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Molybdenum-Promoted Dearomatization of Pyridines

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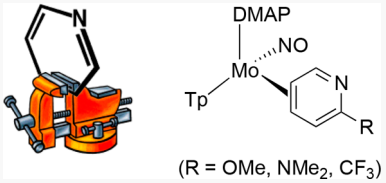
ABSTRACT: A second-row transition metal complex {MoTp(NO)(DMAP)} (DMAP = 4-(dimethylamino)pyridine; Tp = tris(pyrazolyl)borate) is shown to form dihapto-coordinate complexes with a range of substituted pyridines bearing both electron-withdrawing and electron-donating substituents. Subsequent reactivity of the pyridine ligand is demonstrated by protonation and nucleophilic addition reactions.

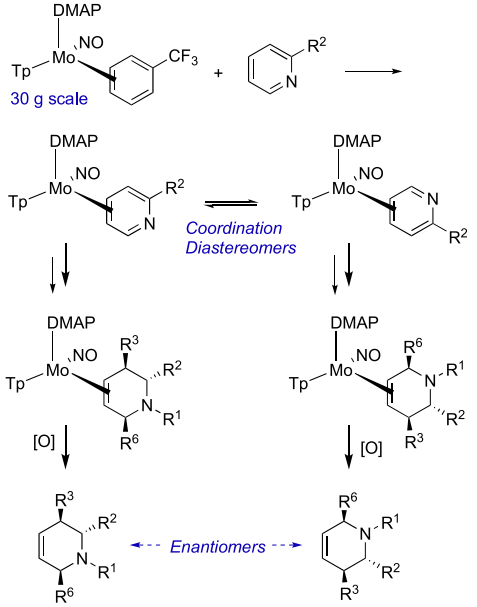


INTRODUCTION

The coordination of benzene by a transition metal across two carbons (η^2) profoundly affects the chemical reactivity of the aromatic ligand. Such action provides access to a wide range of novel organic transformations for the bound aromatic.[1−4] The present study originated from an interest to develop a similar synthetic methodology for η^2-pyridine species. Nitrogen-bound pyridine complexes are ubiquitous in the literature, but other coordination modes are far less common.[5−14] Especially unusual are dihapto-coordinate pyridine complexes, although several examples are known for heavy metals.[8−15] In particular, the tungsten complex [WTp(NO)(PMe_3)(η^2-N-acetylpyridinium)]$^+$ has been shown to undergo an extensive array of pyridine-based reactions leading to tetrahydropyridines. Limited chemistry with η^2-pyridines bearing electron-donating substituents has also been reported.[16−22]

Known second-row η^2-pyridine complexes have tended to involve nitrogen (C,N-η^2).[23,24] However, given the chemical similarities of the {WTp(NO)(PMe_3)} and {MoTp(NO)(DMAP)} systems (DMAP = 4-(dimethylamino)pyridine; Tp = tris(pyrazolyl)borate),[25] we anticipated that C,C-η^2 bound pyridine complexes might be accessible for the latter system. This publication details the syntheses and a preliminary survey of ligand-centered reactivity for pyridine complexes of the form MoTp(NO)(DMAP)(C,C-η^2-pyridine). The ultimate goal of this study is to develop new synthetic routes from pyridines to functionalized tetrahydropyridines (THPs) via a sequence of molybdenum-directed addition reactions (Scheme 1). These THPs could serve as useful precursors for novel piperidine-based drug candidates.[20,21] However, given that MoTp(NO)(DMAP)(η^2-benzene) is substantially less stable ($t_{1/2}$ ∼ 30 s in solution at 25 °C) than the analogous tungsten complex ($t_{1/2}$ ∼ 1 h),[25] it was uncertain whether such dihapto-coordinate molybdenum pyridine complexes, with this or any other second-row metal, would be amenable to isolation and subsequent organic transformations.

Scheme 1. Synthesis of Tetrahydropyridines from Pyridine via Metal-Promoted Dearomatization



RESULTS

Since nitrogen coordination could preempt the desired dihapto-coordination, various pyridines, in which either the 2-position or nitrogen was substituted, were tested as possible ligands for {MoTp(NO)(DMAP)} (Figure 1). Owing to the ability of sodium to reduce organic pyridines, Mo(0) pyridine

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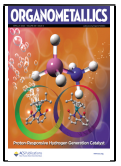

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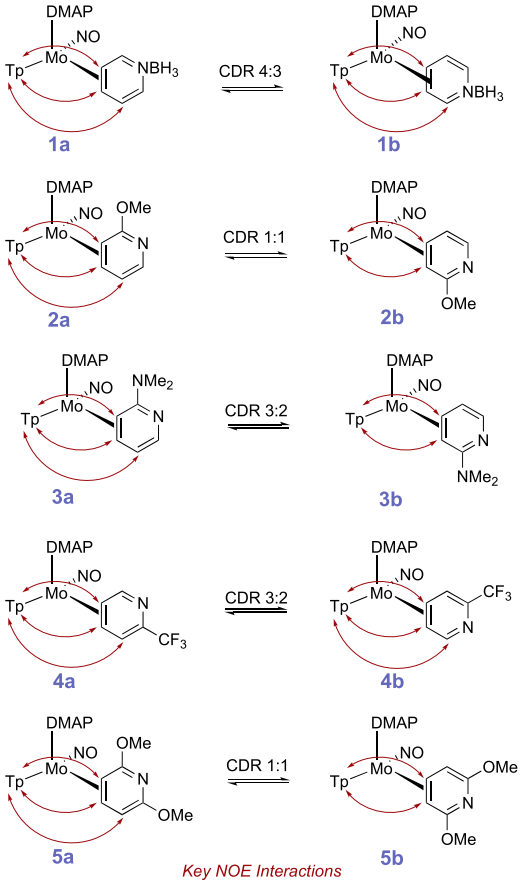

Figure 1. η^2-Molybdenum pyridine complexes in equilibrium coordination diastereomer ratio (cdr) and assignment of stereochemistry via NOE interactions.

complexes cannot be formed cleanly via direct reduction of MoTp(NO)(DMAP)I in a pyridine solution. Instead, the precursor complex MoTp(NO)(DMAP)(η^2-PhCF$_3$) was first prepared[25] (30 g scale) and then allowed to undergo ligand exchange in a THF solution of pyridine borane (**1a**/**1b**), 2-methoxypyridine (**2a**/**2b**), 2-(dimethylamino)pyridine (**3a**/**3b**), 2-(trifluoromethyl)pyridine (**4a**/**4b**), or 2,6-dimethoxypyridine (**5a**/**5b**). Complexes **1**−**5** are all formed as a thermodynamic mixture of coordination diastereomers (Figure 1), differing by which face of the prochiral ligand is coordinated. All compounds were prepared cleanly with coordination diastereomer ratios (cdr) ranging from 1:1 to 3:2, with the exception of the pyridine-borane complex.[26] Coordination stereo- and regiochemistry was determined by 1D and 2D ^{1}H NMR techniques. The protons attached to the metal-bound carbons are significantly more shielded than those in the free ligand due to the influence of the metal. Protons H4 and H5 in complex **4a**, for example, have upfield signals at 3.68 and 3.11 ppm, respectively. Furthermore, these protons have characteristic NOE correlations with a proton of the Tp pyrazole ring trans to the NO. A third NOE correlation is also sometimes present with the "allylic" pyridine proton, away from the DMAP ligand, and a pyrazole ring proton trans to the DMAP (complexes **1a**−**5a**; **1b**, **4b**). These NOESY data, in conjunction with COSY correlations, allowed unambiguous assignment of relative stereochemistries for **1**−**5**.[15]

An ORTEP diagram is provided for the SC-XRD for complex **4a** (Figure 2), which confirms coordination across C4

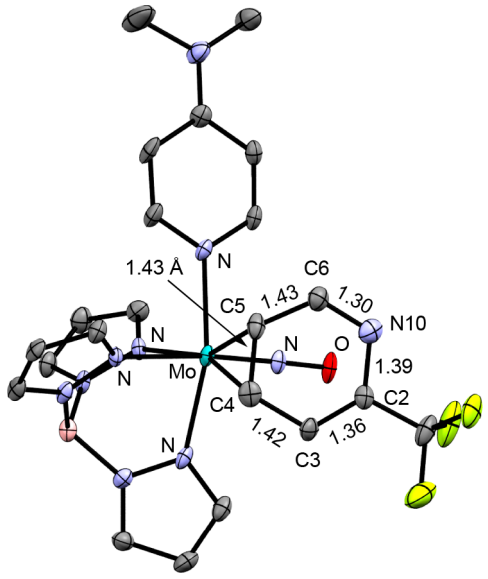

Figure 2. ORTEP of the solid-state structure for the trifluoropicoline complex **4a**, showing significant dearomatization. Only one of the two chemically equivalent but crystallographically distinct units are shown. Hydrogen atoms omitted for clarity.

and C5. The C4−C5 bond length has been increased to an average of 1.43 Å (cf. 1.40 (CC), 1.34 (CN) free ligand, Å). Further, expanded C3−C4 (1.42 Å) and C2−N (1.39 Å) bonds and contracted C2−C3 (1.36 Å) and N−C6 (1.30 Å) bonds indicate significant dearomatization.

Cyclic voltammograms of complexes **1**−**5** revealed $E_{p,a}$ values in the range of +0.08 V to −0.45 V (Table 1). As

Table 1. Cyclic Voltammetry and IR Data for Neutral Molybdenum Pyridine Complexes[a]

compound	$E_{p,a}$ (V)	ν_{NO} (cm^{-1})
5	−0.38	1567
3	−0.45	1573
2	−0.27	1577
4	+0.08	1584
1	+0.05	1607
6	+0.53	1601
7	+0.44	1591
8	+0.83	1623

[a]V, NHE @ 100 mV/s in CH$_3$CN.

anticipated, complexes with more electron-rich pyridine ligands (e.g., **2**, **3**, **5**) have lower $E_{p,a}$ values and are more readily oxidized. Conversely, the NO stretching frequencies are higher for the more electron-deficient pyridine complexes (e.g., **1**, **4**), indicating these ligands are more π-acidic. In cases where comparative data are available, each of these $E_{p,a}$'s was found to be several hundred millivolts more negative than for the analogous tungsten complexes,[16,27] which indicates that the molybdenum complexes are significantly more sensitive to oxidation. This observation is consistent with the trend noted previously with the related η^2-PhCF$_3$ and η^2-napthalene complexes of these metals.[15,25,28]

Several other pyridines were also screened, including unsubstituted pyridine, 2-picoline, 3-picoline, 4-picoline, 2-ethylpyridine, and 2-isopropylpyridine, all of which coordinated through nitrogen, as evidenced by a chemically reversible

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couple around $E_{1/2}$ = −0.9 V.[27] Of note, the reaction of bipy (2,2′-bipyridine) and MoTp(NO)(DMAP)(η^2-PhCF$_3$) produces a complex (**28**) that differs significantly in appearance (deep magenta) from the other pyridine complexes (**1**−**5**, yellow-orange). Electrochemical data indicate a complex that is more reducing ($E_{p,a}$ = −0.42 V, NHE), and H NMR data fail to show any upfield ring-protons. These data suggest a complex in which both the bipy and the Tp are bound κ^2-N,N. This structure was confirmed by SC-XRD (**28**; Figure 3). Inspection of the unit cell packing for **28** does not reveal any H-bonding or π stacking interactions that could stabilize the uncoordinated pyrazole ring.

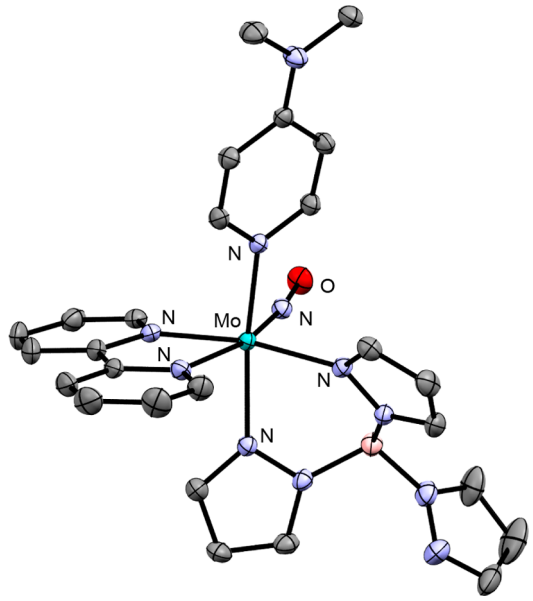
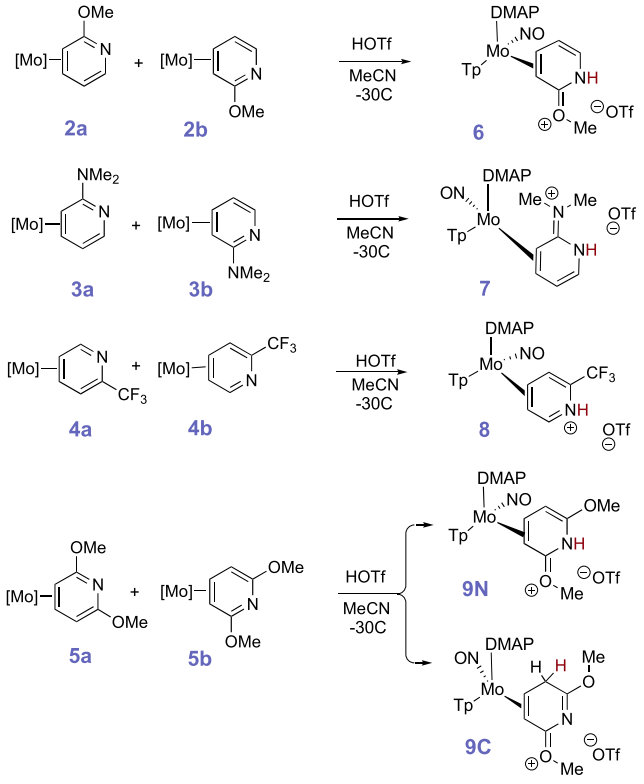


Figure 3. ORTEP diagram (50% ellipsoids) of the solid state structure determination of Mo(κ^2-Tp)(NO)(κ^2-bpy) (**28**). Solvent molecules, H atoms, and noncoordinating bpy omitted for clarity.

Attempted exchanges of MoTp(NO)(DMAP)(η^2-PhCF$_3$) with pyridinium triflate and methylpyridinum triflate were unsuccessful, leading only to oxidation. 2-Chloropyridine, 2-fluoropyridine, and 2-hydroxypyridine also resulted in apparent oxidation of the molybdenum, as evidenced by lack of ^{1}H NMR signals, as well as cyclic voltammetric data inconsistent with either η^2 or κN coordination.

Initial investigations of the reactivity of the dihapto-coordinate pyridine complexes focused on protonation. These molybdenum complexes are highly susceptible to acid oxidation,[29] and thus *strong* acid and low temperatures are required to ensure complete and irreversible protonation at nitrogen. Once protonated in this manner, the Mo(I)/Mo(0) reduction potential is shifted dramatically positive (vide infra), minimizing the chance of metal oxidation. Thus, the complexes of 2-methoxypyridine, 2-(dimethylamino)pyridine, 2-(trifluoromethyl)pyridine, and 2,6-dimethoxypyridine protonate at nitrogen using 0.25 M HOTf in MeCN at −30 °C, as shown in Scheme 2 to yield **6**, **7**, **8**, and **9N**, respectively. Attempts to protonate at ambient temperature resulted in immediate oxidation of the metal. Cyclic voltammetry of these N-protonated complexes revealed $E_{p,a}$ values shifted significantly positive (∼800 mV) from those of the neutral precursors (see Table 1). In addition to protonation at nitrogen (**9N**), the 2,6-dimethoxypyridine complex was found

Scheme 2. Nitrogen and Carbon Protonation of Pyridine Complexes



to protonate at carbon to produce complex **9C**, analogous to the chemistry of the related tungsten system.[27] A set of diastereotopic methylene protons with a coupling constant of 22.5 Hz was evident in the ^{1}H NMR spectrum of **9C**. The ratio of carbon protonation to nitrogen protonation in the precipitated solid was 3:1. Significantly, all of the protonated complexes (**6**−**9**) could be isolated as single coordination diastereomers, and recovered in moderate yield (30−50%) through selective precipitation. To the extent that this selectivity involves isomerization,[30] we believe the process likely occurs through the action of an undefined base, which yields the deprotonated form of the η^2-pyridinium complex (Scheme 3), where backbonding interactions are weaker. Whether the face-flip occurs through a sigma complex or oxidative addition intermediate, weaker backbonding in the neutral complex is expected to facilitate this isomerization.[31] Subsequent reactions of these protonated complexes with nucleophiles (e.g., NaCN, MeMgBr, lithium dimethylmalonate) returned only starting material or deprotonated product.

Complexes **2**−**4** could also be methylated using MeOTf in MeCN (complex **5** was oxidized under these conditions), but once in their methylated forms, interconversion of diastereomers was not thermally accessible, owing to the significantly enhanced backbonding interaction between the molybdenum and η^2-pyridinium ligand (Scheme 3).[16,31] Further, separation by chromatography or solubility differences was unsuccessful, making these derivatives impractical for organic modifications.

Fortuitously, it was discovered that stirring the *neutral* 2-(trifluoromethyl)pyridine complex **4** in MeCN for 2 h permits facile isolation of a single coordination diastereomer (**4a**) in 70% percent yield. In this case, the driving force for the isomerization is the lower solubility of **4a** compared to **4b** in acetonitrile. Once **4a** is isolated in solid form (SICKUS

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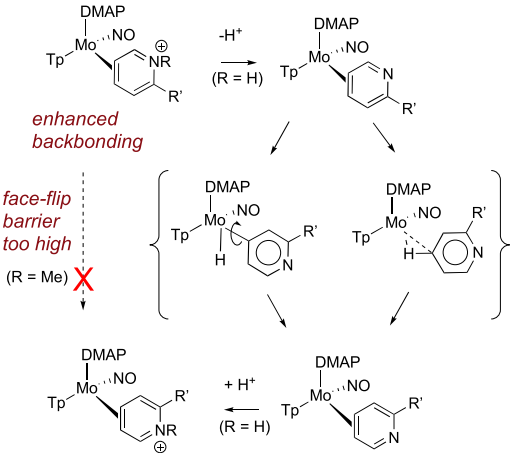
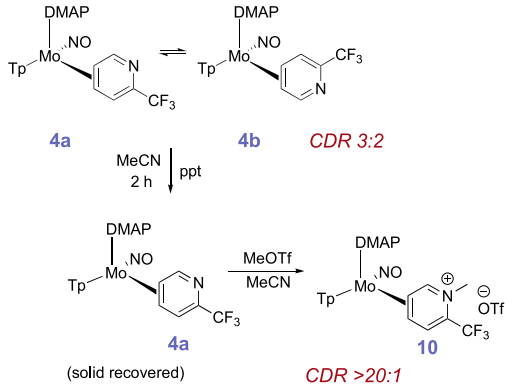
Scheme 3. Intramolecular Face-Flip Isomerization for η^2-Pyridinium Complexes[a]



[a]**6**–**8**; R = H; R′ = OMe, NMe_2, CF_3.

method),[32] it is reintroduced into solution containing methyl triflate. Methylation occurs rapidly, pre-empting the reformation of the **4a**/**4b** equilibrium. The electron-withdrawing trifluoromethyl substituent also appeared to make the complex more resistant to oxidation than the analogues bearing electron-donating groups. Thus, this complex was selected as a model for more thorough exploration of organic reactivity (Scheme 4). Treatment of solid **4a** with MeOTf predissolved

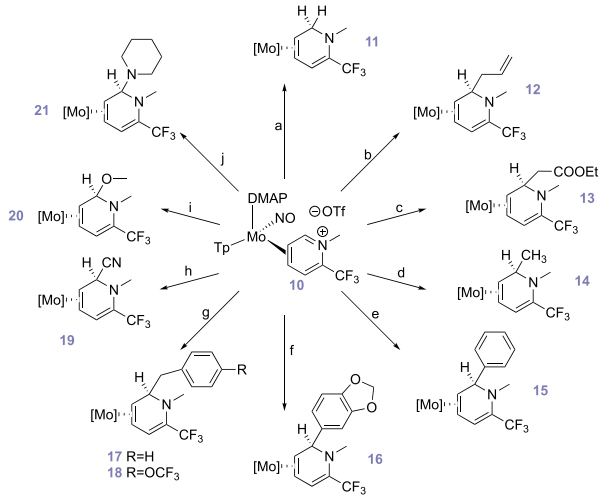
Scheme 4. Synthesis of a Single Coordination Diastereomer via Solid-State Induced Control of Kinetically Unstable Isomer (SICKUS) Method[32]



in MeCN results in quantitative *N*-methylation to form complex **10**. Once methylated, isomerization is no longer an issue on the time scale of organic reactions, with no change in the coordination diastereomer ratio observed by ^{1}H NMR after 24 h at 25 °C in MeCN.

Complex **10** was then subjected to a range of nucleophiles to effect the formation of dihydropyridine complexes (Scheme 5). The reactions were conducted at room temperature using hydride, organomagnesium, and organozinc reagents, among others. In every case, addition was found to take place stereoselectively *anti* to the metal at C6. The details of some of these organic reactions have been disclosed separately.[33] Remarkably, these include cases of amine and alkoxy additions to C6 of pyridine. ORTEP diagrams of the solid-state structures for **20** and **21** are provided in Figure 4, showing the addition *anti* to metal coordination.

Scheme 5. Nucleophilic Additions to the Methylpyridinium Complex[a]



[a](a) KBH_4, MeOH (**11**); (b) $BrCH_2CHCH_2$, Zn, THF (**12**); (c) $BrCH_2CO_2Et$, Zn, THF (**13**); (d) MeMgBr, THF (**14**); (e) PhMgBr, THF (**15**); (f) 3,4-(methylenedioxy)PhMgBr, THF (**16**); (g) BnMgBr, THF (**17**, **18**); (h) NaCN, MeCN (**19**); (i) NBu_4OH, MeOH (**20**); (j) piperidine (**21**) (yields average ∼60%; see ref 33).

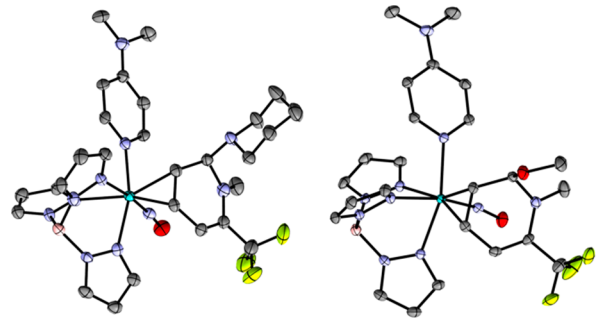


Figure 4. ORTEP diagrams of methoxy (**20**) and piperidine (**21**) additions to pyridinium complex **10**. Hydrogen atoms are omitted for clarity, as is a noncoordinating piperidine molecule in **21**.

Subsequently, the hydride addition product **11** was carried on to further reactions in hopes of finding conditions to perform addition across the remaining uncoordinated double bond (Scheme 1). Treatment of the η^2-dienamine **11** with 0.25 M HOTf in MeCN resulted in oxidation of the metal, even at −40 °C. Attempted protonation with 0.25 M HOTf in MeOH gave an unexpected product, which was ultimately determined to be the ring-opened cation **22A**, which isomerizes over a period of hours to **22B** (Scheme 6). A single crystal of **22B** was analyzed by XRD, and the solid-state structure is shown in Figure 5. C2−C3, C3−C4, and C4−C5 bond lengths of the azatriene ligand are all close to 1.4 Å, indicating significant delocalization (cf. for benzene 1.39 Å), which could be attributed to significant π backbonding of the molybdenum into the iminium group. Compound **22B** can be deprotonated with NEt_3 to yield the neutral complex **23B**. Alternatively, **22A** can immediately be deprotonated to form **23A**. All attempts to convert **11** into a tetrahydropyridine product via protonation were ultimately preempted by either oxidation of the Mo(0) or the ring-opening of **11H** to form **22B** (Scheme 6).

We questioned whether the CF_3 group played an important role in the ring-opening of the methylated dihydropyridinium

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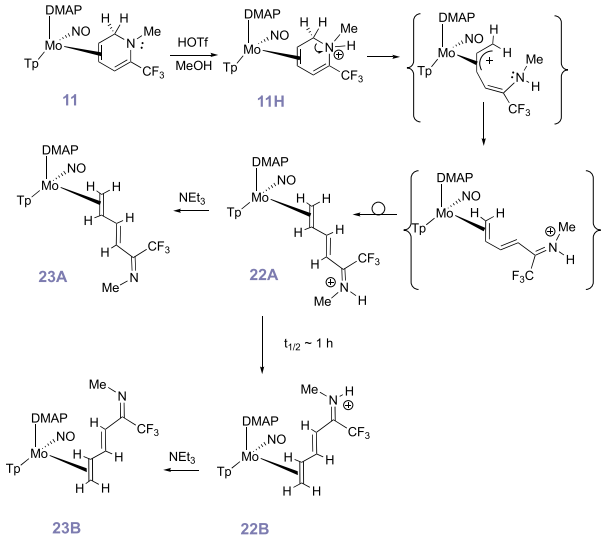
Scheme 6. Ring-Opening of a Dihydropyridine Complex[a]



[a]Triflate anions omitted.

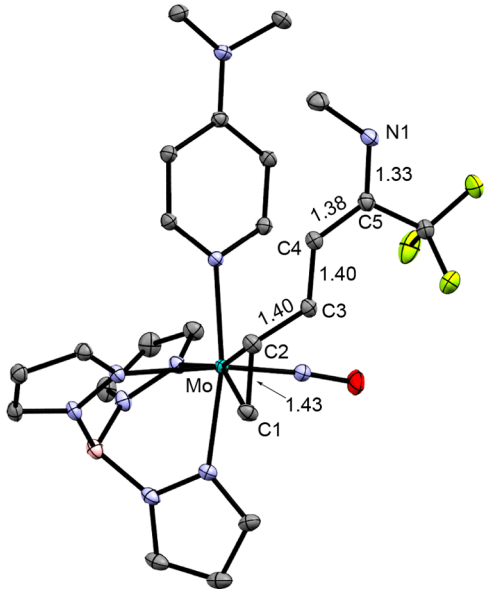
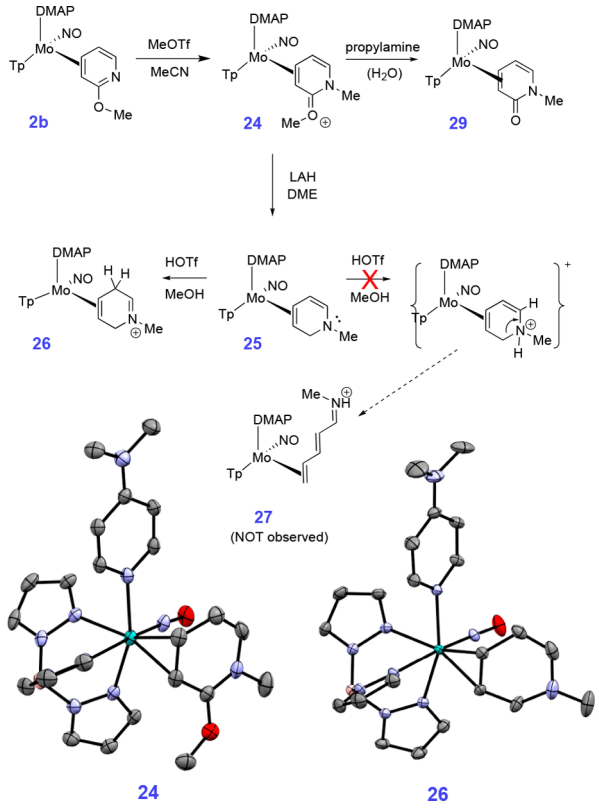


Figure 5. ORTEP of ring-opened-complex **22B**. The solvent, triflate anion, and H atoms have been omitted for clarity.

ligand of **11H**. To get at this issue, the 2-methoxypyridine complex **2b** was first methylated to form the pyridinium salt **24**, then this complex was reduced with LAH in DME. Gratifyingly, reduction of the oxonium was immediately followed by elimination of methanol and a further reduction to the parent methyldihydropyridine complex **25**. Parenthetically, **24** can also be hydrolyzed to the 1-methyl-2-pyridone complex **29**. Complex **25** was found to be extraordinarily susceptible to oxidation at the metal as the π-donation from the nitrogen into the diene is expected to shift the Mo(I)/Mo(0) reduction potential negative ($E_{p,a}$ = −0.23 V). In contrast to the nitrogen protonation observed for **11**, protonation of **25** is driven by the π-donation from the ring-nitrogen into the C5═C6 bond (i.e., an enamine; Scheme 7). This reaction provides a rare example of a dihapto-coordinated 2,5-dihydropyridinium complex **26**.

Scheme 7. Preparation of the 1-Methyldihydropyridine Complex 25 and Its Nitrogen-Directed Protonation to Make an η^2-2,5-Dihydropyridinium Complex (26)[a]



[a]ORTEP diagrams rendered at 50% probability.

Finally, efforts were made to separate a dihydropyridine from the metal center. It was found that the free organics could be obtained in good yield (70−90%) via oxidative decomplexation by treating the dihydropyridine complexes with $FeCp_2PF_6$ or I_2 in acetone. To demonstrate the utility of these molecules in organic synthesis, several were allowed to undergo a Diels−Alder reaction with various dienophiles. The details for the syntheses of these molecules have been published previously.[34]

DISCUSSION

In contrast to the tungsten analogue, {TpW(NO)(PMe_3)}, the molybdenum core is less π-basic, resulting in substantial chemical differences. Molybdenum η^2 complexes undergo exchange and isomerization much more readily; for example, while TpW(NO)(PMe_3)(3,4-η^2-pyridine) converts to its κN isomer with a half-life of 78 min at 22 °C,[27] the corresponding molybdenum complex completely isomerizes within seconds at the same temperature, as determined by cyclic voltammetry. The $E_{p,a}$ values for molybdenum η^2-pyridine and arene complexes are consistently about 0.4 V more negative than those of tungsten,[16,27] signaling increased susceptibility to oxidation. Though such differences give rise to distinct challenges in the molybdenum system, there are several advantages as well. The oxidative decomplexation of the final organic products proceeds under milder conditions (O_2 or I_2),[25,33] resulting in increased functional group tolerance (functional groups susceptible to oxidants) and higher yields. Processes that rely upon isomerization, such as conversion to a

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single coordination diastereomer, proceed more quickly, as exploited in the synthesis of the 2-(trifluoromethyl)pyridine complex (**4**).

Synthesizing complexes of η^2-azatrienes such as **22** or **23** directly from the conjugated ligand would be difficult, given the many potential binding sites and stereochemistries. The pyridine ring-opening encountered is reminiscent of the Zincke–König reaction, in which highly activated pyridinium salts react with secondary amines to produce, after hydrolysis, 5-amino-2,4-pentadienals.[35,36] So called "Zincke aldehydes" have been widely used in organic synthesis and their literature has been reviewed.[37−39] Whereas in the Zincke–König reaction, the amine plays a key role as a π-donor (Figure 6),

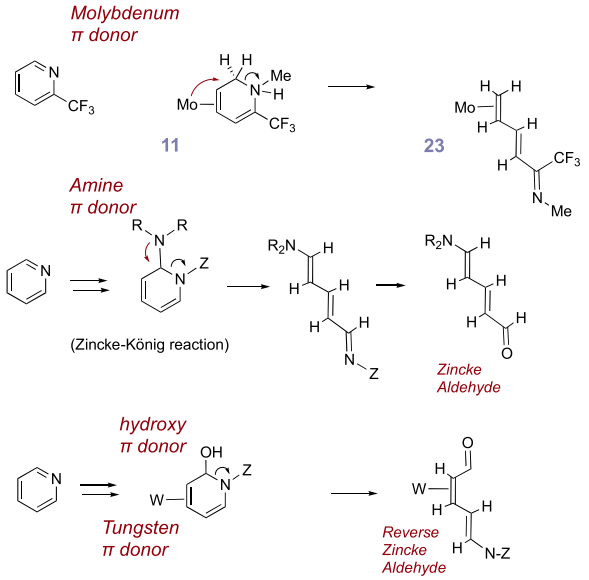

Figure 6. Comparison of molybdenum ring-opening to the Zincke–König reaction and a related tungsten reaction.

in the case of the conversion of **11** to **22B**, the molybdenum itself plays this key role. Thus, an azatriene is formed, lacking the more traditional "push–pull" architecture. In this regard, the mechanism of pyridine ring scission (Scheme 6) is relevant to the hydrodenitrogenation process, which often involves molybdenum on a solid support.[40,41] Wolczanski et al. have reported the ring scission of dihapto-coordinated pyridines forming a binuclear niobium complex,[41,42] and more recently, a report from our own group demonstrated the formation of η^2-cyanine and η^2-merocyanine complexes by treatment of WTp(NO)(PMe_3)(η^2-*N*-acetylpyridinium) with certain nucleophiles.[19] Here it appears that both the O donor and the tungsten are needed to effect ring-cleavage. Returning to molybdenum, the trifluoromethyl substituent on pyridine appears to play a key role in the ring-opening reaction as well. The parent methyldihydropyridine complex was prepared as a control and subjected to HOTf/MeOH, but in this case, without an EWG on either the nitrogen or adjacent ring-carbon, ring scission is not facilitated and only a 2,5-dihydropyridinium complex resulted (**26**). Unfortunately, when ring-opening does occur, it is irreversible and precludes further modification of the dihapto-coordinate ligand, as treatment with nucleophiles (MeMgBr, NaCN, $NaBH_3CN$) only results in deprotonation.

CONCLUSION

Molybdenum can successfully form a range of dihapto-coordinate pyridine complexes, which are stable enough to isolate and utilize for subsequent organic reactions. Although the tetrahydropyridines initially sought were inaccessible with the system that was probed, molybdenum-promoted dearomatization was successful in selectively yielding functionalized 1,2-dihydropyridines, which are useful for an array of organic transformations, as exemplified by the synthesis of isoquinuclidines via Diels–Alder chemistry (vide supra). It has also been demonstrated that a single enantiomer of the 2-(trifluoromethyl)pyridine complex may be synthesized, ultimately resulting in enantiopure organic products. Thus, dihapto-coordinate molybdenum chemistry presents a novel way of preparing compounds with potential applications in medicinal chemistry.[33]

EXPERIMENTAL SECTION

General Methods. NMR spectra were obtained on a 600 or 800 MHz spectrometer (22–25 °C). All chemical shifts are reported in ppm, and proton and carbon shifts are referenced to tetramethylsilane (TMS) utilizing residual ^{1}H or ^{13}C signals of the deuterated solvents as an internal standard. Coupling constants (J) are reported in hertz (Hz). Infrared spectra (IR) were recorded as a glaze on a spectrometer fitted with a horizontal attenuated total reflectance (HATR) accessory or on a diamond anvil ATR assembly. Electrochemical experiments were performed under a nitrogen atmosphere. Cyclic voltammetry data were taken at ambient temperature (22–25 °C) at 100 mV/s in a standard three-electrode cell with a glassy carbon working electrode, *N*,*N*-dimethylacetamide (DMA) or acetonitrile (MeCN) solvent, and tetrabutylammonium hexafluorophosphate (TBAH) electrolyte (approximately 0.5 M). All potentials are reported versus NHE (normal hydrogen electrode) using cobaltocenium hexafluorophosphate ($E_{1/2}$ = −0.78 V), ferrocene ($E_{1/2}$ = +0.55 V), or decamethylferrocene ($E_{1/2}$ = +0.04 V) as an internal standard. The peak-to-peak separation was less than 100 mV for all reversible couples. Unless otherwise noted, all synthetic reactions were performed in a glovebox under a dry nitrogen atmosphere. Deuterated solvents were used as received. Pyrazole (Pz) protons of the (trispyrazolyl)borate (Tp) ligand were uniquely assigned (e.g., "Pz3B") using a combination of two-dimensional NMR data and 4-(dimethylamino)pyridine–proton NOE interactions. When unambiguous assignments were not possible, Tp protons were labeled as "Pz3/5 or Pz4". All J values for Pz protons are 2 (±0.2) Hz. BH ^{1}H NMR peaks (around 4–5 ppm) are not identified due to their quadrupole broadening; IR data are used to confirm the presence of a BH group (around 2500 cm^{-1}). Compounds **4** and **10**–**18** have previously been reported.[34]

Synthesis of MoTp(NO)(DMAP)(4,5-η^2-pyridine-borane) (1). To a 50 mL round-bottom flask charged with a stir egg was added MoTp(NO)(DMAP)(η^2-$PhCF_3$) (2.04 g, 3.36 mmol), followed by pyridine-borane complex (3.10 g, 33.4 mmol) and THF (6.0 mL). This orange mixture was stirred for 3.25 h. The resulting violet solution was added slowly to stirring Et_2O (150 mL). The resulting precipitate was then isolated on a 30 mL fine porosity fritted disc, washed with Et_2O (3 × 25 mL), and desiccated to yield an orange solid, **1** (1.32 g, 58.9%). CV (DMAc) $E_{p,a}$ = +0.05 V (NHE). IR: ν_{NO} = 1607 cm^{-1}. Two coordination diastereomers. **A**:**B** = 4:3 ^{1}H NMR (acetone-d_6, δ): **A** 8.30 (broad, 1H, H2), 8.06 (d, 1H, PzC5), 8.02 (d, 1H, PzA3), 7.96 (d, 1H, PzA5), 7.90 (d, 1H, PzB5), 7.80 (broad s, 2H, DMAP A), 7.62 (d, 1H, PzC3), 7.02 (d, 1H, PzB3), 6.87 (t, J = 6.3 Hz, 1H, H5), 6.77 (d, J = 7.1 Hz, 1H, H6), 6.72 (broad s, 2H, DMAP B), 6.40 (t, 1H, PzC4), 6.38 (t, 1H, PzA4), 6.15 (t, 1H, PzB4), 3.63 (dd, J_{H4} = 6.3 Hz, J_{H2} = 7.1 Hz, 1H, H3), 3.27 (t, J = 6.3, 1H, H4) 3.10 (s, 6H, DMAP Me). **B** 8.54 (broad d, 1H, H2), 8.08 (d, 1H, PzC5), 7.98 (d, 1H, PzA5), 7.91 (d, 1H, PzB5), 7.83 (d, 1H, PzA3), 7.80 (broad s, 2H, DMAP A), 7.54 (d, 1H, PzC3), 6.94 (d,

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1H, PzB3), 6.75 (d, J = 7.1 Hz, 1H, H6), 6.72 (broad s, 2H, DMAP B), 6.50 (dd, J = 7.1 Hz, 6.3 Hz, 1H, H5), 6.44 (t, 1H, PzA4), 6.41 (t, 1H, PzC4), 6.15 (t, 1H, PzB4), 3.80 (t, J = 6.3, 1H, H4), 3.10 (s, 6H, DMAP Me), 3.06 (dd, J = 6.3 Hz, 6.0 Hz, 1H, H3). ^{13}C NMR (acetone-d_6, δ): **A** 166.6 (C2), 155.1 (DMAP C), 150.4 (DMAP A), 142.3 (Pz3), 141.6 (Pz3), 141.4 (Pz3), 137.2 (Pz5), 136.7 (Pz5), 135.9 (Pz5), 127.7 (C5), 127.0 (C6), 108.4 (DMAP B), 106.8 (Pz4), 106.5 (Pz4), 106.2 (Pz4), 74.3 (C4), 72.7 (C3), 38.9 (DMAP Me). **B** 167.7 (C2), 155.1 (DMAP C), 150.4 (DMAP A), 144.2 (PzA3), 142.4 (PzB3), 141.0 (PzC3), 137.8 (PzC5), 136.6 (PzA5), 135.2 (PzB5), 127.9 (C5), 127.4 (C6), 108.1 (DMAP B), 106.3 (PzC4), 106.2 (PzA4), 106.1 (PzB4), 77.0 (C4), 70.4 (C3), 38.9 (DMAP Me) Calculated for $C_{21}H_{28}B_2MoN_{10}O$: C, 45.52; H, 5.09; N, 25.28. Found: C, 45.17; H, 5.13; N, 24.59.

Synthesis of MoTp(NO)(DMAP)(3,4-η^2-2-methoxypyridine) (2). To a 50 mL round-bottom flask charged with a stir egg was added MoTp(NO)(DMAP)(η^2-PhCF$_3$) (4.03 g, 6.64 mmol), followed by 2-methoxypyridine (8.30 g, 76.1 mmol) and THF (36.0 mL). This orange mixture was stirred for 4 h. The resulting heterogeneous golden brown mixture was added slowly to stirring Et$_2$O (300 mL). The resulting precipitate was then isolated on a 60 mL fine porosity fritted disc, washed with Et$_2$O (4 × 30 mL), and desiccated to yield a yellow solid, **2** (3.00 g, 79.2%). CV (DMAc) $E_{p,a}$ = −0.27 V (NHE). IR: ν_{NO} = 1577 cm^{-1}. Two coordination diastereomers. **A**:**B** = 4:3 ^{1}H NMR (acetone-d_6, δ): 8.03 (d, 1H, Pz3/5), 8.00 (d, 1H, Pz3/5), 7.92 (d, 1H, Pz3/5), 7.87 (d, 1H, Pz3/5), 7.85 (d, 1H, Pz3/5), 7.75 (bs, 4H, DMAP A **A**/**B**), 7.51 (d, 1H, Pz3/5), 7.50 (d, 1H, Pz3/5), 6.97 (d, 1H, Pz3/5), 6.95 (d, 1H, Pz3/5), 6.67 (bd, 2H, DMAP B **A**/**B**), 6.61 (bd, 2H, DMAP B′ **A**/**B**), 6.58 (d, J = 6.4 Hz, 1H, H6**A**), 6.56 (d, J = 6.4 Hz, 1H, H6**B**), 6.37 (m, 2H, Pz4), 6.33 (t, 1H, Pz4), 6.26 (t, 1H, Pz4), 6.24 (m, 1H, H5**A**), 6.13 (t, 1H, Pz4), 6.12 (t, 1H, Pz4), 5.85 (m, 1H, H5**B**), 3.79 (s, 3H, H7**B**), 3.65 (dd, J = 8.8 Hz, 5.5 Hz, 1H, H4**B**), 3.62 (s, 3H, H7**A**), 3.28 (d, J = 8.8 Hz, 1H, H3**A**), 3.23 (dd, J = 8.8 Hz, 5.5 Hz, 1H, H4**A**), 3.08 (s, 6H, DMAP Me **B**), 3.07 (s, 6H, DMAP Me **A**), 2.96 (d, J = 8.8 Hz, 1H, H3**B**). ^{13}C NMR ($CDCl_3$, δ): 171.4 (C2**B**), 170.7 (C2**A**), 153.9 (DMAP C **B**), 153.8 (DMAP C **A**), 150.7 (broad, DMAP A **A**), 150.1 (DMAP A **B**), 144.0 (Pz3/5), 142.2 (Pz3/5), 142.1 (Pz3/5), 141.9 (Pz3/5), 140.2 (Pz3/5), 139.9 (Pz3/5), 138.7 (Pz3/5), 136.4 (Pz3/5), 136.3 (Pz3/5), 136.0 (Pz3/5), 135.9 (Pz3/5), 134.7 (Pz3/5), 128.4 (C6**A**), 128.0 (C6**B**), 118.2 (C5**A**), 117.3 (C5**B**), 107.4 (DMAP B **B**), 107.4 (DMAP B **A**), 105.9 (Pz4), 105.8 (Pz4), 105.6 (Pz4), 105.5 (Pz4), 105.4 (Pz4), 105.2 (Pz4), 77.2 (C4**B**), 75.4 (C4**A**), 65.0 (C3**A**), 62.4 (C3**B**), 52.4 (C7**A**), 52.1 (C7**B**), 39.3 (DMAP Me). Calculated for $C_{22}H_{27}BMoN_{10}O_2$: C, 46.33; H, 4.77; N, 24.56. Found: C, 46.23; H, 4.93; N, 24.27. HRMS: $C_{22}H_{27}N_{10}O_2BMo$ + H$^+$ obsd (%), calcd (%), ppm: 567.1613 (45), 567.1556 (54), 10.0; 569.1550 (66), 569.1553 (49), −0.5; 570.1533 (88), 570.1552 (81), −3.4; 571.1549 (100), 571.1547 (86), 0.4; 572.1552 (87), 572.1560 (74), −1.3; 573.1544 (92), 573.1546 (100), −0.4; 574.1537 (40), 574.1575 (34), −6.6; 575.1546 (30), 575.1566 (39), −3.4.

Synthesis of MoTp(NO)(DMAP)(3,4-η^2-2-(dimethylamino)-pyridine) (3). To a 4-dram vial charged with a stir pea was added MoTp(NO)(DMAP)(η^2-PhCF$_3$) (2.14 g, 3.52 mmol), followed by 2-(dimethylamino)pyridine (3.10 g, 25.4 mmol) and THF (10.0 mL). This orange mixture was stirred for 16 h. The resulting heterogeneous mixture was filtered through a 30 mL fine porosity fritted disc. The isolated solid was washed with Et$_2$O (4 × 15 mL) and desiccated to yield a yellow solid, **3** (1.58 g, 76.9%). CV (MeCN) $E_{p,a}$ = −0.45 V (NHE). IR: ν_{NO} = 1573 cm^{-1}. Two coordination diastereomers. **A**:**B** = 3:2 ^{1}H NMR (acetone-d_6, δ, + 5 °C): **A** 8.18 (d, 1H, PzC5), 8.15 (d, J = 6.7 Hz, 1H, DMAP A), 8.02 (d, 1H, PzA5), 7.92 (d, 1H, PzA3), 7.84 (d, 1H, PzB5), 7.63 (d, 1H, PzC3), 7.09 (d, J = 6.7 Hz, 1H, DMAP A′), 6.81 (d, 1H, PzB3), 6.75 (dd, J = 6.7 Hz, 2.7 Hz, 1H, DMAP B), 6.67 (d, J = 6.4 Hz, 1H, H6), 6.43 (dd, J = 6.7 Hz, 2.7 Hz, 1H, DMAP B′), 6.37 (t, 1H, PzC4), 6.33 (t, 1H, PzA4), 6.09 (t, 1H, PzB4), 5.99 (dd, J = 6.4 Hz, 5.3 Hz, 1H, H5), 3.55 (d, J = 9.2 Hz, 1H, H3), 3.34 (dd, J = 9.2 Hz, 5.3 Hz, 1H, H4), 3.07 (s, 6H, DMAP Me), 2.61 (broad s, 6H, H7). **B** 8.02 (d, 1H, Pz3/5), 7.93 (d, 1H, Pz3/5), 7.90 (broad s, 2H, DMAP A), 7.82 (d, 1H, Pz3/5), 7.63 (d, 1H, Pz3/5), 7.45 (d, 1H, Pz3/5), 6.87 (d, 1H, Pz3/5), 6.68 (broad s, 2H, DMAP B), 6.66 (d, J = 6.4 Hz, 1H, H6), 6.38 (t, 1H, Pz4), 6.26 (t, 1H, Pz4), 6.08 (t, 1H, Pz4), 5.63 (dd, J = 6.4 Hz, 5.3 Hz, 1H, H5), 3.67 (dd, J = 9.2 Hz, 5.3 Hz, 1H, H4), 3.08 (s, 6H, DMAP Me), 2.97 (d, J = 9.2 Hz, 1H, H3), 2.88 (s, 6H, H7). ^{13}C NMR (DCM-d_2, δ, 0 °C): **A** 166.5 (C2), 154.3 (DMAP C), 151.6 (DMAP A), 149.9 (DMAP A′), 142.2 (Pz3/5), 142.0 (Pz3/5), 141.0 (Pz3/5), 137.0 (Pz3/5), 136.4 (Pz3/5), 135.1 (Pz3/5), 131.4 (C6), 111.3 (C5), 107.5 (DMAP B′), 106.8 (DMAP B), 106.1 (Pz4), 105.9 (Pz4), 105.8 (Pz4), 75.8 (C4), 62.3 (C3), 39.5 (DMAP Me), 36.8 (broad, C7). **B** 167.2 (C2), 154.3 (DMAP C), 150.0 (broad, DMAP A), 143.0 (Pz3/5), 142.0 (Pz3/5), 140.4 (Pz3/5), 136.7 (Pz3/5), 136.6 (Pz3/5), 135.3 (Pz3/5), 130.1 (C6), 110.2 (C5), 107.7 (DMAP B), 106.4 (Pz4), 106.0 (Pz4), 105.7 (Pz4), 77.8 (C4), 60.7 (C3), 39.5 (DMAP Me), 37.4 (C7). Calculated for $C_{23}H_{30}BMoN_{11}O{\cdot}1/4\ C_4H_{10}O$: C, 47.89; H, 5.44; N, 25.60. Found: C, 47.36; H, 5.19; N, 25.24.

Synthesis of MoTp(NO)(DMAP)(3,4-η^2-2,6-dimethoxypyridine) (5). To a 4-dram vial charged with a stir pea was added MoTp(NO)(DMAP)(η^2-PhCF$_3$) (1.01 g, 1.66 mmol), followed by 2,6-dimethoxypyridine (2.04 g, 14.66 mmol) and THF (10.0 mL). This heterogeneous mixture was stirred for 3.5 h. The resulting brown heterogeneous mixture was added slowly to stirring Et$_2$O (100 mL). The resulting precipitate was isolated on a 30 mL fine porosity fritted disc, washed with Et$_2$O (4 × 20 mL), and desiccated to yield a yellow solid, **5** (0.784 g, 78.6%). CV (MeCN) $E_{p,a}$ = −0.38 V (NHE). IR: ν_{NO} = 1567 cm^{-1}. Two coordination diastereomers. **A**:**B** = 1:1 ^{1}H NMR (DCM-d_2, δ, + 5 °C): **A** 8.10 (d, 1H, PzA3), 7.83 (d, 1H, PzA5), 7.82 (d, 1H, PzC5), 7.73 (bs, 2H, DMAP A), 7.69 (d, 1H, PzB5), 7.33 (d, 1H, PzC3), 6.95 (d, 1H, PzB3), 6.48 (bs, 2H, DMAP B), 6.32 (t, 1H, PzA4), 6.26 (t, 1H, PzC4), 6.05 (t, 1H, PzB4), 5.46 (d, J = 5.8 Hz, 1H, H5), 3.75 (s, 3H, H7), 3.74 (s, 3H, H8), 3.42 (dd, J = 8.8 Hz, 5.8 Hz, 1H, H4), 3.16 (d, J = 8.8 Hz, 1H, H3), 3.01 (s, 6H, DMAP Me). **B** 7.81 (d, 1H, PzC5), 7.80 (d, 1H, PzA3), 7.78 (d, 1H, PzA5), 7.73 (bs, 2H, DMAP A), 7.70 (d, 1H, PzB5), 7.29 (d, 1H, PzC3), 6.95 (d, 1H, PzB3), 6.41 (d, J = 5.9 Hz, 2H, DMAP B), 6.27 (t, 1H, PzC4), 6.26 (t, 1H, PzA4), 6.05 (t, 1H, PzB4), 5.09 (d, J = 5.7 Hz, 1H, H5), 3.89 (s, 3H, H7), 3.73 (s, 3H, H8), 3.71 (dd, J = 8.8 Hz, 5.7 Hz, 1H, H4), 3.01 (s, 6H, DMAP Me), 2.93 (d, J = 8.8 Hz, 1H, H3). ^{13}C NMR (DCM-d_2, δ, + 5 °C): **A** 172.0 (C2), 154.4 (DMAP C), 154.2 (C6), 150.0 (DMAP A), 142.2 (PzB3), 141.1 (PzA3), 140.8 (PzC3), 136.8 (PzA5), 136.4 (PzC5), 135.2 (PzB5), 107.9 (DMAP B), 106.3 (PzA4), 105.9 (PzC4), 105.8 (PzB4), 89.2 (C5), 77.7 (C4), 62.0 (C3), 54.9 (C7), 52.5 (C8), 39.5 (DMAP Me). **B** 172.4 (C2), 154.7 (DMAP C), 154.0 (C6), 150.8 (DMAP A), 145.5 (PzA3), 142.1 (PzB3), 140.7 (PzC3), 136.8 (PzA5), 136.4 (PzC5), 135.3 (PzB5), 107.1 (DMAP B), 106.3 (PzA4), 105.8 (PzC4), 105.4 (PzB4), 89.0 (C5), 81.0 (C4), 59.2 (C3), 52.9 (C7), 55.0 (C8), 39.5 (DMAP Me). Calculated for $C_{23}H_{29}BMoN_{10}O_3$: C, 46.02; H, 4.87; N, 23.33. Found: C, 46.28; H, 5.03; N, 23.04.

Synthesis of [MoTp(NO)(DMAP)(3,4-η^2-2-methoxypyridinium)]$^+$ (OTf) (6). To a 4-dram vial charged with a stir pea was added **2** (508 mg, 0.891 mmol), followed by MeCN (5.0 mL). This mixture was cooled at −30 °C for 15 min. Next, a 1 M solution of HOTf/MeCN (1.8 mL, 1.8 mmol) at −30 °C was added to the reaction mixture with stirring, and the resulting yellow mixture was allowed to sit at −30 °C for 15 min. After 15 min, the resulting yellow solution was added slowly to stirring Et$_2$O (200 mL). The resulting precipitate was isolated on a 30 mL fine porosity fritted disc, washed with Et$_2$O (4 × 10 mL), and desiccated to yield a yellow solid, **6** (600 mg, 93.5%). CV (MeCN) $E_{p,a}$ = +0.53 V (NHE). IR: ν_{NO} = 1601 cm^{-1}. ^{1}H NMR (acetone-d_6, δ): 11.10 (bs, 1H, H1), 8.15 (d, 1H, PzC5), 8.10 (d, 1H, PzA5), 7.94 (d, 1H, PzB5), 7.80 (bs, 2H, DMAP A), 7.77 (d, 1H, PzC3), 7.62 (d, 1H, PzA3), 7.03 (d, 1H, PzB3), 6.75 (bs, 2H, DMAP B), 6.50 (t, 1H, PzC4), 6.45 (t, 1H, PzA4), 6.42 (m, 1H, H6), 6.31 (m, 1H, H5), 6.18 (t, 1H, PzB4), 4.17 (dd, J = 8.5 Hz, 4.5 Hz, 1H, H4), 3.80 (s, 3H, H7), 3.14 (s, 6H, DMAP Me), 2.92 (d, J = 8.5 Hz, 1H, H3). ^{13}C NMR (acetone-d_6, δ): 175.9 (C2), 155.6 (DMAP C), 150.4 (DMAP A), 143.8 (PzA3), 143.2 (PzB3), 142.0 (PzC3), 138.6 (PzC5), 138.5 (PzA5), 136.8 (PzB5), 120.8 (C6), 114.2 (C5), 108.9 (DMAP B), 107.8 (PzC4), 107.5 (PzA4), 106.9

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(PzB4), 78.2 (C4), 57.9 (C7), 56.1 (C3), 39.2 (DMAP Me). Calculated for $C_{23}H_{28}BF_3MoN_{10}O_5S$: C, 38.35; H, 3.92; N, 19.44. Found: C, 38.62; H, 4.02; N, 19.52. HRMS: $C_{22}H_{28}N_{10}O_2BMo^+$ obsd (%), calcd (%), ppm: 567.1544 (40), 567.1556 (54), −2.2; 569.1545 (64), 569.1553 (49), −1.4; 570.1541 (96),570.1552 (81), −2.0; 571.1561 (89), 571.1547 (86), 2.5; 572.1544 (100), 572.1560 (74), −2.7; 573.1549 (77), 573.1546 (100), 0.5; 574.1586 (40), 574.1575 (34), 2.0; 575.1566(31), 575.1566 (39), 0.0.

Synthesis of [MoTp(NO)(DMAP)(3,4-η^2-2-(dimethylamino)-pyridinium)]$^+$ (OTf) (7). To a 4-dram vial charged with a stir pea was added **3** (500 mg, 0.857 mmol), followed by MeCN (1.2 mL). This mixture was cooled at −30 °C for 15 min. Next, a 1 M solution of HOTf/MeCN (1.4 mL, 1.4 mmol) at −30 °C was added to the reaction mixture with stirring, and the resulting yellow mixture was allowed to sit at −30 °C for 5 min. After 5 min, the resulting yellow solution was added dropwise to stirring Et_2O (175 mL). The resulting precipitate was isolated on a 30 mL fine porosity fritted disc, washed with Et_2O (4 × 20 mL), and desiccated to yield a yellow solid, **7** (577 mg, 91.8%). CV (MeCN) $E_{p,a}$ = +0.44 V (NHE). IR: ν_{NO} = 1591 cm^{-1}. ^{1}H NMR (acetone-d_6, δ): 9.61 (s, 1H, H1), 8.14 (d, 1H, DMAP A), 8.11 (d, 1H, PzC5), 8.00 (d, 1H, PzA3), 7.98 (d, 1H, PzA5), 7.89 (d, 1H, PzB5), 7.84 (d, 1H, PzC3), 7.16 (d, 1H, DMAP A′), 7.02 (d, 1H, PzB3), 7.01 (dd, 1H, DMAP B), 6.53 (dd, 1H, DMAP B′), 6.45 (t, 1H, PzC4), 6.38 (t, 1H, PzA4), 6.30 (t, 1H, H5), 6.28 (t, 1H, H6), 6.16 (t, 1H, PzB4), 3.40 (d, 1H, H3), 3.30 (s, 3H, H8), 3.23 (dd, 1H, H4), 3.11 (s, 6H, DMAP Me), 2.61 (s, 3H, H7). ^{13}C NMR (acetone-d_6, δ): 164.8 (C2), 155.8 (DMAP C), 151.1 (DMAP A), 150.4 (DMAP A′), 143.0 (PzA3), 142.8 (PzB3), 142.2 (PzC3), 138.3 (PzC5), 137.6 (PzA5), 136.3 (PzB5),115.5 (C5), 115.4 (C6), 109.1 (DMAP B), 108.9 (DMAP B′), 107.5 (PzC4), 106.9 (PzA4), 106.8 (PzB4), 71.8 (C4), 57.2 (C3), 39.3 (DMAP Me), 38.9 (C8), 38.7 (C7). Calculated for $C_{24}H_{31}BF_3MoN_{11}O_4S$: C, 39.30; H, 4.26; N, 21.01. Found: C, 38.88; H, 4.33; N, 20.59.

Synthesis of [MoTp(NO)(DMAP)(4,5-η^2-2-(trifluoromethyl)-pyridinium)]$^+$ (OTf) (8). To a 4-dram vial charged with a stir pea was added **4A** (500 mg, 0.822 mmol), followed a 0.25 M solution of HOTf/MeCN (8.0 mL, 2.0 mmol) at −30 °C. The resulting mixture was stirred briefly and then allowed to sit at −30 °C for 5 min. After 5 min, the resulting solution was added dropwise to stirring Et_2O (175 mL). The resulting precipitate was isolated on a 30 mL fine porosity fritted disc, washed with Et_2O (4 × 20 mL), and desiccated to yield a magenta solid, **8** (540 mg, 86.6%). CV (MeCN) $E_{p,a}$ = +0.83 V (NHE). IR: ν_{NO} = 1623 cm^{-1}. ^{1}H NMR (acetone-d_6, δ): 8.40 (d, 1H, H6), 8.04 (d, 1H, PzC5), 7.96 (d, 1H, PzA5), 7.86 (d, 1H, PzB5), 7.68 (broad s, 2H, DMAP A), 7.67 (d, 1H, PzA3), 7.54 (d, 1H, PzC3), 7.43 (d, 1H, H3), 7.10 (d, 1H, PzB3), 6.61 (d, 2H, DMAP B), 6.44 (t, 1H, PzC4), 6.40 (t, 1H, PzA4), 6.16 (t, 1H, PzB4), 3.90 (t, 1H, H5), 3.43 (t, 1H, H4), 3.03 (s, 6H, DMAP Me). Efforts to purify compound resulted in deprotonation.

Synthesis of [MoTp(NO)(DMAP)(3,4-η^2-2,6-dimethoxypyridinium)]$^+$ (OTf) (9N and 9C). To a −30 °C solution of **5** (100 mg, 0.17 mmol) and MeCN (2.0 mL) was added a −30 °C, 1 M solution of HOTf/MeCN (0.7 mL, 0.7 mmol). The resulting orange solution was left at −30 °C for 15 min, and subsequently added dropwise to stirring Et_2O (100 mL), yielding a bright orange precipitate. The precipitate was isolated on a 15 mL fine porosity fritted disc, washed with Et_2O (3 × 15 mL), and desiccated to yield **9** (40 mg, 32%). CV (DMAc) $E_{p,a}$ = +0.98 V (NHE). IR: ν_{NO} = 1615 cm^{-1}. ^{1}H NMR (acetone-d_6, δ): CV (DMAc) $E_{p,a}$ = +0.98 V (NHE). IR: ν(C−H) = 2954 cm^{-1}, ν(B−H) = 2511 cm^{-1}, ν(NO) = 1615 cm^{-1}. ^{1}H NMR (acetone-d_6, δ): 9.93 (1H, bs, N−H **9N**), 8.01 (1H, d, Pz3/5 **9N**), 7.99 (1H, d, Pz3/5 **9N**), 7.98 (1H, d, Pz5A **9C**), 7.93 (1H, d, Pz5C **9C**), 7.82 (1H, d, Pz5B **9C**), 7.74 (1H, d, Pz3C **9C**), 7.73 (2H, buried bs, DMAP-A **9C** and **9N**), 7.58 (1H, d, Pz3/5 **9N**), 7.57 (1H, d, Pz3/5 **9N**), 7.35 (1H, d, Pz3A **9C**), 7.15 (1H, d, Pz3B **9C**), 6.98 (1H, d, Pz3/5 **9N**), 6.83 (2H, m, DMAPB **9N**), 6.66 (2H, bs, DMAP-B **9C**), 6.44 (1H, t, Pz4C **9C**), 6.41 (1H, t, Pz4A **9C**), 6.17 (1H, t, Pz4B **9C**), 6.13 (1H, t, Pz4 **9N**), 5.34 (1H, d, J = 5.8, H5 **9N**), 4.22 (3H, s, OMe **9C**), 4.20 (3H, s, OMe **9C**), 4.11 (1H, t, J = 6.8, H4 **9N**), 4.04 (1H, dd, J = 22.5, 8.4, H5′ **9C**), 3.84 (3H, s, OMe **9N**), 3.73 (1H t, J = 7.9, H4 **9C**), 3.49 (3H, s, OMe **9N**), 3.47 (1H, dt, J = 22.5, 1.3, H5 **9C**), 3.03 (6H, s, NMe **9N**), 3.02 (6H, s, NMe **9C**), 2.94 (1H, dd, J = 7.9, 1.3, H3 **9C**) 2.81 (1H, d, J = 8.3, H3 **9N**). ^{13}C NMR (acetone-d_6, δ): 191.9 (CO), 186.7 (CO), 155.6 (DMAP-C), 149.9 (2C, DMAP-A), 144.8 (Pz3A), 143.1 (Pz3B), 141.9 (Pz3C), 138.7 (Pz5A/5C), 138.3 (Pz5A/5C), 137.4 (Pz5B), 109.5 (2C, DMAP-B), 107.9 (Pz4A/4C), 107.6 (Pz4A/4C), 107.3 (Pz4B), 71.3 (C4), 58.8 (OMe), 58.4 (OMe), 57.0 (C3), 39.4 (DMAPMe), 33.4 (C5). HRMS: C23H30N10O3BMo$^+$ obsd (%), calcd (%), ppm: 597.1692 (50), 597.1662 (54), 5.0; 599.1664 (55), 599.1659 (49), 0.8; 600.1662 (88), 600.1658 (81), 0.6; 601.1654 (93), 601.1653 (86), 0.2; 602.1664 (87), 602.1666 (75), −0.3; 603.1664 (100), 603.1652 (100), 1.9; 604.1700 (41), 604.1681 (35), 3.2; 605.1690 (41), 605.1672 (39), 3.0.

Synthesis of MoTp(NO)(DMAP)(4,5-η^2-2-(trifluoromethyl)-6-cyano-*N*-methyldihydropyridine) (19). Compound **10** (375 mg, 0.486 mmol) and MeOH (2.0 mL) were combined in a 4 dram vial containing a stir pea. NaCN (83 mg, 1.69 mmol) was added to the resulting solution, and the reaction mixture was stirred for 30 min, during which time solid precipitated. The solid was isolated on a 15 mL fine porosity fritted funnel, and washed with H_2O (3 mL) followed by MeOH (3 × 1.0 mL). The solid was desiccated to yield **19** as a pale orange solid (181 mg, 57%). $E_{p,a}$ = +0.34 V (NHE). IR: ν_{NO} = 1579 cm^{-1}. ^{1}H NMR (acetonitrile-d_3, δ): 7.88 (d, 1H, PzC5), 7.84 (d, 1H, PzA5), 7.83 (broad s/buried, 2H, DMAP A), 7.83 (d, 1H, PzA3), 7.76 (d, 1H, PzB5), 7.63 (d, 1H, PzC3), 7.15 (d, 1H, PzB3), 6.64 (d, 2H, DMAP B), 6.34 (d, J = 6.7 Hz, 1H, H3), 6.33 (t, 1H, PzC4), 6.30 (t, 1H, PzA4), 6.14 (t, 1H, PzB4), 4.06 (d, J = 1.5 Hz, 1H, H6), 3.05 (s, 3H, H7), 3.02 (s, 6H, DMAP Me), 3.01 (dd, J = 8.7 Hz, 1.5 Hz, 1H, H5), 2.41 (dd, J = 8.7 Hz, 6.7 Hz, 1H, H4). ^{13}C NMR (acetonitrile-d_3, δ): 155.4 (DMAP C), 150.6 (DMAP A), 144.5 (PzA3), 142.6 (PzB3), 142.2 (PzC3), 138.0 (PzC5), 137.1 (PzA5), 136.4 (PzB5), 123.7 (q, J = 270 Hz, CF3), 123.0 (q, J = 29.6 Hz, C2), 121.7 (CN), 115.0 (q, J = 6.6 Hz, C3), 109.2 (DMAP B), 107.1 (PzC4), 106.9 (PzA4), 106.9 (PzB4), 76.7 (C5), 56.6 (C6), 54.7 (C4), 39.4 (DMAP Me), 38.4 (C7). Efforts to purify compound resulted in decomposition **10**. SC-XRD was carried out for this compound (SI).

Synthesis of MoTp(NO)(DMAP)(4,5-η^2-2-(trifluoromethyl)-6-methoxy-*N*-methyldihydropyridine) (20). Compound **10** (372 mg, 0.482 mmol) was dissolved in MeOH (0.5 mL) in a 4 dram vial. A 1.0 M solution of NEt_4OH in MeOH (0.5 mL) was added to the resulting solution. The reaction mixture was allowed to sit for 30 min, resulting in the precipitation of yellow crystals. The crystals were isolated on a 15 mL fine porosity fritted funnel, rinsed with Et_2O (5 mL) and desiccated to yield **20** as a yellow solid (142 mg, 22%). $E_{p,a}$ = +0.13 V (NHE). IR: ν_{NO} = 1577 cm^{-1}. ^{1}H NMR (acetonitrile-d_3, δ): 7.99 (broad s, 2H, DMAP A), 7.87 (d, 1H, PzC5), 7.86 (d, 1H, PzA3), 7.82 (d, 1H, PzA5), 7.76 (d, 1H, PzB5), 7.57 (d, 1H, PzC3), 7.20 (d, 1H, PzB3), 6.64 (d, 2H, DMAP B), 6.32 (t, 1H, PzC4), 6.28 (t, 1H, PzA4), 6.17 (d, J = 6.4 Hz, 1H, H3), 6.14 (t, 1H, PzB4), 4.46 (d, J = 1.5 Hz, 1H, H6), 3.26 (s, 3H, H7), 3.17 (s, 3H, H8), 3.01 (s, 6H, DMAP Me), 2.94 (dd, J = 9.2 Hz, 1.5 Hz, 1H, H5), 2.48 (dd, J = 9.2 Hz, 6.4 Hz, 1H, H4). ^{13}C NMR (acetonitrile-d_3, δ): 155.0 (DMAP C), 151.1 (DMAP A), 144.0 (PzA3), 142.3 (PzB3), 141.7 (PzC3), 137.8 (PzC5), 136.9 (PzA5), 136.2 (PzB5), 124.3 (CF3, J_{CF} = 270.1 Hz), 123.8 (C2, J_{CF} = 28.5 Hz), 113.0 (C3, J_{CF} = 6.3 Hz), 109.0 (DMAP B), 107.1 (PzC4), 106.7 (PzA4), 106.7 (PzB4), 95.6 (C6), 77.1 (C5), 59.3 (C4), 52.7 (C8), 39.6 (C7), 39.4 (DMAP Me). Efforts to purify compound resulted in elimination to reform **10**. Single crystal grown and analyzed by XRD.

Synthesis of MoTp(NO)(DMAP)(3,4-η^2-2-(trifluoromethyl)-6-(piperidin-1-yl)-*N*-methyldihydropyridine) (21). Compound **10** (102 mg, 0.132 mmol) and piperidine (110 mg, 1.29 mmol) were added to a 4 dram vial. Within minutes, yellow crystals began to precipitate from solution. After 30 min, added a 1.0 M solution of potassium *t*-butoxide in 2-propanol (0.14 mL). Isolated the crystals on a 15 mL fine porosity fritted funnel. Desiccated the collected material to yield **21** as a yellow solid (93 mg, 41%). $E_{p,a}$ = +0.12 V (NHE). IR: ν_{NO} = 1576 cm^{-1}. ^{1}H NMR (acetonitrile-d_3, δ): 8.03

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(broad s, 2H, DMAP A), 7.87 (d, 1H, PzC5), 7.86 (d, 1H, PzA3), 7.81 (d, 1H, PzA5), 7.76 (d, 1H, PzB5), 7.54 (d, 1H, PzC3), 7.20 (d, 1H, PzB3), 6.63 (d, 2H, DMAP B), 6.34 (t, 1H, PzC4), 6.27 (t, 1H, PzA4), 6.13 (t, 1H, PzB4), 5.89 (d, J = 6.4 Hz, 1H, H3), 4.04 (d, J = 1.0 Hz, 1H, H6), 3.16 (s, 3H, H7), 3.00 (s, 6H, DMAP Me), 2.76 (broad t, 2H, H8), 2.74 (dd, J = 9.6 Hz, 1.0 Hz, 1H, H5), 2.47 (dd, J = 9.6 Hz, 6.4 Hz, 1H, H4), 2.41 (broad t, 2H, H8′), 1.44 (m, 4H, H9), 1.39 (m, 2H, H10). ^{13}C NMR (acetonitrile-d_3, δ): 155.1 (DMAP C), 151.0 (DMAP A), 143.7 (PzA3), 142.4 (PzB3), 141.6 (PzC3), 137.8 (PzC5), 137.0 (PzA5), 136.4 (PzB5), 126.6 (q, J = 29.7 Hz, C2), 124.2 (q, J = 270 Hz, CF3), 110.6 (q, J = 6.5 Hz, C3), 108.9 (DMAP B), 83.8 (C6), 74.1 (C5), 60.3 (C4), 49.6 (C8), 40.4 (C7), 39.4 (DMAP Me), 27.3 (C9), 26.0 (C10). Efforts to purify compound resulted in elimination to reform **10**. SC-XRD was carried out for this compound (SI).

Synthesis of Ring-Opened Compound 22B. To a 4-dram vial charged with a stir pea, added **11** (114 mg, 0.183 mmol) followed by a 0.25 M solution of HOTf/MeOH (0.90 mL, 0.22 mmol), resulting in an immediate color change from yellow to vibrant orange. The resulting solution was allowed to stir 5 min, and subsequently added dropwise to stirring Et_2O (50 mL). The precipitate was isolated on a 15 mL fine porosity fritted disc, washed with Et_2O (3 × 5 mL), and desiccated to yield a vermilion solid, **22**, as a mixture of isomers (56 mg, 38.3%). Nearly exclusively the "**B**" isomer can be isolated by letting the reaction mixture stir for 24 h before precipitation. CV (DMAc) $E_{p,a}$ = +0.70 V (NHE). IR: ν_{NO} = 1627 cm^{-1}. ^{1}H NMR (MeOD-d_4, δ): **A** 8.06 (d, 1H, PzC5), 8.02 (d, 1H, PzA5), 8.00 (very broad s, 2H, DMAP A), 7.96 (d, 1H, PzC3), 7.87 (d, 1H, PzB5), 7.47 (d, 1H, PzA3), 7.24 (t, 1H, H4), 7.10 (d, 1H, PzB3), 6.61 (broad s, 2H, DMAP B), 6.51 (t, 1H, PzC4), 6.41 (t, 1H, PzA4), 6.20 (t, 1H, PzB4), 5.28 (d, 1H, H3), 4.35 (ddd, 1H, H5), 3.81 (dd, 1H, H6a), 3.53 (dd, 1H, H6b), 3.05 (broad s, 6H, DMAP Me), 2.83 (s, 3H, H7). **B** 8.10 (d, 1H, PzC3), 8.00 (d, 1H, PzC5), 7.89 (broad s, 2H, DMAP A), 7.86 (d, 1H, PzA5), 7.81 (d, 1H, PzB5), 7.81 (d, 1H, PzA3), 7.53 (d, 1H, PzB3), 7.28 (t, 1H, H4), 6.70 (d, 2H, DMAP B), 6.47 (t, 1H, PzC4), 6.35 (t, 1H, PzA4), 6.19 (t, 1H, PzB4), 5.09 (d, 1H, H3), 4.98 (ddd, 1H, H5), 3.39 (dd, 1H, H6b), 3.07 (s, 6H, DMAP Me), 2.96 (dd, 1H, H6a), 2.59 (s, 3H, H7). ^{13}C NMR (MeOD-d_4, δ): **A** 162.7 (C4), 155.9 (DMAP C), 150.8 (broad, DMAP A), 149.4 (q, J = 32.0 Hz, C2), 145.3 (PzA3), 144.0 (PzB3), 142.5 (PzC3), 139.6 (PzC5), 138.6 (PzA5), 137.3 (PzB5), 121.8 (q, J = 270 Hz, CF3), 109.0 (DMAP A), 108.2 (PzC4), 108.7 (PzA4), 107.3 (PzB4), 101.7 (C3), 95.0 (C5), 75.4 (C6), 39.3 (DMAP Me), 30.8 (C7). **B** 161.0 (C4), 155.5 (DMAP C), 151.0 (broad, DMAP A), 148.7 (q, J = 32.4 Hz, C2), 144.5 (PzA3), 143.5 (PzB3), 143.5 (PzC3), 138.7 (PzC5), 137.5 (PzA5), 137.2 (PzB5), 121.0 (q, J = 275 Hz, CF3), 109.1 (DMAP A), 107.8 (PzC4), 107.7 (PzA4), 107.5 (PzB4), 99.1 (C3), 94.8 (C5), 73.4 (C6), 39.3 (DMAP Me), 30.8 (C7). SC-XRD was carried out for this compound (SI).

Synthesis of Ring-Opened Compound 23A. To a 4-dram vial charged with a stir pea, added **11** (114 mg, 0.183 mmol) followed by a 0.25 M solution of HOTf/MeOH (0.90 mL, 0.22 mmol), resulting in an immediate color change from yellow to vibrant orange. The resulting solution was allowed to stir 5 min, and then triethylamine (50.6 mg, 0.50 mmol) was added. The reaction mixture was stirred for 1 min, and subsequently evaporated. The residue was dissolved in minimal DCM and added dropwise to stirring Et_2O (25 mL). The precipitate was isolated on a 15 mL fine porosity fritted disc, washed with Et_2O (3 × 5 mL), and desiccated to yield an orange solid, **23A,** (35 mg, 31%). $E_{p,a}$ = +0.42 V (NHE). ^{1}H NMR (acetonitrile-d_3, δ): 7.91 (d, 1H, PzC5), 7.88 (d, 1H, PzA5), 7.81 (d, 1H, PzB5), 7.61 (d, 1H, PzA3), 7.59 (broad s, 2H, DMAP A), 7.58 (d, 1H, PzC3), 7.09 (d, 1H, PzB3), 6.86 (m, 1H, H4), 6.51 (d, 2H, DMAP B), 6.34 (t, 1H, PzC4), 6.27 (t, 1H, PzA4), 6.15 (t, 1H, PzB4), 5.48 (d, 1H, H3), 3.16 (s, 3H, H7), 2.98 (s, 6H, DMAP Me), 2.89 (dd, 1H, H5), 2.69 (dd, 1H, H6a), 2.69 (dd, 1H, H6b). ^{13}C NMR (acetonitrile-d_3, δ): 157.1 (C4), 155.3 (C2, J_{CF} = 30.1 Hz), 155.2 (DMAP C), 151.3 (DMAP A), 143.7 (PzA3), 143.1 (PzB3), 141.7 (PzC3), 138.0 (PzA5), 137.8 (PzC5), 136.7 (PzB5), 122.0 (CF$_3$, J_{CF} = 278 Hz) 108.5 (DMAP B), 107.3 (PzC4), 107.1 (PzB4), 106.9 (PzA4), 106.6 (C3), 73.3 (C5), 66.2 (C6), 39.5 (DMAP Me), 38.1 (C7). Attempts to purify by column chromatography were unsuccessful.

Synthesis of [MoTp(NO)(DMAP)(3,4-η^2-2-methoxy-*N*-methylpyridinium)]$^+$ (OTf) (24). To a 4-dram vial was added **2** (1.0 g, 1.7 mmol), CH_3CN (5 mL), and MeOTf (400 mg, 2.44 mmol). This orange mixture was left sitting at room temperature for 10 min, yielding a dark red solution. This solution was added to stirring Et_2O (100 mL) to yield a red precipitate, which was then isolated on a 30 mL fine porosity fritted disc, washed with Et_2O (3 × 30 mL), and desiccated to yield the dark orange product **24** (1.72 g, 89% yield). CV (DMAc) $E_{p,a}$ = +0.79 V (NHE). IR: ν(C−H) = 3105 cm^{-1}, ν(B−H) = 2484 cm^{-1}, ν(NO) = 1596 cm^{-1}. Product isolated as a 3:1 **A**:**B** ratio. ^{1}H NMR (acetone-d_6, δ): 8.27 (1H, d, J = 7.3, DMAP-A **B**), 8.16 (1H, d, Pz5C **A**), 8.15 (1H, d, Pz5A **A**), 8.13 (1H, d, Pz3/5 **B**), 8.20 (1H, d, Pz3/5 **B**), 7.96 (1H, d, Pz3/5 **B**), 7.94 (1H, d, Pz3/5 **B**), 7.93 (1H, d, Pz5B **A**), 7.79 (2H, bs, DMAP-B **A**), 7.74 (1H, d, Pz3C **A**), 7.65 (1H, d, Pz3A **A**), 7.28 (1H, d, J = 7.3, DMAP A **B**), 7.09 (1H, d, Pz3B **B**), 7.02 (1H, bs, DMAP-B **B**), 7.00 (1H, d, Pz3B **A**), 6.75 (2H, bs, DMAP-B **A**), 6.61 (1H, bs, DMAP-B **B**), 6.51 (1H, t, Pz4C **A**), 6.49 (1H, t, Pz4A **A**), 6.48 (1H, t, Pz4 **B**), 6.43 (1H, d, J = 7.2, H6 **A**), 6.34 (1H, t, J = 6.3, H5 **A**), 6.39 (1H, t, Pz4 **B**), 6.18 (1H, t, Pz4 **B**), 6.17 (1H, t, Pz4B **A**), 4.21 (1H, dd, J = 8.6, 6.3, H4 **A**), 3.75 (3H, s, NMe **A**), 3.69 (1H, d, J = 8.6, H3 **B**), 3.54 (1H, dd, J = 8.6, 5.8, H4 **B**), 3.50 (3H, s, OMe **A**), 3.12 (6H, s, NMe **A**), 3.00 (1H, d, J = 8.6, H3 **A**). ^{13}C NMR (acetone-d_6, δ) **A**: 175.7 (OMe), 155.89 (DMAP-C), 150.5 (2C, DMAP-A), 143.9 (Pz3A), 143.2(Pz3B), 142.1 (Pz3C), 138.9 (Pz5A/5C), 138.6 (Pz5A/5C), 136.9 (Pz5B), 120.9 (C5/C6),120.8 (C5/C6), 109.1 (2C, DMAP-B), 108.1 (Pz4A/4C), 107.9 (Pz4A/4C), 106.9 (Pz4B),78.1 (C4), 58.5 (OMe), 55.9 (C3), 39.3 (DMAP-Me), 37.3 (NMe). **B** (signals are too small for unambiguous assignment): 175.6, 155.9, 150.2, 143.0, 142.5, 138.5, 137.8, 136.5, 121.5, 121.2, 108.9, 107.7, 107.0, 106.9, 76.7, 66.1, 58.3, 56.4, 39.3, 29.8, 15.6. HRMS: $C_{23}H_{30}N_{10}O_2BMo^+$ obsd (%), calcd (%), ppm: 581.1728 (49), 581.1713 (54), 2.6; 583.1713 (48), 583.1710 (49), 0.6; 584.1723 (75), 584.1709 (81), 2.4; 585.1716 (85), 585.1704 (86), 2.1; 586.1716 (73), 586.1716 (74), −0.1; 587.1721 (100), 587.1703 (100), 3.0; 588.1724 (32), 588.1731 (34), −1.3; 589.1738 (39), 589.1723 (39), 2.6.

Synthesis of MoTp(NO)(DMAP)(3,4-η^2-*N*-methyldihydropyridine) (25). To a solution of **24** (500 mg, 0.679 mmol) and dimethoxyethane (5 mL) was added lithium aluminum hydride (LAH) (75 mg, 1.97 mmol). The resulting dark red solution was then stirred at room temperature for 5 min. This solution was then added to stirring H_2O (30 mL) in a 50 mL round-bottom flask, yielding a green precipitate. This mixture was stirred at room temperature for 20 h. The resulting yellow precipitate was isolated on a 30 mL medium porosity fritted disc, washed with H_2O (3 × 20 mL) and hexanes (3 × 20 mL) (Note: do not stir the precipitate with washing solvent, just wash through), and dried in vacuo 1 h. This precipitate was then triturated in stirring hexanes (20 mL) for 20 h, and the resulting precipitate was isolated on a 15 mL fine porosity fritted disc, washed with hexanes (3 x10 mL), and desiccated to yield **26** (360 mg, 95% mass recovery). CV (DMAc) $E_{p,a}$ = −0.23 V (NHE). IR: ν(C−H) = 2922 cm^{-1}, ν(B−H) = 2468 cm^{-1}, ν(NO) = 1566 cm^{-1}. Product isolated as a 4:1 **A**:**B** ratio. ^{1}H NMR (acetone-d_6, δ): 7.95 (1H, d, Pz3A **A**), 7.90 (1H, d, Pz5A/C **A**), 7.88 (2H, buried bs, DMAP-A **A**), 7.85 (1H, d, Pz5A/C **A**), 7.77 (1H, d, Pz5B **A**), 7.49 (1H, d, Pz3C **A**), 7.04 (1H, d, Pz3B **A**), 6.66 (2H, m, DMAP-B **B**), 6.58 (2H, m, DMAP-B **A**), 6.30 (2H, t, Pz4A and C **A**), 6.28 (1H, t, Pz4 **B**), 6.24 (1H, t, Pz4 **B**), 6.12 (1H, t, Pz4 **B**), 6.11 (1H, t, Pz4B **A**), 5.50 (1H, d, J = 7.4, H6 **A**), 5.44 (1H, d, J = 7.4, H6 **B**), 5.06 (1H, ddd, J = 7.4, 4.6, and 0.9, H5 **B**), 4.75 (1H, ddd, J = 7.4, 4.6, and 0.9, H5 **A**), 3.81 (1H dd, J = 10.9 and 2.8, H2 **A**), 3.61 (1H, dd, J = 10.9 and 5.0, H2′ **A**), 3.05 (6H, s, N-Me **A**), 2.62 (3H, s, N-Me **A**), 2.59 (1H, m, H4 **A**), 2.03 (1H, m, H3 **A**). ^{13}C NMR (acetone-d_6, δ): **A** 155.0 (DMAP-C), 151.1 (2C, DMAP-A), 143.5 (Pz3A), 142.0 (Pz3B), 141.3 (Pz3C), 137.1 (Pz5A/C), 136.7 (Pz5A/C), 135.5 (Pz5B), 131.6 (C6), 107.9 (DMAP-B), 106.5 (Pz4A/C), 106.2 (Pz4A/C), 106.1 (Pz4B), 103.6 (C5), 63.5 (C4), 61.7 (C3), 53.9 (C2), 43.2 (NMe), 39.1 (DMAP-Me). HRMS: $C_{22}H_{29}N_{10}OBMo+H^+$ obsd (%), calcd

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(%), ppm: 553.1769 (36), 553.1764 (54), 1.0; 555.1762 (65), 555.1760 (49), 0.3; 556.1734 (77), 556.1760 (82), −4.6; 557.1730 (92), 557.1754 (86), −4.3; 558.1783 (80), 558.1767 (74), 2.9; 559.1740 (100), 559.1754 (100), 2.4; 560.1814 (46), 560.1782 (34), 5.7; 561.1866 (44), 561.1773 (39), 16.6.

Synthesis of [MoTp(NO)(DMAP)(3,4-η^2-*N*-methyldihydropyridinium)]$^+$ (OTf) (26). **25** (28 mg, 0.050 mmol) and a 0.167 M solution of HOTf in MeOH (0.6 mL) were combined in a 4 dram vial containing a stir pea. The reaction mixture was stirred for 5 min and then added to stirring Et_2O (15 mL). The suspension was stirred for 45 min, and then the suspended solid was isolated on a 15 mL fine porosity fritted funnel. The solid was washed with Et_2O (2 × 3 mL) and desiccated under a vacuum to yield **27** as a pale yellow solid (33 mg, 93%). CV (MeCN) $E_{p,a}$ = +0.39 V (NHE). IR: ν_{NO} = 1623 cm^{-1}. ^{1}H NMR (acetone-d_6, δ): 8.97 (bs, 1H, H6), 8.00 (d, 1H, Pz3/5), 7.99 (d, 1H, Pz3/5), 7.97 (d, 1H, Pz3/5), 7.95 (bs, 2H, DMAP A), 7.83 (d, 1H, Pz3/5), 7.72 (d, 1H, Pz3/5), 7.25 (d, 1H, Pz3/5), 6.70 (d, 2H, DMAP B), 6.41 (t, 1H, Pz4), 6.38 (t, 1H, Pz4), 6.16 (t, 1H, Pz4), 4.94 (d, J = 17.5 Hz, 1H, H2), 4.67 (d, J = 17.5 Hz, 1H, H2′), 3.97 (s, 3H, H7), 3.92 (bd, J = 22.6 Hz, 1H, H5), 3.45 (bd, J = 22.6 Hz, 1H, H5′), 3.06 (s, 3H, H7), 2.55 (dd, J = 10.6 Hz, 6.1 Hz, 1H, H4), 2.14 (dd, J = 10.6 Hz, 4.9 Hz, 1H, H3). ^{13}C NMR (acetone-d_6, δ): 178.6 (C6), 155.3 (DMAP C), 150.6 (DMAP A), 143.6 (Pz3), 142.3 (Pz3), 141.6 (Pz3), 138.9 (Pz5), 137.7 (Pz5), 136.3 (Pz5), 109.0 (DMAP B), 107.2 (Pz4), 107.1 (Pz4), 106.5 (Pz4), 55.6 (C3), 55.3 (C2), 54.2 (C4), 39.2 (DMAP Me), 33.6 (C5). Attempts to purify by column chromatography were unsuccessful. SC-XRD was carried out for this compound (SI).

Synthesis of Mo(κ^2-Tp)(NO)(κ^2-bpy) (28). MoTp(NO)(DMAP)(η^2-PhCF$_3$) (720 mg, 1.18 mmol) and THF (7.0 mL) were combined in a 4 dram vial with stir pea. 2,2′-bipyridyl (2.0 g, 12.8 mmol) was added to the resulting solution. The reaction mixture was allowed to stir for 3 h, becoming vivid magenta in color. The reaction mixture was added dropwise to stirring pentane (50 mL). The precipitated solid was collected on a 15 mL fine porosity fritted funnel, washed with Et_2O (4 × 10 mL), and desiccated to yield **28** as a magenta solid (709 mg, 89% after accounting for 1/3 equiv bipy impurity). CV (MeCN) $E_{p,a}$ = −0.42 V (NHE). ^{1}H NMR (acetonitrile-d_3, δ): 8.89 (broad s, 1H), 8.11 (broad, 1H), 7.95 (d, 1H, Pz3/5), 7.91 (m, 1H), 7.79 (d, 1H, Pz3/5), 7.49 (ddd, J = 8.5 Hz, 6.9 Hz, 1.5 Hz, 1H), 7.41 (bs, 2H, DMAP A), 7.24 (m, 1H), 7.23 (d, 1H, Pz3/5), 7.02 (d, 1H, Pz3/5), 6.98 (d, 1H, Pz3/5), 6.57 (ddd, J = 6.9 Hz, 6.0 Hz, 1.1 Hz, 1H), 6.47 (d, 2H, DMAP B), 6.39 (m, 2H, Pz4 and Pz3/5), 6.31 (t, 1H, Pz4), 6.11 (m, 2H), 5.93 (t, 1H, Pz4), 2.94 (s, 6H, DMAP Me). Single crystal grown and analyzed by XRD. Highly air-sensitive nature of **28** made bulk purification difficult.

Synthesis of TpMo(NO)(DMAP)(3,4-η^2-*N*-methylpyridin-2(1*H*)-one) (29). Compound **24** (1.0 g, 0.0013 mol), DCM (5 mL), and propylamine (1.2 g, 0.020 mol) were added to a 4 dram vial containing a stir pea. This solution was stirred overnight at room temperature (20 h). The resulting green solution was washed with saturated aqueous $NaHCO_3$ (10 mL), and the aqueous layer was back-extracted with DCM (3 × 5 mL). The organic layers were combined and subsequently dried with $MgSO_4$. The $MgSO_4$ was removed on a 15 mL medium porosity fritted disc, washed with DCM (3 × 5 mL), and the resulting filtrate was evaporated in vacuo to an oil. This oil was then dissolved in DCM (15 mL), and the resulting solution was added to stirring pentane (200 mL), yielding a pale green precipitate. This precipitate was isolated on a 30 mL fine porosity fritted disc, washed with pentane (3 × 10 mL) and desiccated to yield **29** as a pale green solid (728 mg, 98% yield). CV (DMAc) $E_{p,a}$ = +0.08 V (NHE). IR: ν(C−H) = 2927 cm^{-1}, ν(B−H) = 2481 cm^{-1}, ν(CO) = 1615 cm^{-1}, ν(NO) = 1579 cm^{-1}. ^{1}H NMR (acetone-d_6, δ): 8.44 (1H, d, Pz5A **A**), 8.01 (1H, d, Pz3/5 **B**), 7.99 (1H, d, Pz3/5 **B**), 7.98 (1H, d, Pz5C **A**), 7.91 (1H, d, Pz3/5 **B**), 7.84 (1H, d, Pz5B **A**), 7.83 (1H, d, Pz3A **A**), 7.78 (2H, bs, DMAP-A **A**), 7.71 (3H, d, Pz3/5 and DMAP-A **B**), 7.60 (1H, d, Pz3C **A**), 7.51 (1H, d, Pz3/5 **B**), 7.03 (1H, d, Pz3B **A**), 7.00 (1H, d, Pz3/5 **B**), 6.63 (2H, bd, DMAP-B **A**), 6.51 (2H, bd, DMAP-B **B**), 6.37 (1H, t, Pz4 **B**), 6.35 (1H, t, Pz4C **A**), 6.30 (1H, t, Pz4 **B**), 6.21 (1H, t, Pz4A **A**), 6.12 (1H, t, Pz4B **A**), 6.11 (1H, t, Pz4 **B**), 6.08 (1H, d, J = 7.5, H6 **B**), 6.07 (1H, d, J = 7.5, H6 **A**), 5.73 (1H, t, J = 7.4, H5 **B**), 5.33 (1H, dd, J = 7.5, 5.4, H5 **A**), 3.48 (1H, dd, J = 8.6, 5.4, H4 **A**), 3.29 (3H, s, NMe **A**), 3.28 (3H, s, NMe **B**), 3.07 (6H, s, NMe **A**), 3.05 (6H, s, NMe **A**), 3.00 (1H, m, H3 **B**), 2.69 (1H, d, J = 8.6, H3 **A**), 1.69 (1H, m, H4 **B**). ^{13}C NMR (acetone-d_6, δ): 173.6 (CO), 155.2 (DMAP-C), 150.5 (DMAP-A), 146.7 (Pz5A), 142.5 (Pz3B), 141.6 (Pz3C), 137.7 (Pz5C), 136.7 (Pz3A/5B), 135.8 (Pz3A/5B), 123.4 (C6), 109.8 (C5), 108.3 (DMAP-B), 106.9 (Pz4C), 106.4 (Pz4B), 105.7 (Pz4A), 75.3 (C4), 62.8 (C3), 39.1 (DMAP-Me), 34.6 (NMe). Highly air-sensitive nature of **29** made purification difficult.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.0c00047.

^{1}H and ^{13}C NMR of all new compounds (PDF)

Accession Codes

CCDC 1975738−1975748 and 1978999 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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