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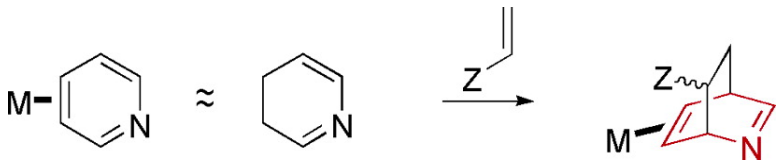

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Facile Diels−Alder Reactions with Pyridines Promoted by Tungsten

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Abstract: The isoquinuclidine (2-azabicyclo[2.2.2]octane) core is found in numerous molecules of biological and medicinal importance, including the widely investigated *Iboga* alkaloids and their related bisindole *Cantharanthus* alkaloids (Sundberg, R. J.; Smith, S. Q. *Alkaloids (San Diego, CA, United States)* **2002**, *59*, 281−386). A diverse range of synthetic methods for the stereoselective construction of this architecture is required for the efficient development of related pharmaceuticals. Here, we report a fundamentally new methodology that constructs the isoquinuclidine core directly from pyridines, using a π-basic tungsten complex to disrupt the aromatic stabilization of these otherwise inert heterocycles. By this approach, common pyridines are found to undergo stereoselective Diels−Alder reactions with electron-deficient alkenes under mild reaction conditions, thus providing access to a broad range of functionalized isoquinuclidines. Further, by using the common terpene α-pinene, a single enantiomer of the tungsten fragment can be isolated and used to provide access to enantio-enriched isoquinuclidines from pyridines.

Introduction

Ubiquitous in nature and readily available from commercial sources, pyridines are attractive as potential feedstocks for the synthesis of polycyclic alkaloids. However, their synthetic value is often marginalized by their inherent aromatic stabilization. For example, whereas dihydropyridines,[1−6] pyridinones,[7−9] and 2-azadienes[10,11] are often used as precursors to the 2-azabicyclo-[2.2.2]octadiene core, the corresponding Diels−Alder reaction with pyridines is virtually unknown. 2,6-(Dimethylamino)-3,4-dicarbomethoxypyridine undergoes cycloaddition with DMAD, but the corresponding cycloadduct is unstable.[12]

Previous studies have shown that benzene can be dearomatized by its η^2 coordination to a π-basic transition metal.[13,14] In a similar vein, we envisioned an approach to the cycloaddition of pyridines that involved its pre-coordination to the powerful π base {TpW(NO)(PMe_3)}.[15] Functioning like a protecting group, the tungsten could effectively isolate the bound C═C fragment from the remainder of the pyridine's π system, thus rendering the bound heterocycle chemically similar to a 2-aza-diene. As a consequence, a Diels−Alder reaction might be feasible with an electron-deficient alkene (Figure 1).

Results and Discussion

Although examples of η^2-pyridine complexes have been previously reported,[16−22] in no case has the bound pyridine been shown to undergo chemical modification. Typically, pyridine binds transition metals through nitrogen, and, unfortunately, this was also the case when TpW(NO)(PMe_3)(η^2-benzene) was allowed to react with an excess of pyridine.[23] However, this coordination mode is discouraged when the pyridine has a

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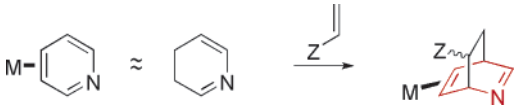


Figure 1. A metal-mediated Diels−Alder reaction with pyridine to construct the isoquinuclidine core.

substituent at the 2-position. Dihapto-coordinated complexes of 2,6-lutidine (**1**) and 2-(dimethylamino)pyridine (**3**) were readily prepared from TpW(NO)(PMe_3)(η^2-benzene) under "low solubility" conditions. Specifically, the desired pyridine is added to the benzene complex in pentane, and the resulting heterogeneous mixture is then stirred for 24−48 h. Isolation of the resulting yellow precipitate is achieved by simple filtration with yields typically greater than 80%. Other pyridine complexes (2-methoxy, 2,6-dimethoxy, 2-TMS, 2-*tert*-butyl) have also been prepared and will be described elsewhere.

Due to the chiral nature of the metal center and the high rotational barrier of the W−(C═C) bond, four coordination diastereomers are possible for each of several available linkage isomers. Fortunately, both complexes **1** and **3** are isolated as single isomers, bound across C3 and C4 of the pyridine. Proton NMR spectra for the lutidine complex **1** indicate the presence of a minor species, **1H** (3:1 ratio), which is the product of an oxidative addition of tungsten across the lutidine C4−H bond. A downfield doublet (J = 99.5) at 8.93 ppm with ^{183}W satellites (J = 32.9) indicates a tungsten hydride, similar to that observed for other reported tungsten hydride complexes.[24] The $[Os(NH_3)_5]^{2+}$ [16] and $(silox)_3Ta$[21] lutidine complexes undergo a similar oxidative addition. If an acidified acetone-d_6 solution is added to a solid sample of **1**, the only complex observed by ^{1}H NMR is **2**, the conjugate acid of **1**. Alternatively, when acid is added to a predissolved solution of **1** (acetone-d_6), complexes **2** and **2H** are observed in a 3:1 ratio, where **2H** is the conjugate acid of the hydride **1H**. When the base DBU is added to either NMR tube, the original 3:1 ratio of **1** to **1H** returns in less than 5 min. Together, these observations indicate that the hydride **1H** is in equilibrium with **1** in solution, but that in the solid state **1H** is not present (Figure 2).

In contrast to **1**, spectra of the (dimethylamino)pyridine analogue **3** do not indicate the presence of a hydridic isomer. Like the lutidine counterpart, **3** is present in solution as a single stereoisomer with the tungsten bound 3,4-η^2. X-ray diffraction data obtained from a single crystal of complex **3** led to confirmation of its molecular structure (Figure 3). Bond lengths for the pyridine ring in **3** indicate significant distortions relative to the uncoordinated ligand and indicate that the unbound portion of the ring resembles the structure of a 2-azadiene. A short C2−N2 bond length (1.376 Å vs 1.42 Å for $C_{Ar}-N_{sp3}$)[25] also indicates a significant π interaction with the amino group.

When combined with acrylonitrile, both pyridine complexes smoothly undergo Diels−Alder reactions to give 2-azabicyclo-[2.2.2]octadiene complexes **4** and **5** (3:1 mixture of **5**(exo):**5**(endo)), respectively. The bicyclic ligands then can be liberated from the metal by treatment with a one-electron oxidant such as silver triflate (eq 1).

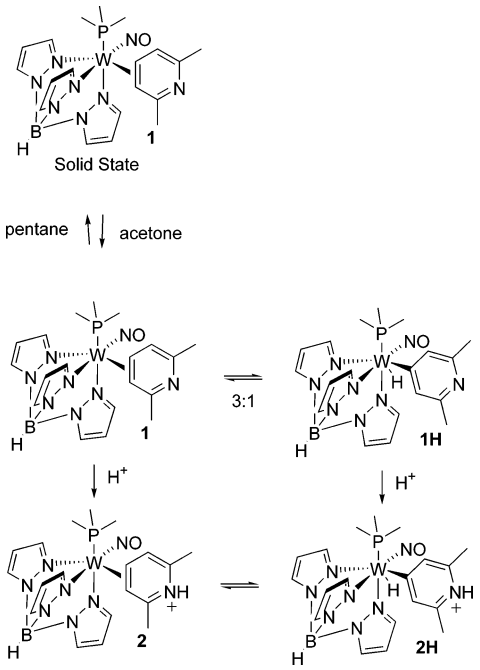


Figure 2. η^2-Lutidine complex (**1**) in equilibrium with lutidinyl hydride (1H).

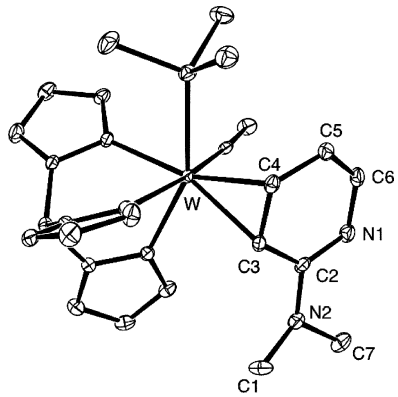
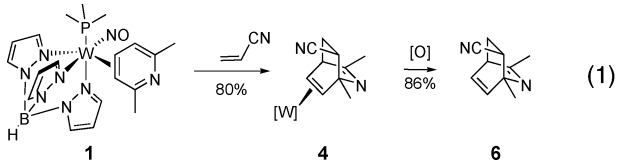


Figure 3. Crystal structure of **3** (30% ellipsoids). Selected bond lengths (Å): W−C4 2.229(4); W−C3 2.241(4); C4−C3 1.448(6); C3−C2 1.454(5); N1−C2 1.318(5); N1−C6 1.386(6); C6−C5 1.332(6); C5−C4 1.456(5); C2−N2 1.376(5).



(1)

Careful examination of NMR data for both complexed cycloadduct **5** and the free cycloadduct **7** indicated a different constitutional isomer than was predicted from the regiochemistry of the aminopyridine complex **3**. A crystal structure of complex **5** confirms that the dimethylamino group is not at the bridgehead position (Figure 4). To obtain the observed product, the 2-(dimethylamino)pyridine ligand of **3** must undergo both a linkage isomerization (ring-walk) and a face-flip to form intermediate **3B**, prior to its undergoing the cycloaddition reaction (Figure 5).

(23) This assignment was supported by electrochemical and IR data, which indicate a metal center more electron-rich than those observed for eta-2 pyridine complexes.

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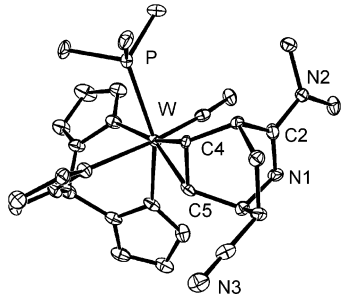

Figure 4. ORTEP diagram of **5** (30% ellipsoids).

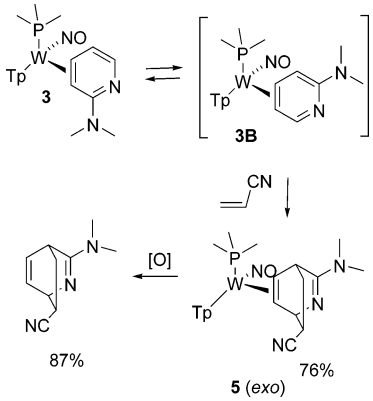

Figure 5. Diels−Alder reaction of **3** with acrylonitrile.

Table 1. Diels−Alder Reactions of Pyridine Complexes **1** and **3**

complex	dienophile	product ratio (exo:endo)	yield
1	acrylonitrile	>20:1	80%
1	*N*-methylmaleimide	<1:20	92%
3	acrylonitrile	3:1	76%
3	ethyl vinyl ketone	1:1	60%
3	methyl acrylate	2:1	20%

Rates have been measured for both face-flip and ring-walk isomerizations for dihapto-coordinated arene,[26] and pyridine complexes,[27] and these occur on a somewhat faster time scale than that observed for cycloaddition. However, it is unclear why the specific rate of cycloaddition for **3B** would be so much greater than that for **3**. The amidine resonance stabilization in **5** likely makes this cycloadduct thermodynamically more stable than one in which the dimethylamino group is at a bridgehead position. Apparently, the transition states of cycloaddition are sufficiently late that they are influenced by the stability of these products.

Table 1 shows preliminary data for Diels−Alder reactions with **1** and **3** and a range of dienophiles. (Attempted cycloaddition reactions with pyridinium complexes such as **2** were unsuccessful.) Three new stereocenters are created in these Diels−Alder products. As expected, the stereochemistry at the newly formed bridgehead positions is controlled for both **4** and **5** by the metal. Because the tungsten fragment blocks one face of the pyridine, the dienophile must approach the pyridine from the opposite face. The remaining stereocenter is derived from the endo/exo approach of the dienophile. Both cycloadducts **4** and **5** are formed with a preference for exo stereochemistry;

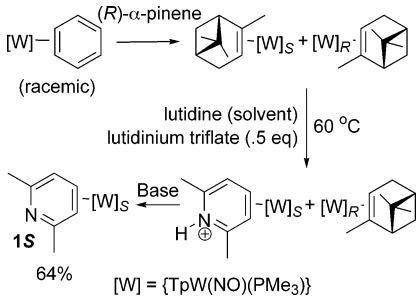

Figure 6. Pinene resolution of lutidine complex **1**.

for **5** this preference is only modest (3:1), while for **4**, the exo isomer is observed exclusively. For the cycloadduct of *N*-methylmaleimide and **1**, however, the endo product dominates. Interestingly, this behavior parallels the selectivity observed for the Diels−Alder reactions of organic cyclic 2-azadienes; acyclic dienophiles give selectivity for exo cycloadducts, and cyclic dienophiles give selectivity for endo cycloadducts.[11]

To demonstrate the ability to control the absolute stereochemistry of the cycloaddition products, an enantio-enriched sample of lutidine complex **1** was prepared using α-pinene in a procedure originally conceived and demonstrated with the rhenium analogue {TpRe(CO)(MeIm)},[28] as follows. The racemic TpW(NO)(PMe_3)(η^2-benzene) complex was first stirred with (*R*)-α-pinene (97% ee) overnight to give a mixture of α-pinene coordination diastereomers $\{W\}_R$,(*R*)-α-pinene (match), and $\{W\}_S$,(*R*)-α-pinene (mismatch). The stability of the two diastereomers with respect to substitution is strikingly different, because the (*R*)-α-pinene must place the methyl group into a sterically encumbered region of the *S* metal fragment. Thus, upon heating to 60 °C in lutidine, this mismatch form exchanges to form the (*S*)-lutidine complex, while the match pinene complex remains intact. The lutidine complex was found to be unstable at this elevated temperature, so 0.5 equiv of the acid lutidinium triflate was added to convert it to **2**. This conversion also allows the easy separation of the match pinene and (*S*)-lutidinium complexes, because only the latter precipitates from an ether solution. Deprotonation gives the resolved (*S*)-lutidine complex in 64% yield based on the available enantiomer (Figure 6).

The enantio-enriched lutidine complex (**1*S***) undergoes cycloaddition with acrylonitrile and subsequent demetalation under conditions and yields similar to those of the racemic mixture. Analysis of the enantio-enriched cycloadduct **6** by chiral HPLC indicates an enantiomer ratio of 90:10 (ee = 80%). The reduced ee of the product in comparison to α-pinene (97%) is tentatively attributed to a partial epimerization of the metal as a result of heating in acid.[28]

Conclusion

The availability and diversity of commercially available pyridines, the exceptionally mild conditions under which cycloaddition occurs, and the ease with which the tungsten fragment can be resolved make the dearomatization of pyridines a potentially valuable new synthetic tool. Although our preliminary data suggest that the methodology may be limited to

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(27) The face-flip isomerization for the analogous 2-(TMS)pyridine complex occurs with a half-life on the order of minutes at 25 °C.
(28) Meiere, S. H.; Valahovic, M. T.; Harman, W. D. *J. Am. Chem. Soc.* **2002**, *124*, 15099−15103.
(29) Sundberg, R. J.; Smith, S. Q. *Alkaloids (San Diego, CA, United States)* **2002**, *59*, 281−386.

2-substituted pyridines, we are currently exploring a full range of pyridines and their proclivity to undergo cycloaddition reactions.

Experimental Section

NMR spectra were obtained on a 300 or 500 MHz spectrometer (Varian INOVA or Avance Bruker). All chemical shifts are reported in ppm and 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). Resonances in the ^{1}H NMR due to pyrazole ligands (Tp) are listed by chemical shift and multiplicity only (all coupling constants are 2 Hz). Infrared spectra (IR) were recorded on a MIDAC Prospect Series (model PRS) spectrometer as a glaze on a Horizontal Attenuated Total Reflectance (HATR) accessory (Pike Industries). Electrochemical experiments were performed under a dinitrogen atmosphere using a BAS Epsilon EC-2000 potentiostat. Cyclic voltammetry data were taken at ambient temperature at 100 mV/s (25 °C) (unless otherwise specified) in a standard three-electrode cell from +1.7 to −1.7 V with a glassy carbon working electrode, *N*,*N*-dimethylacetamide (DMA) solvent, and tetrabutylammoniumhexaflurophosphate (TBAH) electrolyte (∼0.5 M). All potentials are reported versus NHE (normal hydrogen electrode) using cobaltocenium hexafluorophosphate ($E_{1/2} = -0.78$ V) or ferrocene ($E_{1/2} = 0.55$ V) as an internal standard. The peak-to-peak separation was less than 100 mV for all reversible couples. Mass spectra were obtained on either a JEOL JMS600 using FAB^+, or a Finnagan MAT TSQ7000 using ESI^+; no counterions were observed. Elemental analyses (EA) were performed with a Perkin-Elmer 2400 Series II CHN analyzer. Unless otherwise noted, all synthetic reactions and electrochemical experiments were performed under a dry nitrogen atmosphere. CH_2Cl_2, benzene, THF (tetrahydrofuran), and hexanes were purged with nitrogen and purified by passage through a column packed with activated alumina. Other solvents and liquid reagents were thoroughly purged with nitrogen prior to use. Lutidine was distilled before use. Pyridinium, lutidinium, and diphenylammonium triflate were synthesized by addition of triflic acid to the appropriate conjugate base. Deuterated solvents were used as received from Cambridge Isotopes. Stereochemistries were determined through the analysis of NOE, chemical shift, proton-phosphorus, and proton−proton coupling data, as has been previously described.[26]

TpW(NO)(PMe$_3$)(3,4-η^2-2,6-lutidine) (1) + TpW(NO)(PMe$_3$)(H)-(4-(2,6-lutidinyl)) (1H) (3:1 ratio of **1** to **1H** in solution). TpW(NO)-(PMe$_3$)(η^2-benzene) (1.18 g, 2.03 mmol) was dissolved in neat lutidine (4.2 g). Pentane (5 mL) was added, and the resulting heterogeneous mixture was stirred vigorously for 2 d. (The reaction was monitored by taking an aliquot, removing the pentane with a nitrogen stream, dissolving the residue in acetone-d_6, and then subjecting the sample to ^{1}H NMR.) The reaction mixture was added to more pentane (50 mL) to ensure compete precipitation, and then the solid was collected on medium porosity frit and dried in vacuo to give a yellow powder (1.05 g, 1.72 mmol, 85%). Analytical sample recrystallized from lutidine/pentane. IR (HATR glaze): $\nu_{NO} = 1565$ cm^{-1}. CV (DMA, TBAH, 100 mV/s, vs NHE): $E_{p,a} = -0.07$ V, +0.80 V. MS (ESI^+): m/z = 609 $[M - H]^+$. ^{1}H NMR (acetone-d_6, δ) (3:1 ratio of **1** (major) to **1H** (minor)): 8.93 (1H, d (J = 99.5), sat dd (J = 99.5, 32.8), W−H minor), 8.16 (1H, d, Tp minor), 8.03 (1H, d, Tp minor), 8.00 (1H, d, Tp minor), 7.98 (1H, d, Tp major), 7.93 (1H, d, Tp major), 7.92 (1H, d, Tp major), 7.89 (1H, d, Tp major), 7.85 (1H, d, Tp major), 7.82 (1H, d, Tp minor), 7.68 (1H, d, Tp minor), 7.38 (1H, d, Tp major), 7.09 (1H, d, Tp minor), 6.84 (2H, br s, minor 3 and 5), 6.42 (2H, t, 2 Tp minor), 6.32 (2H, overlapping t's, 2 Tp major), 6.29 (1H, t, Tp major), 6.03 (1H, d (J = 4.1), 5 major), 5.97 (1H, t, Tp minor), 4.11 (1H, ddd (J = 4.1, 9.5, 16.0), 4 major), 2.33 (3H, s, 7 or 8 major), 2.25 (1H, d (9.5), 3 major), 2.09 (6H, s, 7 + 8 minor), 2.06 (3H, s, 7 or 8 major), 1.59 (9H, d (J = 9.5), PMe$_3$ minor), 1.32 (9H, d (J = 8.2), PMe$_3$ major). ^{13}C NMR ($CDCl_3$, δ): 191.3 (s, 4 minor), 175.5 (br s, 2 or 6 minor), 157.3 (s, 2 major), 153.0 (br s, 2 or 6 minor), 144.9 (s, Tp major), 144.7 (s, Tp minor), 144.0 (s, Tp major), 143.5 (s, Tp major), 141.2 (s, Tp minor), 139.5 (s, Tp major), 136.8 (s, Tp minor), 136.5 (s, Tp minor), 136.4 (s, Tp minor), 135.9 (s, Tp major), 135.8 (s, Tp major), 128.2 (s, 6 major), 120.2 (s, 5 major), 115.5 (br s, 3 or 5 minor), 115.2 (br s, 3 or 5 minor), 106.3 (br s, 2 Tp major + 2 Tp minor), 105.4 (s, Tp major), 105.2 (s, Tp minor), 64.4 (d (J = 9.2), 4 major), 61.6 (s, 3 major), 29.0 (br s, 7 or 8 minor), 24.2 (s, 7 or 8 major), 22.0 (br s, 7 or 8 minor), 17.4 (d (J = 33.0), PMe$_3$ minor), 13.0 (d (J = 28.1), PMe$_3$ major). ^{31}P: (acetone-d_6, δ): −12.07 (satellite d (J = 309.8), PMe$_3$ major), −3.66 (satellite d (J = 108.7), PMe$_3$ minor).

(*S*)-TpW(NO)(PMe$_3$)(3,4-η^2-2,6-lutidine) (1*S*). TpW(NO)(PMe$_3$)-(η^2-benzene) (365.2 mg, 0.6285 mmol) was dissolved in DME (10 mL), and (*R*)-α-pinene (1.7 g) and K_2CO_3 (1 g) were added. The reaction was stirred overnight (∼18 h). The K_2CO_3 was then filtered out with a medium porosity frit, and the solvent was removed under reduced pressure. The resulting residue was taken in 6 mL of lutidine and transferred to a pressure tube to which was also added lutidinium triflate (86.0 mg, 0.335 mmol, 0.5 equiv) in 2 mL of lutidine. The pressure tube was then sealed and heated to 60 °C in an oil bath overnight (24 h). The solvent was then removed under reduced pressure, and the residue was taken in 3 mL of CH_2Cl_2 and added to Et_2O to give a brown precipitate that was collected on a medium porosity frit. The filtrate containing the "match" form of the α-pinene complex was set aside and could be isolated by precipitation from pentane. The brown precipitate was dissolved in 10 mL of acetone to which was added DBU (81 mg, 0.8 equiv). Et_2O was added to the resulting solution, and the precipitate was collected on a medium porosity frit and discarded. The solvent of the filtrate was removed under reduced pressure, and the residue was dissolved in 3 mL of DME and added to 50 mL of pentane to give a yellow precipitate, which was collected on a medium porosity frit and dried in vacuo to give 122.0 mg (0.200 mmol, 32% yield) of a yellow powder.

TpW(NO)(PMe$_3$)(3,4-η^2-2,6-lutidinium)(OTf) (2). To **1** (37.8 mg, 0.0620 mmol) was added pyridinium triflate (14.8 mg, 0.0646 mmol, 1.04 equiv) in THF (6 mL). The reaction sat for 5 min and was then added to pentane (20 mL). The resulting precipitate was collected on a medium porosity frit and dried in vacuo to give **2** (42.4 mg, 0.0558 mmol, 90%) as an orange powder. IR (HATR glaze): $\nu_{NO} = 1592$ cm^{-1}. CV (DMA, TBAH, 100 mV/s, vs NHE): $E_{p,a} = +0.68$ V. MS (ESI^+): m/z = 611 $[M]^+$. ^{1}H NMR (acetone-d_6, δ): 11.08 (1H, br s, 1 (N−H)), 8.12 (1H, d, Tp), 8.06 (1H, d, Tp), 8.05 (1H, d, Tp), 7.97 (1H, d, Tp), 7.85 (1H, d, Tp), 7.68 (1H, d, Tp), 6.61 (1H, d (J = 4.9), 5), 6.46 (1H, d, Tp), 6.43 (1H, d, Tp), 6.37 (1H, d, Tp), 4.13 (1H, ddd (J = 19.0, 8.2, 4.9), 4), 2.52 (3H, s, 7), 2.49 (3H, s, 8), 2.39 (1H, d (J = 8.2), 3), 1.34 (9H, d (J = 8.9), PMe$_3$). ^{13}C NMR (acetone-d_6, δ): 183.1 (s, 2), 146.0 (s, Tp), 144.8 (s, Tp), 142.2 (s, Tp), 138.6 (s, Tp), 138.4 (s, Tp), 138.2 (s, Tp), 125.4 (s, 6), 121.4 (s, 5), 107.9 (s, 2 Tp), 107.1 (s, Tp), 68.5 (d (J = 12.2), 4), 61.2 (s, 3), 25.0 (s, 8), 16.4 (s, 7), 12.7 (d (J = 29.0), PMe$_3$). ^{31}P (acetone-d_6, δ): −11.25 (satellite d (J = 296.0), PMe$_3$).

TpW(NO)(PMe$_3$)(3,4-η^2-(2-(dimethylamino)-pyridine)) (3). In a 50 mL round-bottom flask were added 2-(dimethylamino)pyridine (5 mL) and pentane (15 mL) to TpW(NO)(PMe$_3$)(η^2-benzene) (3.0 g), forming a suspension that was stirred for 3 d. The mixture then was added to pentane (200 mL), and the precipitate was collected on a fine porosity frit, washed with pentane (30 mL) and acetone (10 mL), and dried in vacuo. TpW(NO)(PMe$_3$)(3,4-η^2-(2-(dimethylamino)pyridine)) (2.75 g, 85% yield) was isolated as a yellow solid. ^{1}H NMR (acetone-d_6): δ 7.91 (1, d, J = 1.9 Hz, Tp), 7.82 (1, d, J = 1.9 Hz, Tp), 7.80 (1, d, J = 2.1 Hz, Tp), 7.73 (1, d, J = 2.3 Hz, Tp), 7.68 (1, d, J = 2.3 Hz, Tp), 7.17 (1, d, J = 2.1 Hz, Tp), 6.45 (1, d, J = 6.8 Hz, 6), 6.29 (1, t, J = 2.1, 2.3 Hz, Tp 4), 6.25 (1, t, J = 2.1, 2.3 Hz, Tp 4), 6.20 (1, t, J = 2.1, 2.3 Hz, Tp 4), 5.73 (1, dd, J = 4.1, 6.6 Hz, 5), 4.03 (1, ddd, J = 4.3, 10.0, 10.5 Hz, 4), 3.17 (3, s(br), N-Me), 2.2 (3, s(br), N-Me), 2.12 (1, d, J = 10.5 Hz, 3), 1.32 (9, d, J = 8.1 Hz, PMe$_3$). ^{13}C NMR

(acetone-d_6): δ 144.0 (Tp), 142.8 (Tp), 139.7 (Tp), 136.9 (Tp), 136.5 (Tp), 136.2 (Tp), 128.2 (6), 109.5 (5), 106.4 (Tp 4), 106.3 (Tp 4), 106.0 (Tp 4), 60.7 (4), 49.5 (3), 13.3 (d, J = 28.3 Hz, PMe_3). $E_{p,a}$ = −0.17 V, $E_{p,a}$ = 8.07 V. MS (FAB^+): m/z = calcd 626.2. Found: 626.1. IR: $\nu_{N\equiv O}$ = 1570 cm^{-1}.

TpW(NO)(PMe_3)(7,8-η^2-(1,3-dimethyl-2-aza-bicyclo[2.2.2]octa-2,7-diene-6-carbonitrile)) (4). To **1** (99.6 mg, 0.1633 mmol) were added 1 mL of DME and 1 mL of lutidine. To this solution was added 2 mL of acrylonitrile. The reaction was then stirred overnight (18 h). The solvent of the reaction mixture was then removed under reduced pressure to give a residue that was taken in 4 mL of CH_2Cl_2 and added to Et_2O (40 mL). The resulting precipitate was then filtered out with a medium porosity frit and discarded. The solvent of the ether filtrate was subsequently removed under reduced pressure to give a light brown residue. This residue was taken in 2 mL of CH_2Cl_2 and added to 60 mL of pentane, which resulted in a precipitate that was collected on a medium porosity frit and dried in vacuo to give **4** (87.6 mg, 0.1313 mmol, 80%) as a white powder. IR (HATR glaze): ν_{NO} = 1557 cm^{-1}, ν_{CN} = 2232 cm^{-1}. CV (DMA, TBAH, 100 mV/s, vs NHE): $E_{p,a}$ = +0.58 V, +1.10 V. MS (ESI^+): m/z = 663 $[M]^+$. ^{1}H NMR ($CDCl_3$, δ): 8.24 (1H, d, Tp), 8.02 (1H, d, Tp), 7.72 (1H, d, Tp), 7.67 (1H, d, Tp), 7.56 (1H, d, Tp), 7.42 (1H, d, Tp), 6.24 (1H, t, Tp), 6.20 (1H, t, Tp), 6.16 (1H, t, Tp), 3.23 (1H, br s, 4), 2.53 (1H, dd (J = 4.6, 10.4), 6), 2.46 (1H, ddd (J = 4.6, 10.2, 15.5), 8), 2.18 (3H, s, 10), 2.12 (1H, ddd (J = 2.3, 10.2, 10.4), 5), 1.97 (1H, ddd (J = 2.3, 4.6, 12.4), 5), 1.85 (3H, s, 9), 1.61 (1H, dd (J = 2.3, 10.2), 7), 1.22 (9H, d (J = 8.2), PMe_3). ^{13}C NMR ($CDCl_3$, δ): 177.3 (s, 3), 147.2 (s, Tp), 142.7 (s, Tp), 104.2 (s, Tp), 136.6 (s, Tp), 135.8 (s, Tp), 135.5 (s, Tp), 123.6 (s, CN), 106.3 (s, Tp), 106.2 (s, Tp), 105.4 (s, Tp), 64.6 (s, 1), 55.4 (s, 7), 53.1 (d (J = 14.9), 8), 43.6 (s, 4), 38.7 (s, 6), 36.9 (s, 5), 27.1 (s, 9), 25.3 (d (J = 27.6), 10), 13.6 (s, PMe_3). ^{31}P (acetone-d_6, δ): −11.58 (satellite d (J = 262.6), PMe_3). Anal. Calcd for $C_{22}H_{31}BN_9OPW$: C, 39.84; H, 4.71; N, 19.01. Found: C, 39.69; H, 4.55; N, 19.33.

TpW(NO)(PMe_3)(7,8-η^2-(3-dimethylamino-2-aza-bicyclo[2.2.2]-octa-2,7-diene-6-carbonitrile)) (5). To **3** (109.0 mg, 0.1744 mmol) was added 3 mL of DME. To this solution was added 3 mL of acrylonitrile. The reaction was then stirred overnight (18 h). The solvent of the reaction mixture was then removed under reduced pressure to give a residue that was taken in 6 mL of CH_2Cl_2 and added to Et_2O (20 mL). The resulting precipitate was then filtered out with a medium porosity frit and discarded. The solvent of the ether filtrate was subsequently removed under reduced pressure to give a light brown residue. This residue was taken in 2 mL of CH_2Cl_2 and added to 60 mL of pentane, which resulted in a precipitate that was collected on a medium porosity frit and dried in vacuo to give **5** (92.0 mg, 0.1329 mmol, 76%) as a white powder. ^{1}H NMR (acetonitrile-d_3, δ): 3:1 ratio of exo:endo, only exo reported, 8.06 (1H, d, Tp), 8.01 (1H, d, Tp), 7.88 (1H, d, Tp), 7.82 (1H, d, Tp), 7.73 (1H, d, Tp), 7.34 (1H, d, Tp), 6.38 (1H, t, Tp), 6.30 (1H, t, Tp), 6.25 (1H, t, Tp), 4.53 (1H, m, 1), 3.74 (1H, dd (J = 2.8, 5.6), 4), 2.86 (6H, br s, N-Me, N-Me), 2.61 (1H, ddd (J = 3.1, 10.4, 13.6), 8), 2.04 (1H, dd (J = 2.1 9.6), 5a), 1.90 (1H, m, 5b), 1.31 (1H, dd (J = 1.9, 8.7), 7), 1.23 (9H, d (J = 8.5), PMe_3). ^{13}C NMR (acetonitrile-d_3): δ 144.3 (s, Tp), 142.4 (s, Tp), 140.3 (s, Tp), 136.5 (s, Tp), 136.0 (s, Tp), 134.8 (s, Tp), 106.1 (s, Tp), 105.9 (s, Tp), 105.7 (s, Tp), 58.9 (s, 1), 55.6 (s, 7), 52.7 (s, 8), 37.1 (s, 6 or N-Me), 35.9 (s, 4), 33.6 (s, 5), 30.7 (s, 6 or N-Me), 12.6 (d (J = 28.4), PMe_3). ^{31}P (acetone-d_6, δ): −15.35 (satellite d (J = 271.7)), PMe_3 exo, −13.42 (satellite d not observed), PMe_3 endo. IR (HATR glaze): ν_{NO} = 1557 cm^{-1}, ν_{CN} = 2232 cm^{-1}. CV (DMA, TBAH, 100 mV/s, vs NHE): $E_{p,a}$ = +0.51 V, +0.93 V. MS (FAB^+): calcd 678.2. Found: 678.0.

1,3-Dimethyl-2-aza-bicyclo[2.2.2]octa-2,7-diene-6-carbonitrile (6). Complex **4** (0.106 g, 0.160 mmol) was dissolved in acetone (1 mL). AgOTf (0.101 g, 0.393 mmol) was added, and the solution was stirred at room temperature overnight. The mixture was filtered through a silica plug (4 cm), washed with acetone (1 mL × 3), and the filtrate was concentrated to a dark red oil. The oil was chromatographed on a preparatory TLC plate using 20% acetone/EtOAc as the eluent. The desired band was cut out, extracted with acetone, and rotary evaporated to dryness to afford **6** (22.0 mg, 86%) as a light yellow oil. ^{1}H NMR ($CDCl_3$, δ): 6.46 (dd, J = 7.5, 6.3 Hz, 1H, 8), 6.26 (d, J = 7.5 Hz, 1H, 7), 3.75 (m, 1H, 4 (bridgehead)), 2.30 (dd, J = 9.6, 5.1 Hz, 1H, 6), 2.10 (s, 3H, 10), 1.96 (s, 3H, 9), 1.84 (ddd, J = 12.6, 9.6, 3.0 Hz, 1H, 5a), 1.54 (ddd, J = 12.3, 4.8, 2.4 Hz, 1H, 5b). ^{13}C NMR ($CDCl_3$): 178.2, (*C*N), 136.2 (8), 132.2 (7), 121.4 (3), 63.1 (1), 42.1 (4), 33.5 (6), 30.7 (5), 23.5 (10), 23.4 (9).

3-Dimethylamino-2-aza-bicyclo[2.2.2]octa-2,7-diene-6-carbonitrile (7). Compound **5** (15 mg) was dissolved in acetone-d_6 (0.7 mL), AgOTf (41 mg) and durene (integration standard, 1.9 mg) were added, and the reaction was allowed to stand for 18 h. Proton NMR data indicated a yield of 87% for the decomplexation. For further characterization, a protonated sample of **7** (**8**) was prepared as follows: Compound **5** (54 mg) was placed in acetone-d_6 (0.7 mL), DPhAT (25 mg) and AgOTf (41 mg) were added, and the reaction sat for 18 h. The solution was added to ether (20 mL), and the filtrate was collected on a fine porosity frit and discarded. The ether was evaporated, and the remaining oil was dissolved in chloroform (1 mL) and added to a 2.5 cm silica gel plug wet with benzene in a pipet. The silica was then rinsed with benzene and EtOAc, and then the product was eluted with MeOH. The MeOH was evaporated, and compound **8** was isolated as a 3:1 exo:endo mixture of products. ^{1}H NMR (acetone-d_6, δ): 3:1 ratio of exo:endo, only exo isomer is reported, 9.57 (1H, s, N−H), 6.90 (1H (ddd, J = 1.1, 5.3, 12.8), 6), 6.78 (1H, ddd (J = 1.7, 7.9, 13.9), 5), 5.20 (1H, dddd (J = 1.7, 3.2, 5.1, 8.5), 1), 4.77 (1H, m, 4), 3.54 (3H, s, N-Me), 3.43 (1H, ddd (J = 1.3, 4.5, 9.4), 7), 3.20 (3H, s, N-Me), 2.52 (1H, dddd (J = 2.3, 9.4, 13.0, 22.6), 8a), 1.85 (1H, dddd (J = 3.0, 4.5, 13.0, 17.5), 8b). ^{13}C NMR (acetone-d_6): δ 167.9 (3), 134.3 (6), 133.6 (5), 51.2 (1), 41.2 (N-Me), 40.1 (N-Me), 36.4 (4), 28.8 (7), 27.7 (8).

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Supporting Information Available: Crystallographic details for compounds **3** and **5** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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