 10 mL) after isolation on a fine 15 mL fritted disc and allowed to desiccate for 3 h (0.096 g, 82.1%).

CV (DMA): $E_{p,a}$= + 1.34 V (NHE), $E_{p,c}$ = - 1.54 V (NHE). IR: ν(BH) = 2519 cm^{-1}, ν(NO) = 1602 cm^{-1}, ν(CN iminium) = 1581 cm^{-1}. ^{1}H NMR (acetone-d_6, δ, 25 °C): δ ppm 8.22 (1H, d, Tp3/5C), 8.16 (1H, d, Tp5B), 8.07 (2H overlapping, d, Tp5A and Tp3/5), 8.03 (1H, d, Tp3C), 7.49 (1H, d, Tp3A), 7.27 (1H, broad s, Tp3/5C), 6.55 (1H, t, Tp4C), 6.49 (1H, t, Tp4B), 6.47 (1H, t, Tp4A), 4.00 (1H, m, H5), 3.80 (3H, s, NMe$_A$), 3.74 (1H, d, J = 22.4, H2), 3.47 (1H, d, J= 22.4, H2’), 2.67 (1H, m, H6), 2.58 (3H, s, NMe$_B$), 1.41 (9H, d, J_{PH} = 9.20, PMe$_3$). ^{13}C NMR {^{1}H} (acetone-d_6, δ, 25 °C): 181.7 (C1), 145.9 (Tp3/5C), 143.1 (Tp3/5), 142.7 (Tp3/5), 142.6 (Tp3C), 139.2 (Tp5B), 138.8 (Tp3/5), 133.6 (C4), 122.3 (CF$_3$, q, J_{CF} = 322.2), 113.0 (C3, q, J_{CF} = 31.6), 108.4 (Tp4), 108.3 (Tp4), 107.8 (Tp4), 61.2 (C5, J_{PC} = 12.3), 55.3 (C6), 28.6 (C2), 43.1 (NMe$_A$), 41.8 (NMe$_B$) 28.5 (C3, buried) 13.5 (PMe$_3$, d, J_{CP} = 31.7). ^{19}F {^{1}H} NMR (acetone-d_6, δ, 25 °C): -78.28 (s, CF$_3$). ^{31}P {^{1}H} NMR (acetone-d_6, δ, 25 °C): -11.16 (J_{WP} = 281).

MoTp(NO)(DMAP)(4,5-η^2-(1,2-bis(trifluoromethyl)benzene)) (24)

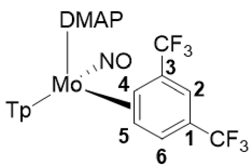


24

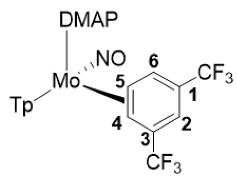
An oven-dried 15 mL vial was charged with complex **1** (0.230 g, 0.379 mmol) followed by 1,2-bis-trifluoromethylbenzene (1.95 g, 1.07 mmol) and DME (4 mL). This initially heterogeneous orange reaction mixture was capped and stirred at room temperature for 3 h. This mixture was then slowly added to a -60 °C solution of stirring pentane (50 mL) yielding an orange precipitate. The precipitate was then isolated on a 15mL fine porosity fritted disc, washed with pentane (3 x 10mL) and desiccated to yield **24**. A vibrant orange-red solid was obtained (0.074 g, 28.9%).

CV (DMA) $E_{p,a}$ = - 0.06 V (NHE). IR: ν_{BH} = 2478 cm^{-1}, ν_{NO} = 1597 cm^{-1}. ^{1}H NMR (acetone-d_6, δ, 25 °C): 8.07 (1H, d, Tp5C), 7.97 (1H, d, Tp3/5). 7.90 (1H, d, Tp3/5), 7.84 (1H, d, Tp3/5), 7.80 (broad, 2H, DMAP-2/6), 7.66 (1H, d, J = 6.50, H3),7.58 (1H, d, Tp3C), 7.29 (1H, d, J = 6.39, H6), 6.97 (1H, d, Tp3/5), 6.72 (2H, d, J = 5.97, DMAP-3/5), 6.41 (1H, t, Tp4C), 6.40 (t, 1H, Tp4), 6.14 (1H, t, Tp4), 3.68 (1H, t, J = 7.10, H5), 3.19 (1H, t, J = 7.23, H4), 3.11 (s, 6H, NMe_2). ^{13}C {^{1}H} NMR (acetone-d_6, δ, 25 °C): 155.4 (DMAP-4), 150.6 (DMAP-2/6), 142.8 (Tp3/5), 142.7 (Tp3/5), 141.8 (Tp3C), 140.8 (C3), 140.3 (C6), 137.9 (Tp5C), 137.2 (Tp3/5), 136.2 (Tp3/5), 125.6 (-CF_3, q, J_{CF} = 272.0), 125.5 (-CF_3, q, J_{CF} = 271.2), 113.5 (2C, overlapping m, C1/C2) 108.6 (DMAP-3/5), 107.2 (Tp4), 106.7 (Tp4), 106.6 (Tp4), 75.5 (C5), 73.2 (C4), 39.2 (NMe_2).^{19}F {^{1}H} NMR (acetone-d_6, 25 °C): δ ppm -58.03 (6F, s, overlapping, CF_3s). Calculated for $C_{24}H_{24}BF_6MoN_9O$: Calculated: C, 42.69; H, 3.58; N, 18.67. Found: C, 42.90; H, 3.56; N, 18.93. A SC-XRD study confirms the identify of this compound (SI).

MoTp(NO)(DMAP)(4,5-η^2-(1,3-bis(trifluoromethyl)benzene)) (25)



25A



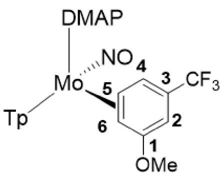
25B

A 15 mL vial was charged with complex **1** (0.500 g, 0.820 mmol) 1,3-bis-trifluoromethylbenzene (2.00 g, 9.34 mmol) and DME (5 mL). This mixture was capped and stirred at room temperature for 3 h. This mixture was then slowly added to a -60 °C solution of stirring pentane (50 mL) yielding an orange precipitate. The precipitate was then isolated on a 15mL fine porosity fritted disc, washed with pentane (3 x 10 mL) and desiccated to yield **25**. An orange solid was obtained (0.240 g, 43.2%). The complex is isolated in an approximate 3:1 ratio of A:B.

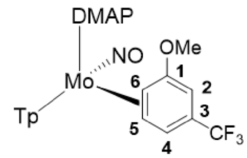
CV (DMA): $E_{p,a}$= -0.10 V (NHE). IR: ν_{BH}= 2488 cm^{-1}, ν_{NO}= 1585 cm^{-1}. Characterization of **25A** ^{1}H NMR (acetone-d_6, δ, 3 °C): 8.10 (1 H, d, Tp3/5), 7.99 (1H, d, Tp3/5), 7.88 (1H, d, Tp3/5), 7.86 (1H, d, Tp3/5), 7.71 (1H, d, Tp3C), 7.70 (1H, d, J = 6.34, H6), 6.96 (1H, d, Tp3/5), 6.76 (2H, broad, DMAP-3/5), 6.65 (1H, s, H2), 6.45 (1H, buried,Tp4), 6.41 (1H, t, Tp4), 6.11 (1H, buried, H4), 3.89 (1H, d, J = 8.48, H4), 3.19 (1H, t, J = 8.48, H5), 3.07 (6H, s, NMe_2). ^{13}C {^{1}H} NMR (acetone-d_6, δ, 3 °C): 155.1 (DMAP-4), 150.6 (DMAP-2/6), 142.8 (Tp3/5), 142.4 (Tp3/5), 141.8 (Tp3/5), 141.2 (C6), 137.9 (Tp3/5), 137.2 (Tp3/5), 136.2 (Tp3/5), 126.0 (-CF_3, q, J_{CF} = 269.0), 125.5 (-CF_3, q, J_{CF} = 274.0), 116.4 (2C, overlapping, C1/C3), 112.2 (C2), 108.6 (DMAP-3/5), 108.4 (Tp4), 106.4 (Tp4), 106.2 (Tp4), 75.9 (C5), 73.1 (C4), 39.1 (NMe_2). ^{19}F {^{1}H} NMR (acetone-d_6, δ, 25 °C): -61.52 ppm (-CF_3), -62.66 ppm (CF_3') –overlapping for both diastereomers.

Characterization of **25B** ^{1}H NMR (acetone-d_6, δ, 3 °C): 8.10 (1 H, buried, Tp3/5), 7.97 (1H, d, Tp3/5), 7.59 (1H, d, Tp3/5), 7.55 (1H, d, Tp3/5), 7.32 (1H, d, J = 5.20, H6), 6.93 (1H, d, Tp3/5), 6.71 (1H, s, H2), 6.46 (1H, buried, Tp4), 6.30 (1H, t, Tp4), 6.11 (1H, buried,Tp4), 3.72 (1H, broad t, J = 6.56, H5), 3.36 (1H, d, J = 8.20, H4), 3.11 (6H, s, -NMe_2). ^{13}C {^{1}H} NMR (acetone-d_6, δ, 25 °C): 155.1 (DMAP-4), 150.6 (DMAP-2/6), 142.5 (Tp3/5), 141.3 (Tp3/5), 140.1 (C6), 140.1 (Tp3/5), 137.4 (Tp3/5), 136.0 (Tp3/5), 135.7 (Tp3/5), 135.5 (Tp3/5), 126.0 (-CF_3, q, J_{CF} = 269.0), 125.5 (-CF_3, q, J_{CF} = 274.0), 112.1 (C2), 108.6 (DMAP-3/5), 108.4 (Tp4), 106.4 (Tp4), 106.2 (Tp4), 75.9 (C5), 73.1 (C4), 39.1 (NMe_2). A SC-XRD study confirms the identify of this compound (SI).

MoTp(NO)(DMAP)(5,6-η^2-(3-methoxytrifluorotoluene)) (26)



26B



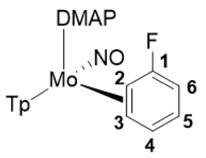
26A

A 15 mL vial was charged with complex **1** (0.217 g, 0.357 mmol) along with 3-(Trifluoromethyl)anisole (1 mL, 6.91 mmol) and DME (1 mL). This mixture was capped and stirred at room temperature for 4 h. This mixture was then loaded onto a medium 30 mL fritted disc filled with silica (~ 2 cm) that had been set in diethyl ether. The column was then eluted with diethyl ether (~ 100 mL) to elute a vibrant yellow band. The eluent was collected in a filter flask and the solvent was removed in vacuo until a minimal amount of solvent remained (< 10 mL). To this solution was added pentane (50 mL) to induce precipitation. Upon addition of pentane a vibrant yellow solid precipitates from solution. The precipitate was then isolated on a 15mL fine porosity fritted disc, washed with pentane (3 x 10 mL) and desiccated under dynamic vacuum for 3 h to yield **26**. A yellow solid was obtained (0.106 g, 46.7%). The complex is isolated as an approximate 2.5:1 ratio of A:B.

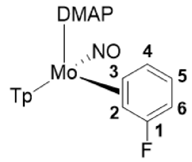
CV (DMA): $E_{p,a}$= -0.260 V. IR: ν_{BH}= 2458 cm^{-1}, ν_{NO}= 1575 cm^{-1}. Characterization of **26A:** ^{1}H NMR (acetone-d_6, δ, 25 °C): δ ppm 8.02 (1 H, d, Tp3/5), 7.94 (1H, d, Tp3/5), 7.93 (1H, d, Tp3/5), 7.85 (1H, d, Tp3/5), 7.80 (2H, broad, DMAP-2/6), 7.52 (1H, d, Tp3/5), 7.01 (1H, d, J = 6.1, H4), 6.93 (1H, d, Tp3/5), 6.63 (2H, broad d, J = 6.3 DMAP-3/5), 6.38 (1H, t overlapping with minor isomer, Tp4), 6.36 (1H, t, Tp4), 6.11 (1H, t overlapping with minor isomer, Tp4), 5.43 (1H, s, H2), 3.56 (3H, s, -OMe), 3.52 (1H, d, J = 9.1, H6), 3.19 (1H, m, H5), 3.08 (6H, s, NMe_2).^{13}C {^{1}H} NMR (acetone-d_6, 0 °C): 166.9 (C1), 155.0 (DMAP-C4), 150.6 (DMAP-C2/6), 142.5 (Tp3/5), 142.4 (Tp3/5), 141.6 (Tp3/5), 137.5 (Tp3/5), 136.9 (Tp3/5), 135.9 (Tp3/5), 126.4 (-CF_3, q, J_{CF} = 269.6), 126.1 (C4, overlapping m), 119.4 (C3, q, J_{CF} = 30.1), 108.3 (DMAP-3/5), 107.0 (Tp4), 106.4 (Tp4), 106.3 (Tp4), 85.8 (C2), 73.7 (C6), 72.8 (C5), 54.2 (-OMe), 39.1 (NMe_2). ^{19}F {^{1}H} NMR (acetone-d_6, δ, 25 °C): -60.5 (-CF_3).

Characterization of **26B** ^{1}H NMR (acetone-d_6, δ, 25 °C): 8.02 (1 H, d, Tp3/5), 7.87 (1H, d, Tp3/5), 7.84 (1H, d, Tp3/5), 7.81 (1H, d, Tp3/5), 7.80 (2H, broad overlapping with major isomer, DMAP-2/6), 7.55 (1H, buried, H4), 6.95 (1H, d, Tp3/5), 6.68 (2H, broad d, J = 6.21, DMAP-3/5), 6.38 (1H, t overlapping with major isomer, Tp4), 6.25 (1H, t,Tp4), 6.11 (1H, t overlapping with minor isomer, Tp4), 5.50 (1H, s, H2), 3.63 (1H, m, H5), 3.45 (3H, s, -OMe), 3.19 (1H, buried, H6), 3.09 (6H, s, NMe_2).^{13}C {^{1}H} NMR (acetone-d_6, δ, 0 °C): 167.3 (C1), 154.9 (DMAP-C4), 150.6 (overlapping DMAP-C2/C6), 144.2 (Tp3/5), 142.5 (Tp3/5), 142.4 (Tp3/5), 141.5 (Tp3/5), 136.8 (Tp3/5), 135.8 (Tp3/5), 126.3 (-CF_3, q, J_{CF} = 269.6), 126.1 (C4, overlapping m with major isomer), 119.1 (C3, q, J_{CF} = 29.5), 108.3 (2C, overlapping with major isomer, DMAP-3/5), 112.2 (C2), 107.0 (Tp4), 106.3 (Tp4), 105.5 (Tp4), 86.3 (C2), 75.6 (C5), 71.0 (C6), 54.5 (-OMe), 39.1 (NMe_2). ^{19}F {^{1}H} NMR (acetone-d_6, δ, 25 °C): -61.7. A SC-XRD study confirms the identify of this compound (SI).

MoTp(NO)(DMAP)(2,3-η²-(fluorobenzene)) (27)



27A

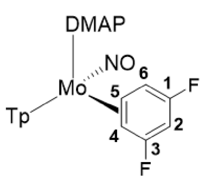


27B

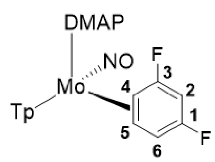
A 15 mL vial was charged with **1** (0.500 g, 0.820 mmol) and fluorobenzene (8.03 g, 83.6 mmol). This mixture was capped and stirred at room temperature for 3 h. This mixture was then slowly added to a -60 °C solution of pentane yielding a yellow precipitate. The precipitate was then isolated on a 15mL fine porosity fritted disc, washed with pentane (3 x 10 mL) and desiccated to yield **27**. A yellow solid was obtained (0.233 g, 50.8%). The complex is isolated as an approximate 1:1 ratio of A:B.

CV (DMA): $E_{p,a}$ = - 0.36 V (NHE). IR: ν_{BH}= 2481 cm^{-1}, ν_{NO}= 1574 cm^{-1}. Two coordination diastereomers **A** : **B** = 1:1. ^{1}H NMR (acetone-*d₆*, δ, -20 °C): 8.07 (2H, overlapping d, Tp3/5 for **A** and/or **B**), 7.99 (2H, overlapping d, Tp3/5 for **A** and/or **B**), 7.97 (2H, overlapping d, Tp3/5 for **A** and/or **B**), 7.94 (1H, d, Tp3/5 for **A** or **B**), 7.90 (3H, overlapping d, **Tp3/5** for **A** and/or **B**), 7.89 (4H, overlapping broad resonances, DMAP-2/6 for **A** and **B**), 7.56 (1H, d, Tp3/5), 7.54 (1H, d, Tp3/5), 6.70 (1H, m, H4**B**), 6.68 (1H, m, H4**A**), 6.66 (4H, overlapping broad resonances, DMAP-3/5 for **A** and **B**), 6.39 (2H, overlapping triplets, Tp **A** and **B**), 6.34 (1H, t, Tp**A**/**B**), 6.30 (1H, t, Tp**A**/**B**), 6.13 (2H, overlapping triplets, Tp **A** and **B),** 6.09 (1H, m, H5**A**), 6.06 (1H, m, H5**B**), 5.74 (1H, m, H6**B**), 5.70 (1H, m, H6**A**), 3.80 (1H, m, H3**B**), 3.64 (1H, t, *J* = 9.84, H2**A**), 3.35 (1H, m, H3**A**), 3.23 (1H, t, *J* = 9.90, H2**B**), 3.08 (12H, overlapping singlets, NMe for **A** and **B**). ^{19}F {^{1}H} NMR (acetone-d_6, 25 °C): -97.6 (-F**A/B**), -100.0 (-F**A/B**). Attempts at elemental analysis were thwarted by the thermal instability of this complex and its sensitivity to oxidation.

MoTp(NO)(DMAP)(4,5-η²-(1,3-difluorobenzene)) (28)



28B

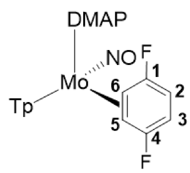


28A

A 15 mL vial was charged with **1** (0.500 g, 0.82 mmol), 1,3-difluorobenzene (1.00 g, 8.76 mmol), and DME (3 mL). The mixture was capped and stirred at room temperature for 3 h. This mixture was then slowly added to 30 mL solution of stirring pentane at -60 °C to generate a yellow precipitate. The precipitate was then isolated on a 15mL fine porosity fritted disc, washed with pentane (3x10mLs), and desiccated to yield **5**. A yellow solid was obtained (0.330 g, 70%).

CV (DMA): $E_{p,a}$ = - 0.35 V (NHE). IR: ν_{BH}= 2472 cm^{-1}, ν_{NO}= 1580 cm^{-1}. ^{1}H NMR (acetone-d_6, δ, 25 °C): Two coordination diastereomers **A** : **B** = 1:1. 8.03 (2H, overlapping doublets, Tp **A** and **B**), 7.97 (2H, overlapping doublets, Tp**A/B**), 7.94 (1H, d, Tp**A/B**), 7.92 (1H, d, Tp**A/B**), 7.90 (1H, d, Tp**A/B**), 7.86 (1H, d, Tp**A/B**), 7.82 (4H, broad, DMAPs A for **A** and **B)** 7.55 (1H, d, Tp**A)**, 7.53 (1H, d, Tp**B)**, 6.97 (2H, overlapping doublets, Tp **A** and **B**), 6.70 (2H, broad, DMAP B **A/B**), 6.64 (2H, broad, DMAP B **A/B**), 6.40 (2H, overlapping triplets, Tp **A** and **B**), 6.38 (1H, t, Tp**A/B**), 6.31 (1H, t, Tp**A/B**), 6.25 (1H, m, H6**A**), 6.13 (2H, overlapping triplets, Tp **A** and **B**), 5.83 (1H, dd, J_{HF} = 11.43, *J* = 5.79, H6**B**), 5.79 (1H, t, *J* = 10.10, H2**A/B**), 5.74 (1H, t, *J* = 9.80, H2**A/B**), 3.68 (1H, m, H5**B**), 3.53 (1H, t, *J* =9.44, H4**A**), 3.18 (1H, m H5**A**), 3.09 (1H, buried, H4**B**), 3.07 (12H, overlapping singlets, NMe_2). ^{19}F {^{1}H} NMR (acetone-d_6, δ, 25 °C): -94.9 (-F for **A/B**), -97.3 (-F for **A/B**), -125.8 (-F for **A/B**), -126.2 (-F for **A/B).** Attempts at elemental analysis were thwarted by the thermal instability of this complex and its sensitivity to oxidation.

MoTp(NO)(DMAP)(5,6-η²-(1,4-difluorobenzene)) (29)

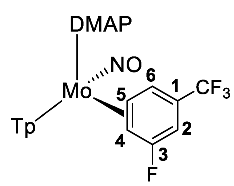


29

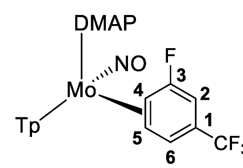
A 15 mL vial was charged with **1** (0.500 g, 0.82 mmol), 1,4-difluorobenzene (1.00g, 8.76 mmol) and 3 mLs of DME. The heterogeneous red reaction mixture was capped and stirred at room temperature for 3 h during which time it turns to a homogeneous brown/black coloration. This mixture was then slowly added to 50 mL of pentane that had been cooled to – 60 C and upon addition, a yellow precipitate forms. The yellow solid was then isolated on a 15mL fine porosity fritted disc, washed with pentane (3 x 10 mL), and desiccated under static vacuum for 16 h to yield 1**5**. (0.416 g, 87.8%).

CV (DMA) $E_{p,a}$ = - 0.21 V (NHE). IR: ν_{BH}= 2472 cm^{-1}, ν_{NO}= 1581 cm^{-1}. ^{1}H NMR (acetone-d_6, δ, 15 °C): 8.04 (1H, d, Tp5C), 7.93 (1H, d, Tp3A), 7.91 (1H, d, Tp3/5B), 7.90 (2H, broad, DMAP- 2/6), 7.87 (1H, d, Tp), 7.57 (1H, d, Tp3C), 6.99 (1H, d, Tp3/5A), 6.63 (2H, broad, DMAP B), 6.40 (1H, t, Tp4C), 6.29 (1H, t, Tp4A), 6.13 (1H, t, Tp4B), 5.59 (1H, m, H3), 5.54 (1H, m, H2), 3.74 (1H, m, H6), 3.27 (1H, m, H5), 3.07 (6H, s, NMe_2).^{13}C {^{1}H} NMR (acetone-d_6, δ, 15 °C): 165.0 (C1/C4, d, J_{CF} = 248.6), 164.9 (C1/C4, d, J_{CF} = 246.8), 155.1 (DMAP-C), 150.5 (DMAP-2/6), 142.5 (Tp3/5), 141.6 (Tp3/5), 137.7 (Tp3/5), 137.0 (Tp3/5), 135.9 (Tp3/5), 107.4 (DMAP-3/5), 107.1 (Tp4C), 106.4 (Tp4B), 106.1 (Tp4A), 95.1 (C3, dd, J_{CF} = 9.9, 26.0), 94.7 (C2, dd, J_{CF} = 9.7, 24.6), 71.0 (C6, dd, J_{CF} = 8.5, 30.1), 68.4 (C5, dd, J_{CF} = 8.4, 29.6), 39.1 (NMe_2). ^{19}F {^{1}H} NMR (acetone-d_6, δ, 25 °C): -107.3 (1F, m), -109.5 (1F, m). Attempts at elemental analysis were thwarted by the thermal instability of this complex and its sensitivity to oxidation.

MoTp(NO)(DMAP)(4,5-η²-(3-fluorobenzotrifluoride)) (30)



30B



30A

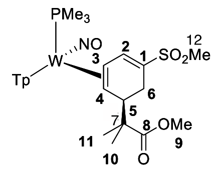
A 15 mL vial was charged with MoTp(NO)(DMAP)(η^2-2,5-dimethylfuran) (0.250 g, 0.410 mmol) and 3-fluorobenzotrifluoride (1.50 g, 9.14 mmol).[35] This mixture was capped and stirred at room temperature for 5 days. This mixture was then isolated on a 15 mL fine porosity fritted disc. The precipitate was washed with pentane (3 x 10mL) and desiccated to yield **30**. An orange solid was obtained (0.135 g, 48.0%). Initially the ratio of **30A : 30B** is approximately 9:1 due to what we believe is selective precipitation that results in a high population of **30A** in the solid state under the precipitation conditions described. Over time (6 h) a 1:1 equilibrium is established between the two coordination diastereomers.

CV (DMA): $E_{p,a}$= - 0.05 V (NHE). IR: ν_{BH}= 2490 cm^{-1}, ν_{NO}= 1590 cm^{-1}. Two coordination diastereomers A : B = 1:1 after 6 hours in solution. Characterization for **30A** ^{1}H NMR (acetone-d_6, δ, 25 ˚C): A (initial major): 8.05 (1H, d, Tp5C), 7.96 (1H, d, Tp5A), 7.88 (1H, d, Tp5B), 7.85 (1H, d, Tp3A), 7.80 (2H, broad, DMAP-2/6), 7.58 (1H, d, Tp3C), 7.19 (1H, d, J = 6.25, H6), 6.96 (1H, d, Tp3B), 6.65 (2H, d, J= 6.53, DMAP-3/5), 6.40 (1H, t, Tp4C), 6.38 (1H, t, Tp4A), 6.13 (1H, t, Tp4B), 5.79 (1H, dt, J= 11.71, 1.26, H2), 3.65 (1H, t, J= 9.66, H4), 3.24 (1H, m, H5), 3.08 (6H, s, NMe^2). ^{13}C {^{1}H} NMR (acetone-d_6, δ, 25 ºC): 169.4 (C3), 155.3 (DMAP 4), 142.7 (Tp3B), 142.6 (Tp3A), 141.7 (Tp3C), 137.7 (Tp5C), 137.2 (Tp5A), 136.1 (Tp5B), 131.1 (H6), 108.4 (DMAP-3/5), 107.2 (Tp4C), 106.6 (Tp4), 106.5 (Tp4), 91.6 (H2), 74.1 (H5), 70.4 (H4), 39.1 (NMe$_2$). ^{19}F NMR {^{1}H} (acetone-d_6, δ, 25 ºC): δ -62.18 (3F, -CF$_3$), -99.54 (1F, F).

Characterization for **30B** ^{1}H NMR (acetone-d_6, δ, 25 ˚C): B (initial minor): 8.07 (1H, d, Tp3/5), 8.05 (1H, d, Tp3/5), 7.97 (1H, d, Tp3/5), 7.84 (1H, d, Tp3/5), 7.86 (2H, broad, DMAP-2/6), 7.56 (1H, d, Tp3/5), 7.34 (1H, d, Tp3/5), 6.82 (1H, d, J= 5.76, H6), 6.71 (2H, d, J = 6.48, DMAP-3/5), 6.40 (1H, t, Tp4), 6.31 (1H, t, Tp4), 6.14 (1H, t, Tp4), 5.84 (1H, dt, J = 11.67, 1.17, H2), 3.74 (1H, m, H5), 3.19 (1H, t, J= 8.49 , H4), 3.10 (6H, s, NMes). ^{19}F {^{1}H} NMR (acetone-d_6, δ, 25 ºC): -62.2 (3F, -CF$_3$), -97.05 (-F). Calculated for $C_{23}H_{24}BF_4MoN_9O$: Calculated: C, 44.18; H, 3.87; N, 20.16. Found: C, 43.94; H, 4.11; N, 20.41.

WTp(NO)(PMe$_3$)(η^2-3,4-(methyl-2-methyl-2-(5-(methylsulfonyl)cyclohexa-2,4-dien-1-yl)propanoate)) 31.

Compound **16** (1.50 g, 2.27 mmol) and MeCN were combined in a test a tube to form an orange heterogenous solution. The heterogenous mixture was cooled to 0 °C for 15 min. 1 M HOTf/MeCN (4.32 mL, 4.32 mmol, -30 °C) was added to the reaction via syringe. Upon addition, the reaction became a dark red, homogeneous mixture. After 2 min, 1-methoxy-2-methyl-1-(trimethylsiloxy)propene (1.98 g, 2.31 mL, 11.4 mmol, -30 °C) was added to the reaction mixture. The reaction was stirred for 16 h at 0 °C. Et$_3$N (2.30 g, 3.17 mL, 22.7 mmol, -30 °C) was then added to the reaction. The reaction was removed from the box and evaporated to dryness to form a dark brown oil. A 60 mL medium porosity fine frit was filled ¾ full with silica and set in ether. Minimal acetone was used to pick the reaction oil up and loaded onto the column. Hexanes (100 mL) was eluted through the column, followed by diethyl ether (200 mL) followed by ethyl acetate (250 mL). The ethyl acetate eluted a light brown band, which was evaporated to dryness, redissolved in minimal DCM, then added to 30 mL stirring pentane. An off-white solid precipitated out of the pentane and was collected on a 30 mL fine porosity fitted disc washed with diethyl ether (2 x 10 mL) and hexanes (2 x 15 mL), then desiccated overnight to yield **33** (0.935 g, 1.23 mmol, 54.0%).



CV (DMA): $E_{p,a}$ = +0.74 V (NHE). IR: ν(NO) = 1551 cm^{-1}, ν(SO) = 1409 cm^{-1}. ^{1}H NMR (MeCN-d_3, δ, 25 ºC): 8.07 (1H, d, Tp3A), 8.04 (1H, d, Tp3B), 7.86 (2H, m, Tp5B and Tp5C), 7.80 (1H, d, Tp5A), 7.57 (1H, dd, J = 5.30, 2.82, H2), 7.50 (1H, d, Tp3C), 6.36 (1H, t, Tp4B), 6.32 (1H, t, Tp4A), 6.31 (1H, t, Tp4C) 3.49 (1H, d, J = 8.9, H5), 3.24 (3H, s, H9), 3.01 (1H, m, H3), 2.89 (3H, s, H12), 2.80 (1H, dd, J = 17.39, 9.29, H6y), 2.39 (1H, d, J = 17.39, H6x), 1.25 (3H, s, H10/H11), 1.21 (9H, d, J_{PH} = 8.57, PMe$_3$), 1.09 (3H, s, H10/H11), 0.97 (1H, d, J = 9.85, H4). ^{13}C {^{1}H} NMR (MeCN-d_3, δ, 25 ºC): 179.2 (C8), 145.0 (d, J_{PC} = 2.47, C2), 144.5 (Tp3A), 142.3 (Tp3B), 142.1 (Tp3C), 138.1 (TpB or C5), 137.5 (Tp5A), 137.4 (TpB or C5), 127.7 (C1), 107.6 (Tp4B), 107.3 (Tp4C), 106.7 (Tp4A), 55.0 (C4), 52.3 (C7), 51.6 (C9), 50.0 (d, J_{PC} = 8.81, C3), 44.8 (C12), 43.3 (C5), 23.8 (C10 or 11), 22.9 (C6), 21.9 (C10 or C11), 13.6 (3C, d, J_{PC} = 29.24, PMe$_3$) Anal. Calcd for $C_{24}H_{37}BN_7O_5PSW$: C, 37.87; H, 4.90; N, 12.88. Found: C, 38.11; H, 4.79; N, 12.92. A SC-XRD study confirms the identify of this compound (SI).

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Notes:
The authors declare no competing financial interest.

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Supporting Information Available:

^{1}H and ^{13}C NMR spectra of selected compounds, DFT calculations, and crystallographic information for compounds **16**, **18A**, **20**, **24**, **25A**, **26B**, **33**. This material is available free of charge via the Internet at http://pubs.acs.org. . CCDC 1997383-1997389 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures

References.

1. Liebov, B. K.; Harman, W. D., Group 6 Dihapto-Coordinate Dearomatization Agents for Organic Synthesis. *Chem. Rev.* **2017,** *117*, 13721-13755.
2. Keane, J. M.; Harman, W. D., A New Generation of π-Basic Dearomatization Agents. *Organometallics* **2005,** *24*, 1786-1798.
3. Harman, W. D., The Activation of Aromatic Molecules with Pentaammineosmium(II). *Chem. Rev.* **1997,** *97*, 1953-1978.
4. Lis, E. C.; Salomon, R. J.; Sabat, M.; Myers, W. H.; Harman, W. D., Synthesis of 1-Oxadecalins from Anisole Promoted by Tungsten. *J. Am. Chem. Soc.* **2008,** *130*, 12472-12476.
5. Kolis, S. P.; Kopach, M. E.; Liu, R.; Harman, W. D., Osmium-Promoted Electrophilic Substitution of Anisoles: A Versatile New Method for the Incorporation of Carbon Substituents. *J. Org. Chem.* **1997,** *62*, 130.
6. Kopach, M. E.; Harman, W. D., The Osmium-Promoted [4+2] Cycloaddition Reaction of Anisole and Characterization of the h^2-4H-Anisolium Intermediate. *J. Org. Chem.* **1994,** *59*, 6506-6507.
7. Kopach, M. E.; Gonzalez, J.; Harman, W. D., Electrophilic substitutions on .eta.2-coordinated arenes: an unprecedented Michael addition for phenol and aniline. *J. Am. Chem. Soc.* **1991,** *113*, 8972-8973.
8. Todd, M. A.; Grachan, M. L.; Sabat, M.; Myers, W. H.; Harman, W. D., Common Electrophilic Addition Reactions at the Phenol Ring: The Chemistry of TpW(NO)(PMe3)(η2-phenol). *Organometallics* **2006,** *25*, 3948-3954.
9. Todd, M. A.; Sabat, M.; Myers, W. H.; Smith, T. M.; Harman, W. D., Stereoselective Umpolung Tandem Addition of Heteroatoms to Phenol. *J. Am. Chem. Soc.* **2008,** *130*, 6906-6907.
10. Gonzalez, J.; Sabat, M.; Harman, W. D., A Novel Dearomatization of Anilines via Complexation to Pentaammineosmium(II): Synthesis of Highly Functionalized 3-Aminocyclohexenes from Anilines. *J. Am. Chem. Soc.* **1993,** *115*, 8857.
11. Salomon, R. J.; Todd, M. A.; Sabat, M.; Myers, W. H.; Harman, W. D., Single and Double Electrophilic Addition Reactions to the Aniline Ring Promoted by a Tungsten π-Base. *Organometallics* **2010,** *29*, 707-709.
12. Wilson, K. B.; Myers, J. T.; Nedzbala, H. S.; Combee, L. A.; Sabat, M.; Harman, W. D., Sequential Tandem Addition to a Tungsten–Trifluorotoluene Complex: A Versatile Method for the Preparation of Highly Functionalized Trifluoromethylated Cyclohexenes. *J. Am. Chem. Soc.* **2017,** *139*, 11401-11412.
13. Shivokevich, P. J.; Myers, J. T.; Smith, J. A.; Pienkos, J. A.; Dakermanji, S. J.; Pert, E. K.; Welch, K. D.; Trindle, C. O.; Harman, W. D., Enantioenriched Molybdenum Dearomatization: Dissociative Substitution with Configurational Stability. *Organometallics* **2018,** *37*, 4446-4456.
14. Myers, J. T.; Smith, J. A.; Dakermanji, S. J.; Wilde, J. H.; Wilson, K. B.; Shivokevich, P. J.; Harman, W. D., Molybdenum(0) Dihapto-Coordination of Benzene and Trifluorotoluene: The Stabilizing and Chemo-Directing Influence of a CF_3 Group. *J. Am. Chem. Soc.* **2017,** *139*, 11392-11400.
15. Harman, W. D.; Sekine, M.; Taube, H., Substituent Effects on η^2-Coordinated Arene Complexes of Pentaammineosmium(II). *J. Am. Chem. Soc.* **1988,** *110*, 5725.
16. Fleming, F. F.; Yao, L.; Ravikumar, P. C.; Funk, L.; Shook, B. C., Nitrile-Containing Pharmaceuticals: Efficacious Roles of the Nitrile Pharmacophore. *Journal of Medicinal Chemistry* **2010,** *53*, 7902-7917.
17. Beaumont, K.; Webster, R.; Gardner, I.; Dack, K., Design of ester prodrugs to enhance oral absorption of poorly permeable compounds: challenges to the discovery scientist. *Curr. Drug Metab.* **2003,** *4* (6), 461-85.
18. Chen, X.; Hussain, S.; Parveen, S.; Zhang, S.; Yang, Y.; Zhu, C., Sulfonyl group-containing compounds in the design of potential drugs for the treatment of diabetes and its complications. *Curr. Med. Chem.* **2012,** *19*, 3578-604.
19. Zhou, Y.; Wang, J.; Gu, Z.; Wang, S.; Zhu, W.; Aceña, J. L.; Soloshonok, V. A.; Izawa, K.; Liu, H., Next Generation of Fluorine-Containing Pharmaceuticals, Compounds Currently in Phase II–III Clinical Trials of Major Pharmaceutical Companies: New Structural Trends and Therapeutic Areas. *Chemical Reviews* **2016,** *116*, 422-518.
20. Graham, P. M.; Meiere, S. H.; Sabat, M.; Harman, W. D., Dearomatization of Benzene, Deamidization of N,N-Dimethylformamide, and a Versatile New Tungsten π Base. *Organometallics* **2003,** *22*, 4364-4366.
21. Lis, E. C.; Delafuente, D. A.; Lin, Y.; Mocella, C. J.; Todd, M. A.; Liu, W.; Sabat, M.; Myers, W. H.; Harman, W. D., The Uncommon Reactivity of Dihapto-Coordinated Nitrile, Ketone, and Alkene Ligands When Bound to a Powerful π-Base. *Organometallics* **2006,** *25*, 5051-5058.
22. Welch, K. D.; Harrison, D. P.; Lis, E. C.; Liu, W.; Salomon, R. J.; Harman, W. D.; Myers, W. H., Large-Scale Syntheses of Several Synthons to the Dearomatization Agent {TpW(NO)(PMe3)} and Convenient Spectroscopic Tools for Product Analysis. *Organometallics* **2007,** *26*, 2791-2794.
23. Smith, J. A.; Shouton, A.; Ess, D.; Harman, W. D., PBu_3 study *submitted for publication*.
24. Sheppard, W. A., m-TRIFLUOROMETHYL-N,N-DIMETHYLANILINE. *Organic Syntheses* **1969,** *49*, 111-113.
25. Wang, J.; Sánchez-Roselló, M.; Aceña, J. L.; del Pozo, C.; Sorochinsky, A. E.; Fustero, S.; Soloshonok, V. A.; Liu, H., Fluorine in Pharmaceutical Industry: Fluorine-Containing Drugs Introduced to the Market in the Last Decade (2001–2011). *Chemical Reviews* **2014,** *114* (4), 2432-2506.
26. Liu, W.; Welch, K.; Trindle, C. O.; Sabat, M.; Myers, W. H.; Harman, W. D., Facile Intermolecular Aryl-F Bond Cleavage in the Presence of Aryl C-H Bonds: Is the eta-2-Arene Intermediate Bypassed? *Organometallics* **2007,** *26*, 2589-2597.
27. Keane, J. M.; Chordia, M. D.; Mocella, C. J.; Sabat, M.; Trindle, C. O.; Harman, W. D., Transition Metal-Stabilized Arenium Cations: Protonation of Arenes Dihapto-Coordinated to π-Basic Metal Fragments. *J. Am. Chem. Soc.* **2004,** *126*, 6806-6815.
28. Carbo, J. J.; Eisenstein, O.; Higgitt, C. L.; Klahn, A. H.; Maseras, F.; Oelckers, B.; Perutz, R. N., The reaction of the unsaturated rhenium fragment {Re(η^5-C_5Me_5)(CO)$_2$} with 1,4-difluorobenzene. Thermal intramolecular conversion of a rhenium (difluorophenyl)(hydride) to Re(η^2-$C_6H_4F_2$) and a [1,4]-metallotropic shift. *J. Chem. Soc., Dalton Trans.* **2001,**, 1452-1461.
29. Ladogana, S.; Dobson, G. R.; Smit, J. P., Bonding of halogenated arenes in photogenerated (arene)M(CO)$_5$ complexes (M = Cr, Mo, W). *Inorg. Chim. Acta* **1998,** *278*, 202-208.
30. Bosque, R.; Clot, E.; Fantacci, S.; Maseras, F.; Eisenstein, O.; Perutz, R. N.; Renkema, K. B.; Caulton, K. G., Inertness of the Aryl−F Bond toward Oxidative Addition to Osmium and Rhodium Complexes: Thermodynamic or Kinetic Origin? *J. Am. Chem. Soc.* **1998,** *120*, 12634-12640.
31. Reinhold, M.; McGrady, J. E.; Perutz, R. N., A Comparison of C−F and C−H Bond Activation by Zerovalent Ni and Pt: A Density Functional Study. *J. Am. Chem. Soc.* **2004,** *126* , 5268-5276.
32. Clot, E.; Oelckers, B.; Klahn, A. H.; Eisenstein, O.; Perutz, R. N., cis–trans Isomerisation of CpRe(CO)$_2$(H)(ArF) (ArF = $C_6F_nH_{5-n}$; n = 0–5) is the rate determining step in C–H activation of fluoroarenes: a DFT study. *Dalton Transactions* **2003**, 4065-4074.
33. Clot, E.; Eisenstein, O.; Jasim, N.; Macgregor, S. A.; McGrady, J. E.; Perutz, R. N., C−F and C−H Bond Activation of Fluorobenzenes and Fluoropyridines at Transition Metal Centers: How Fluorine Tips the Scales. *Accounts of Chemical Research* **2011,** *44*, 333-348.
34. Johnson, S. A.; Mroz, N. M.; Valdizon, R.; Murray, S., Characterization of intermediates in the C-F activation of tetrafluorobenzenes using a reactive Ni(PEt_3)$_2$ synthon: combined computational and experimental investigation. *Organometallics* **2011,** *30*, 441-457.
35. Myers, J. T.; Dakermanji, S. J.; Chastanet, T. R.; Shivokevich, P. J.; Strausberg, L. J.; Sabat, M.; Harman, W. D., 4-(Dimethylamino)pyridine (DMAP) as an Acid-Modulated Donor Ligand for PAH Dearomatization *Organometallics* **2017,** *36*, 543-555.
36. Harman, W. D.; Sekine, M.; Taube, H., Redox-promoted linkage isomerizations of aldehydes and ketones on pentaammineosmium. *J. Am. Chem. Soc.* **1988,** *110*, 2439-2445.
37. Dakermanji, S. J.; Smith, J. A.; Westendorff, K. S.; Pert, E. K.; Chung, A. D.; Myers, J. T.; Welch, K. D.; Dickie, D. A.; Harman, W. D., Electron-Transfer Chain Catalysis of η^2-Arene, η^2-Alkene, and η2-Ketone Exchange on Molybdenum. *ACS Catalysis* **2019,** *9*, 11274-11287.

38. Graham, P. M.; Mocella, C. J.; Sabat, M.; Harman, W. D., Dihapto-Coordinated Amide, Ester, and Aldehyde Complexes and Their Role in Decarbonylation. *Organometallics* **2005,** *24*, 911-919.

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