Tungsten-Promoted Diels−Alder Cycloaddition of Pyridines: Dearomatization of 2,6-Dimethoxypyridine Generates a Potent 2-Azadiene Synthon

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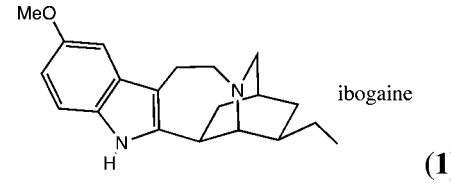
The complex TpW(NO)(PMe_3)(DMP), where DMP is 2,6-dimethoxypyridine, features an η^2-coordinated pyridine ligand that chemically resembles an electron-rich 2-azadiene. As such, it readily reacts with a full range of dienophiles including examples of both alkenes and alkynes to generate azabicyclo[2.2.2]octadiene complexes. Often, one diastereomer spontaneously precipitates from the reaction solution. The bicyclic ligand in these complexes can in some cases be directly removed from the metal by the action of an oxidant (e.g., CAN) and in other cases can be chemically modified prior to its removal. Crystal structures of five tungsten cycloadduct complexes are included. A related complex of 2,6-lutidine is found to react with the nitrile dienophile ethyl cyanoformate to form a new dihapto-coordinated pyridine complex that is derived from a purported diaza[2.2.2]octatriene intermediate.

Introduction

The construction of numerous polyheterocyclic scaffolds has been achieved utilizing hetero-Diels−Alder reactions.[1−5] In particular, the isoquinuclidine skeleton, found in a variety of alkaloids (e.g., ibogaine, **1**) and their pharmaceutically derived analogues,[6−9] has been prepared using azabutadienes,[10−13] dihydropyridines,[14,15] or pyridones,[8] combined with various dienophiles. Common pyridines would be attractive alternatives as sources of azadienes, but their aromatic stability normally renders them unsuitable for such cycloaddition reactions.



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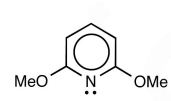
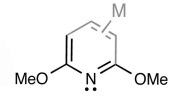
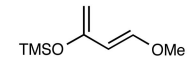
Recently, we reported the ability to form dihapto-coordinated complexes of 2,6-lutidine and 2-(dimethylamino)pyridine with a π-basic tungsten complex.[16,17] Once coordinated, the pyridine ring is *dearomatized*, activating this heterocycle toward cycloaddition reactions. Unfortunately, only a narrow range of dienophiles reacted with these pyridine complexes.[16] We postulated that if 2,6-dimethoxypyridine (η^2-DMP) were bound to {TpW(NO)(PMe_3)}, the uncoordinated portion of this ring should take on a chemical nature similar to that of Danishefsky's diene. Specifically, the combination of π-donation from both tungsten and the methoxy groups was expected to render this pyridine a potent reagent for cycloaddition reactions. The following study explores the potential of TpW(NO)(PMe_3)(4,5-η^2-DMP) as an azadiene synthon for azabicyclic frameworks.



DMP





Danishefsky's Diene

Results and Discussion

The DMP complex TpW(NO)(PMe_3)(4,5-η^2-DMP) (**3**) is prepared by stirring a suspension of the benzene complex

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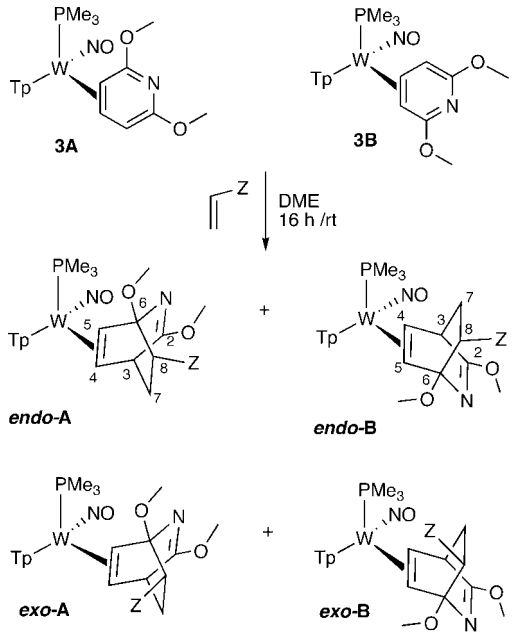
Scheme 1. Cycloaddition Reactions of 2,6-Dimethoxypyridine Complex (3) to Form 4−8



$TpW(NO)(PMe_3)(\eta^2$-benzene) (**2**) and DMP in hexanes for 26 h. The resulting yellow precipitate is isolated in 79% yield as a 1:1 equilibrium mixture of coordination diastereomers (**3A** and **3B**; Scheme 1).[17] While **3** could be obtained from its conjugate acid as a single coordination diastereomer,[17] its rate of re-equilibration ($t_{1/2} \approx 10$ min) is significantly faster than that of cycloaddition. Hence an equilibrium mixture was used in all experiments.

Once coordinated to tungsten, DMP was found to react with a broad range of alkene and alkyne dienophiles to form the isoquinuclidine core (Scheme 1, Figure 1).

In a typical experiment, an excess of the dienophile was dissolved in DME, complex **3** was added, and the resulting solution was allowed to stir for 16 h at ambient temperature. Large differences in the anodic peak currents and $^{183}W-^{31}P$ coupling constants for **3** and its products (**4**−**14**) made cyclic voltammetry and ^{31}P NMR valuable tools for monitoring of these reactions.[16] In most cases (all but **5**, **9**, and **10**), the product spontaneously precipitated from solution. The filtrate was then evaporated under reduced pressure, and the residue was dissolved in THF. This solution was then added to pentane to induce precipitation of any remaining products. Analyses of the product mixtures are reported in Table 1, where the reported yield is the combined mass of all *precipitated* products.

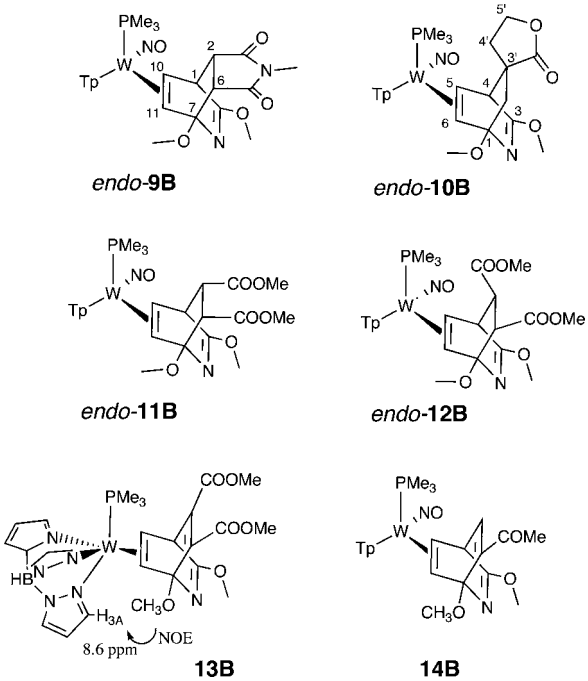


Figure 1. Cycloadduct complexes **9**−**14** (only endo isomer shown for **9**−**12**; for **12B**, the "endo" designation refers to the carbomethoxy group closest to the nitrogen).

Table 1. Cycloadditions with TpW(NO)(PMe$_3$)(η^2-2,6-dimethoxypyridine) (3)

dienophile	dr (A:B)	dr (exo:endo)	yield (isolated)
4 Z = $COCH_3$	1:1.4	1.7:1[a]	84%
5 Z = $COCH_2CH_3$	1:1.4	1.9:1[a]	70%
6 Z = CN	1:1	3.6:1[a]	89%
7 Z = $SO_2C_6H_5$	1:3.3	1:3.0[a]	85%
8 Z = CO_2CH_3	1.0:1	1.4:1[a]	89%
9 α-methylene-γ-butyrolactone	1:1.2	4.6:1[ab]	61%
10 *N*-methylmaleimide	1:1	6.0:1[c]	60%
		1.0:1[a]	
11 dimethyl maleate	1:2.0	1:8.2[a]	81%
12 dimethyl fumarate	1: 1.1	3.2:1[a]	78%
13 DMAD	1: 1.1	N/A	81%
14 3-butyne-2-one	1: 1.5	N/A	80%

[a] Determined for **B** isomer only. [b] Geometry of isomers unknown. [c] Determined by NOE.

Table 2. Isomer(s) Isolated by Precipitation from DME Reaction Mixture

compound	dienophile	major isomer	yield of isolated isomer
4	$H_2CCHCOCH_3$	*exo*/*endo* **4B**	54%
6	H_2CCHCN	*exo* **6B**	32%
7	H_2CCHSO_2Ph	*exo* **7B**	39%
8	H_2CCHCO_2Me	*exo* **8B**	17%
11	dimethyl maleate	*endo* **11B**	40%
12	dimethyl fumarate	*exo* **12B**	39%
13	DMAD	**13B**	55%
14	3-butyne-2-one	**14B**	56%

The structural and stereochemical characterizations of the isolated products (**4**−**14**) were assigned on the basis of CV, IR, ^1H and ^{13}C NMR, NOE, and H−H coupling data, as first described for the lutidine analogue.[17] For example, diagnostic chemical shifts for the **B** diastereomers include proton resonances associated with the tungsten-bound carbons (H4 and H5) near 2.5 ppm (ddd) and 1.8 ppm (dd), respectively. The former exhibits a ^{31}P coupling of ∼10 Hz. The **A** diastereomers have their H5 proton resonances near 2.4 ppm (dd) coupled to ^{31}P (∼10 Hz), and the corresponding H4 signals are multiplets *upfield* of the PMe_3 signal (<1.3 ppm). The most downfield Tp doublet for the **A** diastereomers is near 8.10 ppm, while for the **B**-type isomers, one Tp signal is consistently in the range 8.6−8.8 ppm. NOESY data for the DMAD analogue **13B** indicate that this proton (H_{3A}; see Figure 1) belongs to the pyrazole ring trans to the PMe_3 group and is in close proximity to the bridgehead methoxy group. In every case where a precipitate forms directly from the initial reaction solution, a **B** coordination diastereomer was isolated exclusively (Table 2). Structural and stereochemical assignments for *exo*-**5B**, *exo*-**6B**, *exo*-**8B**, *exo*-**11B**, and *exo*-**12B** were confirmed by X-ray crystallography, and the corresponding ORTEP diagrams appear in Figures 1 and 2.[18]

(18) The crystal structure of *exo*-**7B** shows internal disorder. This prevented us from obtaining meaningful bond lengths, but the stereochemistry was confirmed.

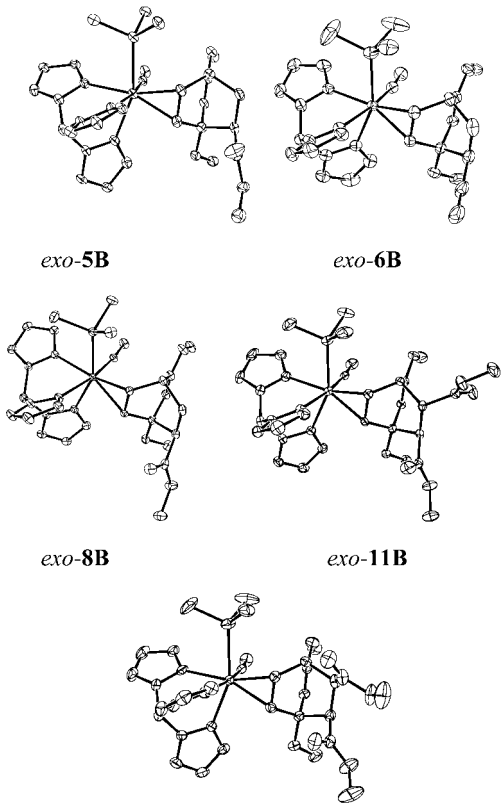
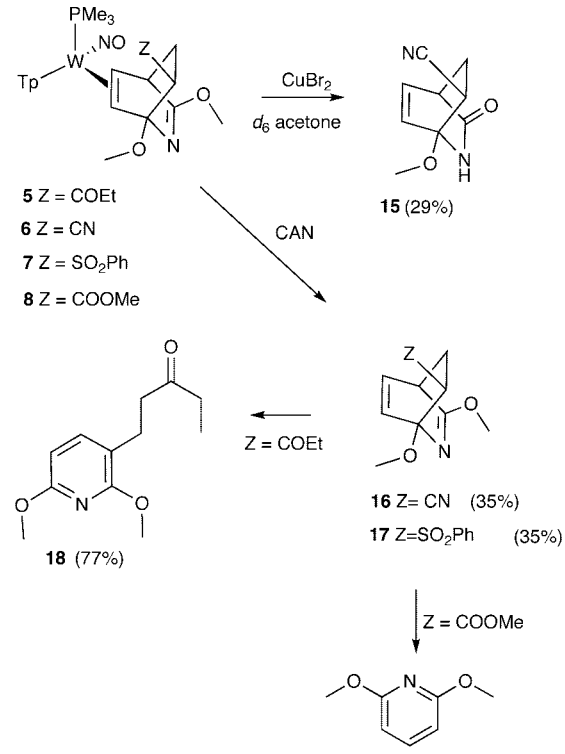


Figure 2. ORTEP diagrams for structures *exo*-**5B**, *exo*-**6B**, *exo*-**8B**, *exo*-**11B**, and *exo*-**12B**.

In order to gain insight into the mechanism of the cycloaddition, we examined the dependence of the reaction rate and stereochemistry on solvent polarity. We postulated that if the reaction was sequential (i.e., a Michael addition reaction followed by an aldol), then it should be accelerated in a more polar solvent. Hence, two solutions of methyl acrylate [6×10^{-4} M] were prepared, one in DME and one in DMF. To each, the pyridine complex **3** [6×10^{-5} M] was added, and the reaction was monitored by ^{1}H NMR spectroscopy. The pseudo-first-order rate constants were determined to be 8.7×10^{-5} and 1.2×10^{-4} s^{-1} (22 °C). While the more polar solvent (DMF) did accelerate the reaction, the solvent effect was minor, corresponding to a difference in $\Delta G^{\ddagger}$ values of only 0.20 kcal/mol. Further, the distribution of stereoisomers in the crude reaction mixture was found to be virtually independent of solvent polarity. These results are in contrast to the solvent dependence predicted for 3,4-dihydropyridines by Ghosez et al.[10] Finally, if the reaction occurred through a stepwise mechanism, a trans stereochemistry would be expected for the two ester groups originating from maleate (**11**) or fumarate (**12**) dienophiles. Indeed, such was the case for cycloaddition reactions with the analogous 2,5-dimethylpyrrole complexes.[19] However, the reactions of **3** with maleate and fumarate methyl esters lead to two different stereoisomers (see Figure 1) with no trace of the complementary epimer. Taken together, these observations suggest a concerted reaction mechanism.

Demetalation of Isoquinuclidine Scaffold. Various one- and two-electron oxidants were screened with the expectation that a more electron-deficient tungsten(I) or tungsten(II) species would release the W–alkene bond in complexes **4**–**14**. A similar strategy was successfully applied in our initial exploration of pyridine cycloaddition reactions.[16] Demetalation of the azabicyclooctadiene core of nitrile **6** was ultimately achieved by subjecting it to 1.1 equiv of ceric ammonium nitrate (CAN) in deuterated acetone (**16**, Scheme 2). The crude ^{1}H NMR spectrum of **16** reveals the disappearance of protons associated with metal-bound carbons (H4/H5) and the formation of two olefinic proton signals near 6.4 ppm with 7 Hz vicinal coupling. Silica chromatography led to the isolation of **16** in 35% yield. This process was repeated with the sulfone cycloadduct (**7**), producing **17** in 35% yield (Scheme 2). Interestingly, the treatment of **6** with a solution of $CuBr_2$ in deuterated acetone or acetonitrile also effected decomplexation, but NMR analysis revealed that the imidate group of the isoquinuclidine was hydrolyzed by adventitious water to form the bicyclic amide **15** in a 30% yield. The ^{1}H NMR spectrum of **15** shows the loss of one of the methoxy groups and the appearance of an amide proton at 7.9 ppm. An IR spectrum of the isolated product revealed signals at 1688 and 1611 cm^{-1}, indicating the presence of an amide.[18] Hydrolysis of the imidate was not observed for any other cycloadduct complex or oxidant.

Scheme 2. Attempted Oxidative Demetalation of Cycloadducts 5–8



When methyl ester **8** was subjected to CAN, the anticipated isoquinuclidine was observed in the ^{1}HNMR spectrum of the crude product, but its signals were dwarfed by those of 2,6-dimethoxypyridine, the product of a retro-cycloaddition reaction. When the ketone-derived cycloadduct **5** was exposed to CAN, the bicyclic structure opened, but in this case the recovered product was the trisubstituted pyridine, **18** (Scheme 2). Aromatic protons at 6.20 and 7.30 ppm were observed in the ^{1}H NMR spectrum of this compound along with two sets of geminal protons near 2.7 ppm.

Speculating that both the retro-cycloaddition and ring-opening decomposition pathways in Scheme 2 were likely facilitated by the electron-withdrawing substituents originating from the dienophile, we endeavored to modify this group prior to

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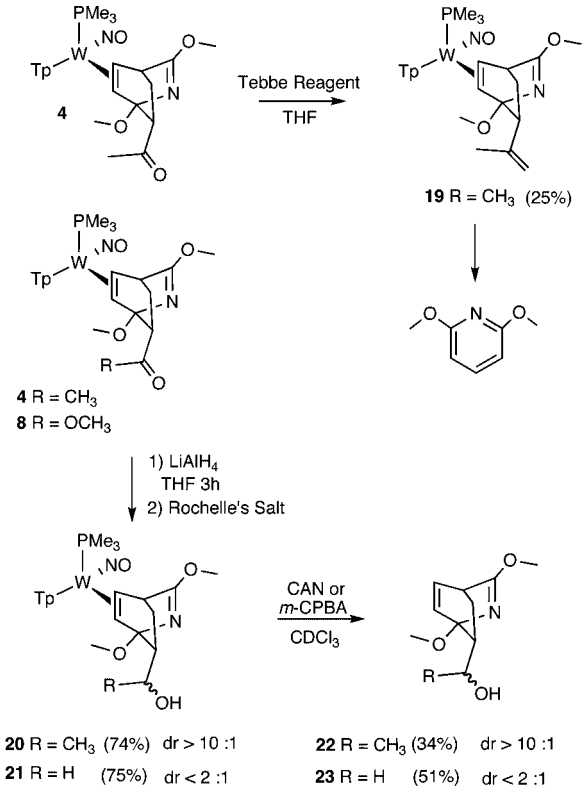
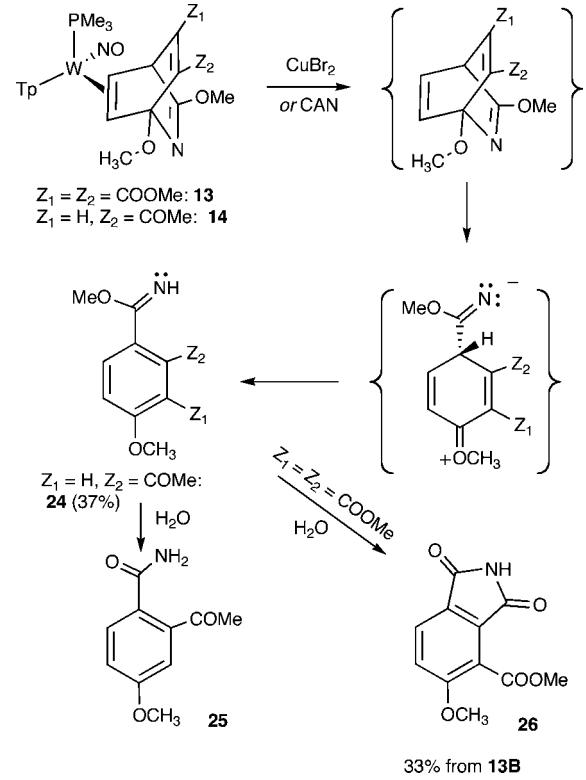
Scheme 3. Reduction and Decomplexation of 4 and 8



decomplexation. This study also allowed us to evaluate the compatibility of the metal system with nucleophilic/basic regents. Reduction of the ketone and ester cycloadducts (**4** and **8**) with $LiAlH_4$ yielded the secondary and primary alcohol isoquinuclidines (**20** and **21**) with overall yields of 74% and 75%. Treating **20** and **21** with either 1 equiv of CAN or 2 equiv of recrystallized *m*-CPBA (*Caution: shock sensitive*) led to the oxidation of the tungsten complex and the isolation of the isoquinuclidines **22** and **23** in a 51% and 34% yield, respectively (Scheme 3). Further, the ketone cycloadduct (**4**) could be olefinated using the Tebbe reagent, to generate **19** (25%; Scheme 3). To our surprise, oxidative demetalation of **19** with CAN, $CuBr_2$, or AgOTf yielded only the retro-cycloaddition product 2,6-dimethoxypyridine.

With the hope of obtaining a rare example of an azabarrelene, we treated the butynone-derived cycloadduct **14** with the mild oxidant AgOTf. The reaction mixture was then subjected to chromatography, and the new product **24** was isolated. ^{1}H NMR and IR spectra indicated an acetyl group, two methoxy groups, and three aromatic protons in the range 7−8 ppm. ^{13}C NMR data and MS confirmed the identity of **24** as a benzimidate derivative (Scheme 4), purportedly the result of the ring-opening of a liberated azabarrelene followed by proton transfer (Scheme 4). Attempts to purify this material were hampered by its slow decomposition to what we suspect is the corresponding benzamide **25**. A proton NMR spectrum of **25** indicates that it is similar to **24** but contains one less methoxy group, and LRMS (ESI+) shows a parent ion of 194 (M + 1). Repeating this decomplexation procedure with the DMAD-derived cycloadduct complex **13** delivers an arene product with only one methoxy group. ^{13}C NMR and LRMS data along with a high-frequency carbonyl stretching absorption at 1762 cm^{-1} indicate that a ring-opening process occurs similar to that postulated for the formation of **24**, but in this case hydrolysis and condensation form the novel phthalimide **26**.

Scheme 4. Oxidative Decomplexation of Azabarrelene Complexes (13 and 14)

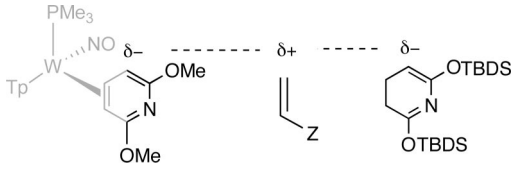


Nitrile Metathesis. The Diels−Alder/retro-Diels−Alder sequence above that ultimately resulted in the conversion of 2,6-dimethoxypyridine to substituted arenes led us to postulate that an analogous reaction might be accessible in which a η^2-pyridine reacts with a nitrile to form a new η^2-pyridine and nitrile combination. While unactivated nitriles have been observed to undergo Diels−Alder reactions only under harsh reaction conditions, Mander's reagent (ethyl cyanoformate) has been documented to undergo such a reaction with dienes at or below 20 °C.[20] Hence, the pyridine complex **3** was subjected to this reagent at −10 °C and the reaction followed by ^{1}H NMR. We also examined the unactivated pyridine complex derived from 2,6-lutidine, **27**, for comparison. While reaction of **3** and Mander's reagent gave a complex mixture of products, when the lutidine complex (**27**) was exposed to ethyl cyanoformate at −10 °C, a single new complex (**28**) was isolated. ^{1}H NMR spectra identify the complex as a new η^2-pyridine species in which one of the methyl groups has been replaced by an ester group, the product of a nitrile metathesis (Scheme 5). Attempts to isolate the diazabicyclooctatriene intermediate were unsuccessful, and the generation of free CH_3CN was not verified.

With the tungsten preferentially coordinating the C4 and C5 carbons of the pyridine in **3**, the uncoordinated portion of the ring is analogous to the TMSO-disubstituted cyclic 2-azadiene extensively explored by Ghosez et al.[13] The regiochemical preference in both systems is distinct, with the positively polarized dienophile carbon forming a bond with the 4-position of the 2-azadiene. Ghosez found the usual kinetic preference for endo cycloaddition with cyclic dienophiles, but open-chain dienophiles showed a distinct exo kinetic selectivity.[13] In Table 1, the exo/endo ratios are not as dramatic as found by Ghosez et al., but the same general trend is observed.

The activation of pyridine through dihapto coordination was first documented using the examples of 2,6-lutidine and 2-(dim-

(20) McClure, C. K.; Link, J. S. *J. Org. Chem.* **2003**, *68*, 8256–8257.



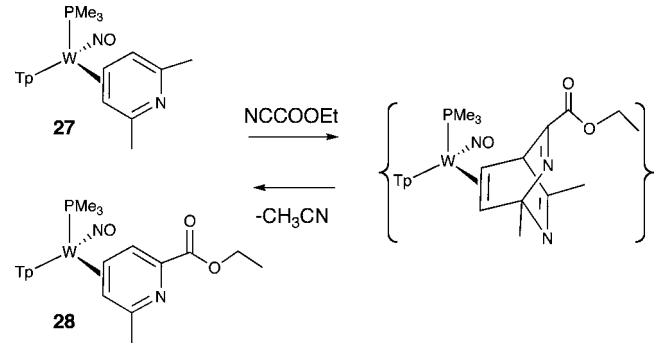
ethylamino)pyridine.[16] Other than this report, the only example that we are aware of involving cycloaddition to a pyridine are those of Gompper[21] and Neunhoeffer,[22] who independently described the cycloaddition of dimethyl 2,6-bis(dimethylamino)pyridine-3,4-dicarboxylate and DMAD (Scheme 6). However, in that case the azabarralene readily rearomatized via a retrocycloaddition, yielding a pentasubstituted benzene. Other relevant examples of pyridinium-like aromatic molecules undergoing cycloaddition include reactions with isoquinolinium[23] and azoniaanthracene.[24] The Diels–Alder reaction of an η^2-benzene complex with *N*-methylmaleimide has also been demonstrated.[25,26]

In conclusion, the coordination of 2,6-dimethoxypyridine by {TpW(NO)(PMe_3)} and subsequent removal of the metal provides the formal equivalent of a Diels–Alder cycloaddition with this heterocycle, a reaction that typically is thermodynamically unfavorable in the absence of extreme pressures. Once formed, the cycloadduct is moderately stable and in some cases can be isolated. The use of a dihapto-coordinated 2,6-dimethoxypyridine allows access to a full range of alkene and alkyne dienophiles, and in some cases, these azabicyclic skeletons can be chemically modified while bound to the tungsten fragment prior to their decomplexation.

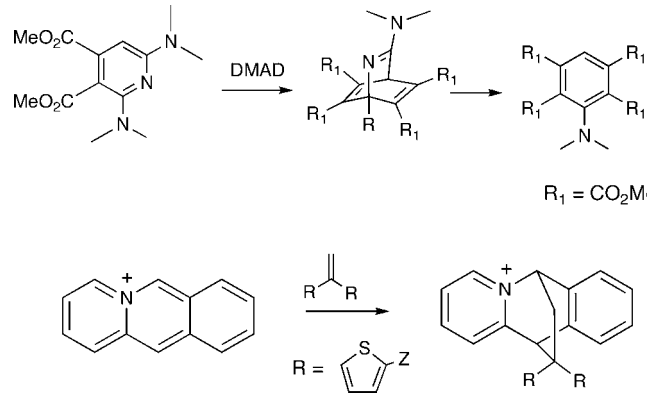
Experimental Section

General Methods. All NMR spectra were obtained on either a 300 or 500 MHz Varian INOVA or Bruker AVANCE spectrometer. All chemical shifts are reported in ppm versus tetramethylsilane using residual shifts of the deuterated solvent as the internal standard. All coupling constants (*J*) are reported in hertz (Hz). All ^{31}P NMR data are reported versus an external standard in acetone (trimethylphosphate, −16.58 ppm). Infrared spectra were obtained on a MIDAC Prospect Series spectrometer as a glaze on a horizontal attenuated total reflectance (HATR) cell from Pike Industries. Electrochemical measurements were taken under a nitrogen atmosphere using a BAS Epsilon EC-2000 potentiostat. Cyclic voltammetry data were obtained in a three-electrode cell from +1.7 to −1.7 V, with a glassy carbon working electrode, a platinum wire auxiliary electrode, and a platinum wire reference electrode. All data were obtained using a 100 mV/s scan rate with tetrabutylammonium hexafluorophosphate (TBAH) as the electolyte in *N,N*-dimethylacetamide (DMA) unless otherwise noted. All potentials were reported versus the normal hydrogen electrode (NHE) using cobalticinium hexafluorophosphate ($E_{1/2} = -0.78$ V) as an internal standard. For reversible waves the peak to peak separation was less than 100 mV. High-resolution mass spectrometry data (HRMS) was obtained using either a 1:1 water:/acetonitrile solution with sodium trifluoroacetate as a standard on a Bruker BioTOF-Q instrument

Scheme 5. Nitrile Metathesis in the Reaction of Ethyl Cyanoformate and Lutidine Bound to Tungsten



Scheme 6. Examples of Pyridine and Azoniaanthracene Cycloaddition



or was performed by the University of Illinois Urbana–Champaign School of Chemical Sciences (UIUC when noted). The data for metal complexes are reported using the five most intense peaks from the isotopic envelope and are listed as *m*/*z* with the intensity relative to the most abundant peak of the isotopic envelope given in parentheses for both the calculated and the observed peaks. The difference between calculated and observed peaks is reported in ppm. For isolated organic products, the monoisotopic peak is reported, with the observed, calculated, and ppm difference again provided. Thin-layer chromatography was performed on a Uniplate silica gel GF from Analtech Inc. Methylene chloride and benzene were run down a column packed with activated alumina and purged with nitrogen prior to use. All other solvents and chemicals were used as received from Sigma-Aldrich, Acros Chemicals, or Fischer Scientific. 3-Chloroperbenzoic acid (*m*-CPBA) was recrystallized by using a procedure from Bortolini et al.[27]

Preparations. The cycloaddition reactions forming compounds **4**–**13** typically resulted in mixtures of several diastereomers. These mixtures were inseparable using column chromatography, and extensive overlap of NMR signals prevented their full characterization. Detailed characterizations were possible only in cases where one or two isomers cleanly precipitated from the reaction mixture (see Table 2). The A/B ratio for each crude reaction mixture was determined on the basis of NMR data (e.g., H4 and H5 chemical shifts). The exo/endo ratio was determined specifically for the **B** isomer, where X-ray data could identify one of the stereoisomers. The only exception to this is compound **10**, where endo isomers were confirmed by NOE interactions between H10 or H11 and protons originating from the maleimide ring (H2 and H6).

[TpW(NO)(PMe_3)(4,5-η^2-1-(1,3-dimethoxy-2-azabicyclo[2.2.2]octa-2,5-dien-7-yl)ethanone))] (4). A 2-dram vial containing 0.100 g of methyl vinyl ketone (1.43×10^{-3} mol, 6 equiv) was solvated with

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1.723 g of DME that was dried over basic alumina. This stock solution was added to a preweighed 2-dram vial containing 0.153 g of **3** (2.379×10^{-4} mol, 1 equiv). The resulting homogeneous mixture was allowed to react at room temperature for 16 h. The resulting heterogeneous mixture was filtered over a 30 mL fine fritted glass disk and washed with 50 mL of fresh Et_2O. An off-white precipitate **4B** was isolated and dried under vacuum. The isolated yield of the pure **B** isomer was 54% in a diastereomer ratio of 1.7:1 *exo*/*endo*. Overall, the reaction yield was 84% (**A** and **B**). ^{1}H NMR ($CDCl_3$, ambient temperature, 300 MHz, δ): **4B** *exo* 8.79 (1H, d, J = 2.0 Hz, Tp), 8.13 (1H, d, J = 2.0 Hz, Tp), 7.69 (1H, d, J = 2.0 Hz, Tp), 7.63 (1H, d, J = 2.0 Hz, Tp), 7.45 (1H, d, J = 2.0 Hz, Tp), 7.29 (1H, d, J = 2.0 Hz, Tp), 7.26 ($CDCl_3$), 6.28 (2H, m, Tp major and minor), 6.12 (2H, m, Tp major and minor), 6.08 (1H, t, J = 2.2, 4.1 Hz, Tp), 3.82 (3H, s, H11), 3.76 (3H, s, H12), 3.39 (1H, dd, J = 4.1,9.8 Hz; H8), 3.06 (1H, m, H3), 2.45 (1H, m, H7), 2.37 (1H, m, H4 major and minor), 2.27 (3H, s, H10), 1.76 (1H, m, H7′) 1.43 (1H, dd, J = 2.6, 10.4 Hz, H5), 1.23 (9H, d, J = 8.4 Hz, PMe_3). **4B** *exo* ^{13}C NMR ($CDCl_3$, ambient temperature, 300 MHz, δ): 210.2 (C9), 168.2 (C2), 149.3 (Tp d), 143.0 (Tp d), 140.8 (Tp d), 136.7 (Tp d), 135.7 (Tp d), 134.6 (Tp d), 106.5 (Tp t), 105.9 (Tp t), 105.2 (Tp t), 100.3 (C6), 77.0 ($CDCl_3$, t), 55.4 (C5), 54.3 (C8), 54.2 (d, J = 16.0 Hz, C4), 53.6 (C11), 49.8 (C12), 41.0 (C3), 34.0 (C7), 32.2 (C10), 14.0 (d, J = 27.5 Hz, PMe_3). **4B** *endo* ^{1}H NMR ($CDCl_3$, ambient temperature, 300 MHz, δ): 8.62 (1H, d, J = 2.0 Hz, Tp), 8.06 (1H, d, J = 2.0 Hz, Tp), 7.71 (1H, d, J = 2.0 Hz, Tp), 7.67 (1H, d, J = 2.0 Hz, Tp), 7.51 (1H, d, J = 2.0 Hz, Tp), 7.26 ($CDCl_3$), 7.24 (1H, d, J = 2.0 Hz, Tp), 6.28 (2H, m, Tp major and minor), 6.21 (1H, t, Tp), 6.12 (2H, m, Tp major and minor), 3.89 (3H, s, H11), 3.55 (1H, dd, J = 4.4,9.6 Hz; H8), 3.23 (3H, s, H12), 3.17 (1H, m, H3), 2.45 (1H, m, H7), 2.37 (2H, m, H4 major and minor), 2.20 (3H, s, H10), 2.05 (1H, m, H7′) 1.43 (2H, dd, J= 2.6, 10.4 Hz, H5 major and minor), 1.28 (9H, d, J = 8.4 Hz, PMe_3). **4B** *endo* ^{13}C NMR ($CDCl_3$, ambient temperature, 300 MHz, δ): 211.5 (C9), 166.8 (C2), 148.4 (Tp d), 143.2 (Tp d), 140.3 (Tp d), 136.9 (Tp d), 135.9 (Tp d), 134.8 (Tp d), 106.6 (Tp t), 105.8 (Tp t), 105.7 (Tp t), 100.8 (C6), 77.0 ($CDCl_3$, t), 58.9 (C8), 54.7 (C11), 54.6 (C5), 53.8 (d, J = 15.1 Hz, C4), 51.3 (C12), 41.2 (C3), 36.0 (C7), 28.9 (C10), 14.2 (d, J = 28.2 Hz, PMe_3). IR: ν(NO) = 1574 cm^{-1} (vs), ν(imidate) = 1648 cm^{-1} (s), ν(CO) = 1698 cm^{-1} (s). CV: $E_{p,a}$ = +0.62 V. HRMS (*m*/*z*, obsd(I); calcd(I); error (ppm)): 711.20967 (94%), 711.20985 (83%), 0.25; 712.21195 (83%), 712.21240 (80%), 0.63; 713.21097 (100%), 713.21228 (100%), 1.83; 714.21493 (47%), 714.21635 (44%), 1.98; 715.21481 (89%), 715.21551 (83%), 0.97.

[TpW(NO)(PMe$_3$)(4,5-η^2-(1-(1,3-dimethoxy-2-azabicyclo[2.2.2]octa-2,5-dien-7-yl)propan-1-one))] (5). The synthesis is similar to compound **4**. ^{1}H NMR (d_6-acetone, ambient temperature, 300 MHz, δ): **5B** *exo* 8.81 (1H, d, J = 1.5 Hz, Tp), 8.17 (1H, d, J = 1.9 Hz, Tp), 7.93 (1H, d, J = 2.3 Hz, Tp), 7.88 (1H, d, J = 2.2 Hz, Tp), 7.62 (1H, d, J = 2.2 Hz, Tp), 7.49 (1H, d, J = 1.9 Hz, Tp), 6.39 (2H, m, Tp major and minor), 6.29 (2H, m, Tp major and minor), 6.12 (1H, t, J = 2.2, 4.1 Hz, Tp), 3.74 (3H, s, H12), 3.72 (3H, s, H13), 3.45 (DME), 3.35 (1H, dd, J = 4.0,9.7 Hz, H8), 3.27 (DME), 3.10 (1H, m, H3), 2.45 (1H, m, H7), 2.37 (1H, m, H4 major and minor), 2.27 (3H, s, H10), 1.76 (1H, m, H7′) 1.43 (1H, dd, J= 2.6, 10.4 Hz, H5), 1.28 (9H, d, J = 8.5 Hz, PMe_3), 0.88 (3H, t, J = 7.2,14.3 Hz, H13). **5B** *exo* ^{13}C NMR (d_6-acetone, ambient temperature, 300 MHz, δ): 210.3 (C9), 167.8 (C2), 148.9 (Tp d), 143.0 (Tp d), 141.0 (Tp d), 136.9 (Tp d), 135.8 (Tp d), 134.6 (Tp d), 106.2 (Tp t), 105.8 (Tp t), 104.8 (Tp t), 100.1 (C6), 71.6 (DME), 57.9 (DME), 54.4 (C5), 53.9 (d, J = 15.2 Hz, C4), 53.4 (C8), 52.6 (C12), 48.7 (C13), 40.8 (C3), 36.6 (C10), 33.9 (C7), 12.8 (d, J = 28.2 Hz, PMe_3) 7.43 (C11). **5B** *endo* ^{1}H NMR (d_6-acetone, ambient temperature, 300 MHz, δ): 8.62 (1H, d, J = 2.0 Hz, Tp), 8.06 (1H, d, J = 2.0 Hz, Tp), 7.71 (1H, d, J = 2.0 Hz, Tp), 7.67 (1H, d, J = 2.0 Hz, Tp), 7.51 (1H, d, J = 2.0 Hz, Tp), 7.26 ($CDCl_3$), 7.24 (1H, d, J = 2.0 Hz, Tp), 6.28 (2H, m, Tp major and minor), 6.21 (1H, t, Tp), 6.12 (2H, m, Tp major and minor), 3.89 (3H, s, H11), 3.55 (1H, dd, J = 4.4,9.6 Hz; J = 4.1, 9.8 Hz, H8), 3.23 (3H, s, H12), 3.17 (1H, m, H3), 2.45 (1H, m, H7), 2.37 (2H, m, H4 major and minor), 2.20 (3H, s, H10), 2.05 (1H, m, H7′) 1.43 (2H, dd, J= 2.6, 10.4 Hz, H5 major and minor), 1.28 (9H, d, J = 8.4 Hz, PMe_3). **5B** *endo* ^{13}C NMR (d_6-acetone, ambient temperature, 300 MHz, δ): 211.5 (C9), 166.8 (C2), 148.4 (Tp d), 143.2 (Tp d), 140.3 (Tp d), 136.9 (Tp d), 135.9 (Tp d), 134.8 (Tp d), 106.6 (Tp t), 105.8 (Tp t), 105.7 (Tp t), 100.8 (C6), 77.0 ($CDCl_3$, t), 58.9 (C8), 54.7 (C11), 54.6 (C5), 53.8 (d, J = 15.1 Hz, C4), 51.3 (C12), 41.2 (C3), 36.0 (C7), 28.9 (C10), 14.2 (d, J = 28.2 Hz, PMe_3). IR: ν(NO) = 1574 cm^{-1} (vs), ν(imidate) = 1648 cm^{-1} (s), ν(CO) = 1698 cm^{-1} (s). CV: $E_{p,a}$ = + 0.62 V. HRMS (UIUC) (*m*/*z*, obsd (%), calcd (%), error (ppm)): 725.2261 (81.7%), 725.2235 (82.8%), 3.6; 726.2286 (80.3%), 726.2256 (80.5%), 4.1; 727.2286 (100%), 727.2248 (100%), 5.2; 728.2325 (45.4%); 728.2314 (45%), 1.5; 729.23180 (83.4%), 729.2300 (83.3%) 2.5.

[TpW(NO)(PMe$_3$)(4,5-η^2-(1,5-dimethoxybicyclo[2.2.2]octa-5,7-diene-2-carbonitrile))] (6). The synthesis is similar to compound **4**. ^{1}H NMR (d_6-acetone, ambient temperature, 300 MHz, δ): 8.90 (1H, d, J = 1.7 Hz, Tp), 8.18 (1H, d, J = 1.8 Hz, Tp), 7.96 (1H, d, J = 2.3 Hz, Tp), 7.91 (1H, d, J = 2.1 Hz, Tp), 7.67 (1H, d, J = 2.4 Hz, Tp), 7.62 (1H, d, J = 2.0 Hz, Tp), 6.42 (1H, t, J = 2.1, 4.3 Hz, Tp), 6.28 (1H, t, J = 2.3, 4.4 Hz, Tp), 6.17 (1H, t, J = 2.1, 4.3 Hz, Tp), 3.73 (3H, s, H10), 3.58 (3H, s, H11), 3.45 (3H, DME), 3.27 (3H, DME), 3.19 (1H, m, H3) 3.16 (1H, dd, J = 4.6, 10.1 Hz, H8), 2.59 (1H, ddd, J= 2.7,10.5, 13.0 Hz, H4), 2.37 (1H, ddd, J= 2.4,10.8, 12.7 Hz, H7′), 2.12 (1H, ddd, J= 2.4, 4.6, 12.4 Hz; H7), 2.05 (d_6-acetone) 1.86 (1H, dd, J = 2.7, 10.5 Hz, H5), 1.29 (9H, d, J = 8.4 Hz, PMe_3). ^{13}C NMR ($CDCl_3$, ambient temperature, 300 MHz, δ): 167.2 (C2), 149.0 (Tp d), 142.7 (Tp d), 140.4 (Tp d), 136.5 (Tp d), 135.6 (Tp d), 134.3 (Tp d), 122.4 (C9), 106.3 (Tp t), 105.7 (Tp t), 105.3 (Tp t), 98.4 (C6), 71.7 (DME), 59.0 (DME), 53.8 (C5), 53.7 (C10), 53.6 (d, J = 15.6 Hz, C4), 49.7 (C11), 40.0 (C8), 37.5 (C7), 33.0 (C3), 13.6 (d, J = 28.2 Hz, PMe_3). IR: ν(NO) = 1562 cm^{-1} (vs), ν(imidate) = 1645 cm^{-1} (s), ν(CN) = 2231 cm^{-1} (w). CV: $E_{p,a}$ = +0.65 V. HRMS (*m*/*z*, obsd(I); calcd(I); error (ppm)): 694.19216 (87%), 694.19452 (84%), 3.40; 695.19634 (82%), 695.19705 (80%), 1.02; 696.19659 (100%), 696.19692 (100%), 0.47; 697.20037 (50%), 697.20099 (44%), 0.88; 698.19977 (95%), 698.20016 (84%), 0.58.

[TpW(NO)(PMe$_3$)(4,5-η^2-(1,3-dimethoxy-7-(phenylsulfonyl)-2-azabicyclo[2.2.2]octa-2,5-diene))] (7). The synthesis is similar to compound **4**. ^{1}H NMR ($CDCl_3$, ambient temperature, 300 MHz, δ): 8.53 (1H, d, J = 1.1 Hz, Tp), 8.08 (1H, m, H13), 8.06 (1H, m, H11), 8.01 (1H, d, J = 1.8 Hz, Tp), 7.70 (1H, d, J = 2.0 Hz, Tp), 7.67 (1H, d, J = 2.0 Hz, Tp), 7.54 (1H, m, H14), 7.52 (1H, m, H10), 7.50 (1H, d, J = 1.3 Hz, Tp), 7.48 (1H, m, H12), 7.26 ($CDCl_3$), 7.22 (1H, d, J = 1.6 Hz, Tp), 6.25 (1H, t, Tp), 6.20 (1H, t, Tp), 6.10 (1H, t, Tp), 4.22 (1H, dd, J = 5.1, 9.7 Hz; 5.5, 10.1 Hz, H8), 3.50 (3H, s, H15), 3.08 (1H, m, H3), 2.92 (3H, s, H16), 2.45 (1H, ddd, J = 2.8, 5.5; 14.0 Hz, H7), 2.33 (1H, ddd, J = 2.0, 10.1, 12.6 Hz, H7′), 2.22 (1H, ddd, J = 2.6, 11.5, 13.4 Hz, H4) 1.59 (1H, dd, J = 2.4, 11.0 Hz, H5), 1.23 (9H, d, J = 8.4 Hz, PMe_3). ^{13}C NMR ($CDCl_3$, ambient temperature, 300 MHz, δ): 165.7 (C2), 148.2 (Tp d), 142.8 (Tp d), 140.4 (C9), 139.9 (Tp, d), 136.6 (Tp d), 135.7 (Tp d), 134.6 (Tp d), 132.7 (C12), 130.1 (C11, C13), 128.4 (C10, C14), 106.3 (Tp t), 105.7 (Tp t), 105.4 (Tp t), 98.8 (C6), 68.5 (C8), 54.1(C4), 53.9 (C15), 52.6 (C5), 51.2 (C16), 40.5 (C3), 34.9 (C7), 13.7 (d, J = 28.2 Hz, PMe_3). IR: ν (NO) = 1565 cm^{-1} (vs), ν(imidate) = 1650 cm^{-1} (s). CV: $E_{p,a}$ = +0.74 V. HRMS (*m*/*z*, obs(I); calc(I); error (ppm)): 809.19249 (69%), 809.19255 (78%); 0.07; 810.19511 (79%), 810.19501 (79%), 0.12; 811.19437 (100%), 811.19480 (100%), 0.53; 812.19890 (50%), 812.19829 (50%), 0.75; 813.19961 (73%), 813.19786 (84%), 2.15.

[TpW(NO)(PMe$_3$)(4,5-η^2-(methyl 1,3-dimethoxy-2-azabicyclo-[2.2.2]octa-2,5-diene-7-carboxylate))] (8). The synthesis is similar to compound **4**. ^{1}H NMR ($CDCl_3$, ambient temperature, 300 MHz, δ): 8.81 (1H, d, J = 1.6 Hz, Tp), 8.11 (1H, d, J = 1.8 Hz, Tp), 7.69 (1H, d, J = 2.0 Hz, Tp), 7.63 (1H, d, J = 2.0 Hz, Tp), 7.44 (1H, d, J = 2.0 Hz, Tp), 7.31 (1H, d, J = 1.6 Hz, Tp), 6.27 (1H, t, J = 2.0, 4.2 Hz, Tp), 6.12 (1H, t, J = 2.2, 4.1 Hz, Tp), 6.08 (1H, t, J = 2.2, 4.1 Hz, Tp), 3.80 (3H, s, H11), 3.67 (3H, s, H12), 3.60 (3H, s, H10), 3.13 (1H, dd, J = 4.6, 10.0 Hz, H8), 3.08 (1H, m, H3), 2.44 (1H, ddd, J = 2.6,10.5, 13.3 Hz, H4), 2.21 (1H, ddd J = 2.1, 4.6, 12.1 Hz; H7), 2.08 (1H, buried, H7′) 1.70 (1H, dd, J = 2.6, 10.5 Hz, H5), 1.23 (9H, d, J = 8.2 Hz, PMe_3). ^{13}C NMR ($CDCl_3$, ambient temperature, 300 MHz, δ): 174.8 (C9), 167.4 (C2), 149.0 (Tp d), 142.7 (Tp d), 140.4 (Tp d), 136.2 (Tp d), 135.4 (Tp d), 134.2 (Tp d), 106.1 (Tp t), 105.6 (Tp t), 105.1 (Tp t), 99.7 (C6), 77.0 ($CDCl_3$, t), 54.5 (C5), 54.4 (d, J = 15.3 Hz, C4), 53.3 (C11), 51.5 (C12), 49.3 (C10), 46.9 (C8), 40.6 (C3), 35.8 (C7), 13.7 (d, J = 27.1 Hz, PMe_3). IR: ν(NO) = 1561 cm^{-1} (vs), ν(imidate) = 1648 cm^{-1} (s), ν(CO_2Me) = 1725 cm^{-1} (w). CV: $E_{p,a}$ = +0.65 V. HRMS (*m*/*z*, obsd (%), calcd (%), error (ppm)): 727.2056 (87.9%), 727.2054 (83.2%), 0.27; 728.2087 (80.9%), 728.2079 (80.2%), 1.10; 729.2083 (100%), 729.2078 (100%), 0.68; 730.2116 (44.1%), 730.2119 (44.4%), 0.41; 731.2111 (84.4%), 731.2110 (83.6%), 0.13.

TpW(NO)(PMe$_3$)(4,5-η^2-(1,3-Dimethoxy-4′,5′-dihydro-2azaspiro[bicyclo[2.2.2]octa-2,5-diene-7-3′-furan]-2′-one)) (9). To **3** (0.085 g, 1.321 × 10^{-4} mol, 1 equiv) was added 4 mL of pentane. To this solution was added a solution of α-methylene-γ-butyrolactone (0.039 g, 3.966 × 10^{-4} mol, 3 equiv) in DME (1 mL). The reaction was then stirred overnight (18 h). The reaction mixture was then added to pentane (50 mL). Residue on the sides of the reaction vessel was taken in DME (1 mL) and also added to the pentane. The resulting precipitate was then collected on a medium-porosity filter funnel and dried *in vacuo* to give **9** (0.059 g, 0.0805 mmol, 61%) as a white powder (dr = 4.6:1 for the **B** isomers). ^{1}H NMR (acetone-d_6, ambient temperature, 300 MHz, δ): 8.17 (1H, d, Tp), 7.92 (1H, d, Tp), 7.90 (1H, d, Tp), 7.67 (1H, d, Tp), 7.59 (1H, d, Tp), 6.39 (1H, d, Tp), 6.27 (1H, d, Tp), 6.17 (1H, d, Tp), 4.32 (1H, ddd (J = 7.2, 7.2, 7.2 Hz), 10a), 4.12 (1H, ddd (J = 7.2, 7.2, 3.2 Hz), 10b), 3.79 (3H, s, 9), 3.61 (3H, s, 8), 3.14 (1H, d (J = 2.4 Hz), 3), 2.88 (1H, ddd (J = 12.9, 7.2, 3.2 Hz), 11a), 2.49 (1H, ddd (J = 12.9, 10.2, 2.4 Hz), 4 (bound)), 2.27 (1H, dd (J = 12.0, 2.6 Hz), 7a), 2.17 (1H, m, 11b), 1.80 (1H, dd (J = 12.0, 2.6 Hz), 7), 1.75 (1H, dd (J = 10.2, 2.4 Hz), 5 (bound)), 1.26 (9H, d (J = 8.5 Hz), PMe_3). ^{13}C NMR (acetone-d_6, ambient temperature, 300 MHz, δ): 181.5 (s, C9), 166.6 (s, C2), 149.3 (s, Tp), 143.9 (s, Tp), 142.0 (s, Tp), 137.8 (s, Tp), 136.7 (s, Tp), 135.6 (s, Tp), 107.0 (s, Tp), 106.6 (s, Tp), 105.7 (s, Tp), 102.3 (s, C6), 66.1 (s, C10), 56.1 (s, C5), 55.2 (d (J = 15.5 Hz), C4), 53.7 (s, C12), 50.9 (s, C13), 47.3 (s, C7), 42.5 (s, C3), 40.8 (s, C8), 36.1 (s, C11), 13.4 (d (J = 28.2 Hz), PMe_3). ^{31}P NMR (acetone-d_6, δ): −12.14 (satellite d (J = 267), PMe_3). IR: ν(NO) = 1561 cm −1, ν(CO) = 1757 cm^{-1}. CV: $E_{p,a}$ = +0.66 V. HRMS (*m*/*z*, obsd(I); calcd(I); error (ppm)): 739.20417 (90%), 739.20478 (83%), 0.82; 740.20656 (81%), 740.20733 (80%), 1.04; 741.20678 (100%), 741.20723 (100%), 0.61; 742.21039 (47%), 742.21125 (45%), 1.16; 743.20936 (82%), 743.21045 (83%), 1.46.

TpW(NO)(PMe$_3$)(4,5-η^2-(7,9-Dimethoxy-4-methyl-4,8-diaza-tricyclo[5.2.2.0^{2,6}]undeca-8,10-diene-3,5-dione)) (10). To **3** (0.069 g, 1.082 × 10^{-4} mol, 1 equiv) was added 2 mL of THF. To this solution was added a solution of NMM (0.143 g 1.288 × 10^{-3} mol, 12 equiv) in THF (1 mL). The reaction was then stirred overnight (18 h). The solid generated by the reaction, presumably NMM polymer, was filtered out with a 15 mL medium-porosity filter funnel. The filtrate was than added to pentane (50 mL). The resulting precipitate was then collected on a medium-porosity filter funnel and dried *in vacuo* to give **10** (48.5 mg, 0.0644 mmol, 60%) as a tan powder. IR: ν(NO) = 1566 cm^{-1}, ν(CO) = 1692 cm^{-1}. CV: $E_{p,a}$ = +0.79 V. ^{1}H NMR ($CDCl_3$, ambient temperature, 300 MHz, δ): 8.70 (1H, d, Tp), 8.05 (2H, d, 2 Tp), 8.03 (1H, d, Tp), 7.70 (1H, d, Tp), 7.69 (1H, d, Tp), 7.67 (2H, d, 2 Tp), 7.54 (1H, d, Tp), 7.49 (1H, d, Tp), 7.24 (1H, d, Tp), 7.19 (1H, d, Tp), 6.28 (1H, t, Tp), 6.26 (1H, t, Tp), 6.20 (1H, t, Tp), 6.19 (1H, t, Tp), 6.17 (1H, t, Tp), 6.14 (1H, t, Tp), 3.78 (3H, s, 13A), 3.76 (3H, s, 12A), 3.72 (3H, s, 12B), 3.67 (1H, dd (J = 2.5, 3.0 Hz), 3A), 3.60 (1H, t (J = 2.8 Hz), 3B), 3.57 (1H, d (J = 7.7 Hz), 8B), 3.45 (3H, s, 13B), 3.43 (1H, d (J = 7.9 Hz), 8A), 3.27 (1H, dd (J = 3.2, 7.7 Hz), 7B), 3.08 (1H, dd (J = 3.0, 7.9 Hz), 7A), 2.90 (1H, s, NMe (A or B)), 2.89 (1H, s, NMe (A or B)), 2.71 (1H, dd (J = 10.4, 12.4 Hz), 5A), 2.26 (1H, ddd (J = 2.8, 10.6, 15.3 Hz), 4B), 1.72 (1H, dd (J = 2.5, 10.6 Hz), 5B), 1.28 (9H, d (J = 8.9 Hz), PMe_3 A), 1.25 (9H, d (J = 8.5 Hz), PMe_3 B), 1.19 (1H, buried, 4A). ^{13}C NMR ($CDCl_3$, ambient temperature, 300 MHz, δ): 177.2 (s, 11A(CO)), 177.1 (s, 11B(CO)), 176.6 (s, 9A(CO)), 174.6 (s, 9B(CO)), 164.6 (s, 2A or B), 164.4 (s, 2A or B), 148.3 (s, Tp), 144.3 (s, Tp), 142.9 (s, Tp), 142.4 (s, Tp), 140.2 (s, Tp), 140.1 (s, Tp), 136.7 (s, Tp), 136.5 (s, Tp), 135.9 (s, Tp), 135.7 (s, Tp), 134.8 (s, Tp), 134.5 (s, Tp), 106.4 (s, Tp), 106.3 (s, Tp), 106.0 (s, Tp), 105.8 (s, Tp), 105.7 (s, Tp), 105.5 (s, Tp), 99.5 (s, 6B), 98.7 (s, 6A), 60.2 (d (J = 14.9 Hz), 5A), 54.5 (s, 8A), 54.3 (s, OMe), 53.9 (s, OMe), 53.3 (s, 4A + 5B), 52.4 (s, 7B), 52.1 (d (J = 16.1 Hz), 4B), 51.9 (s, OMe + 7A), 51.1 (s, OMe), 49.6 (s, 8B), 43.7 (s, 3B), 42.7 (s, 3A), 24.5 (s, NMe A or B), 24.4 (s, NMe A or B), 14.3, 14.0 (d (J = 28.7 Hz), PMe_3 A or B), 13.8. 13.4 (d (J = 28.1 Hz), PMe_3 A or B). ^{31}P NMR: −12.81 (satellite d (J^{PW} = 261 Hz), PMe_3), −13.68 (satellite d (J^{PW} = 272 Hz), PMe_3). HRMS (UIUC) (*m*/*z*, obsd (%), calcd (%), error (ppm)): 752.2006 (81.22%), 752.1997 (82.5%), 1.2; 753.2031 (80.35%), 753.2002 (80.5%), 3.9; 754.2031 (100%), 754.2023 (100%), 1.1; 755.2070 (45.85%), 755.2062 (45.3%), 1.1; 756.2063 (83.41%), 756.2057 (83.3%), 0.8.

[TpW(NO)(PMe$_3$)(4,5-η^2-(dimethyl 1,3-dimethoxy-2-azabicyclo-[2.2.2]octa-2,5-diene-7,8-dicarboxylate))] (11). The synthesis is similar to compound **4**. ^{1}H NMR ($CDCl_3$, ambient temperature, 300 MHz, δ): 8.63 (1H, d, J = 1.8 Hz, Tp), 8.11 (1H, d, J = 1.8 Hz, Tp), 7.70 (1H, d, J = 2.3 Hz, Tp), 7.62 (1H, d, J = 2.1 Hz, Tp), 7.44 (1H, d, J = 2.1 Hz, Tp), 7.28 (1H, d, J = 2.0 Hz, Tp), 6.28 (1H, t, J= 2.0, 4.1 Hz, Tp), 6.12 (1H, t, J = 2.0, 4.1 Hz, Tp), 6.08 (1H, t, J = 2.1, 4.4 Hz, Tp), 3.82 (3H, s, H13), 3.72 (3H, s, H14), 3.71 (3H, s, H11), 3.64 (3H, s, H12), 3.50 (1H d, J = 1.7 Hz, H8), 3.41 (1H, m, H3), 3.11 (1H, ddd, J = 2.7,10.8, 13.6 Hz, H4), 2.97 (1H, dd, J = 1.7, 10.8 Hz, H7), 1.69 (1H, dd, J = 2.7, 10.8 Hz, H5), 1.31 (9H, d, J = 8.4 Hz, PMe_3). ^{13}C NMR ($CDCl_3$, ambient temperature, 300 MHz, δ): 172.9 (C9 or C10), 172.1 (C10 or C9), 167.9 (C2), 148.7 (Tp d), 142.8 (Tp d), 140.5 (Tp d), 136.2 (Tp d), 135.4 (Tp d), 134.1 (Tp d), 106.1 (Tp t), 105.7 (Tp t), 104.9 (Tp t), 100.1 (C6), 56.1 (C5), 51.6 (C11), 51.5 (C12), 49.9 (C8), 49.7 (C7), 49.5 (C14) 49.6 (C14), 47.9 (d, J = 15.3 Hz, C4), 42.6 (C3), 13.8 (d, J = 28.2 Hz, PMe_3). IR: ν(NO) = 1560 cm^{-1} (vs), ν(imidate) = 1646 cm^{-1} (s), ν(CO_2Me) = 1733 cm^{-1} (m). CV: $E_{p,a}$ = +0.66 V. HRMS (UIUC) (*m*/*z*, obsd (%), calcd (%), error (ppm)): 785.2109 (80.7%), 785.2100 (81.8%), 1.1; 786.2134 (80.3%), 786.2112 (80.4%), 2.8; 787.2133 (100%), 787.2139 (100%), 0.8; 788.2173 (46.5%), 788.2158 (46%), 1.9; 789.2166 (83.3%), 789.2141 (83.2%), 3.2.

[TpW(NO)(PMe$_3$)(4,5-η^2-(dimethyl 1,3-dimethoxy-2-azabicyclo-[2.2.2]octa-2,5-diene-7,8-dicarboxylate))] (12). The synthesis is similar to compound **4**. ^{1}H NMR ($CDCl_3$, ambient temperature, 300 MHz, δ): 8.78 (1H, Tp), 8.11 (1H, Tp), 7.70 (1H, Tp), 7.65 (1H, Tp), 7.44 (1H, Tp), 7.29 (1H, Tp), 7.26 ($CDCl_3$), 6.28 (1H, Tp), 6.15 (1H, Tp), 6.09 (1H, Tp), 3.81 (3H, s, H13), 3.72 (3H, s, H14), 3.71 (3H, s, H11), 3.64 (3H, s, H12), 3.50 (2H, s, H7 and H8), 3.38 (1H, m, H3), 2.47 (1H, ddd, J= 2.0,10.2, 12.5 Hz, H4), 1.68 (1H, dd, J = 2.0, 10.2 Hz, H5), 1.25 (9H, d, J = 8.2 Hz, PMe_3). ^{13}C NMR ($CDCl_3$, ambient temperature, 300 MHz, δ): 173.6

(C9 or C10), 173.5 (C10 or C9), 165.4 (C2), 149.1 (Tp d), 142.8 (Tp d), 140.4 (Tp d), 136.4 (Tp d), 135.5 (Tp d), 134.3 (Tp d), 106.3 (Tp t), 105.7 (Tp t), 105.0 (Tp t), 99.3 (C6), 77.0 ($CDCl_3$, t), 54.2 (C5), 53.7 (d, J = 13.7 Hz, C4), 53.6 (C13), 53.3 (C8), 52.1 (C11), 51.9 (C12), 50.5 (C7) 49.6 (C14), 43.9 (C3), 13.7 (d, J = 28.2 Hz, PMe_3). IR: ν(NO) = 1566 cm^{-1} (vs), ν(imidate) = 1650 cm^{-1} (s), $\nu(CO_2Me)$ = 1715 cm^{-1}(m). CV: $E_{p,a}$ = +0.66 V. HRMS (UIUC) (*m*/*z*, obsd (%), calcd (%), error (ppm)): 785.21090 (80.8%), 785.2100 (81.8%), 1.1; 786.213 (80.4%), 786.2133 (80.4%), 0.1; 787.2133 (100%), 787.2114 (100%), 2.4; 788.2173 (46.6%), 788.2185 (46%), 1.5; 789.2166 (83.5%), 789.2158 (83.2%), 1.0.

[TpW(NO)(PMe_3)(4,5-η^2-(dimethyl 1,3-dimethoxy-2-azabicyclo-[2.2.2]octa-2,5,7-triene-7,8-dicarboxylate))] (13). The synthesis is similar to compound **4**. ^{1}H NMR ($CDCl_3$, ambient temperature, 300 MHz, δ): 8.59 (1H, d, J = 1.8 Hz, Tp), 8.14 (1H, d, J = 1.8 Hz, Tp), 7.72 (1H, d, J = 2.2 Hz, Tp), 7.68 (1H, d, J = 2.1 Hz, Tp), 7.47 (1H, d, J = 2.2 Hz, Tp), 7.31 (1H, d, J = 1.8 Hz, Tp), 6.30 (1H, t, J = 2.3, 4.3 Hz, Tp), 6.16 (1H, t, J = 2.3, 4.3 Hz, Tp), 6.13 (1H, t, J = 2.2, 4.4 Hz, Tp), 4.37 (1H, d, J = 2.8 Hz, H3), 3.90 (3H, s, H13), 3.83 (3H, s, H12), 3.80 (3H, s, H11), 3.74 (3H, s, H14), 2.73 (1H, ddd, J = 3.0, 10.6, 13.2 Hz, H4), 2.16 (1H, dd, J = 2.8, 10.4 Hz, H5), 1.23 (9H, d, J = 8.4 Hz, PMe_3). ^{13}C NMR ($CDCl_3$, ambient temperature, 300 MHz, δ): 169.7 (C2), 168.4 (C10), 164.3 (C9), 160.4 (C7), 148.6 (Tp), 142.9 (Tp), 140.8 (Tp), 136.7 (C8), 136.4 (Tp), 135.8 (Tp), 134.3 (Tp) 106.3 (Tp), 105.6 (Tp), 105.4 (Tp), 104.4 (C6), 77.0 ($CDCl_3$, t), 63.6 (C5), 63.3 (d, J = 2.9 Hz, C4), 59.0 (C13), 55.0 (C14), 53.4 (C12), 52.1 (C11), 48.1 (C3), 13.8 (d, J = 29.0 Hz, PMe_3). IR: ν(NO) = 1571 cm^{-1} (vs), ν(imidate) = 1649 cm^{-1} (s), $\nu(CO_2Me)$ = 1730 cm^{-1}(s). CV: $E_{p,a}$ = +0.87 V. HRMS (UIUC) (*m*/*z*, obsd (%), calcd (%), error (ppm)): 783.1952 (80.70%), 783.1946 (81.8%), 0.8; 784.1978 (80.26%), 784.1976 (80.4%), 0.3; 785.1977 (100%), 785.1979 (100%), 0.3; 786.2017 (46.49%), 786.2018 (46.0%), 0.1; 787.2009 (83.33%), 787.2007 (83.2%), 0.3.

TpW(NO)(PMe_3)(4,5-η^2-(1,3-Dimethoxy-2-azabicyclo[2.2.2]octa-2,5,7-trien-6-yl)ethanone) (14). To **3** (0.041 g, 6.372 × 10^{-4} mol, 1 equiv) was added 4 mL of pentane. To this solution was added a solution of 3-butyne-2-one (0.018 g, 4 equiv) in DME (1 mL). The reaction was then stirred overnight (18 h). The reaction mixture was then added to pentane (50 mL). Residue on the sides of the reaction vessel was taken in DME (1 mL) and also added to the pentane. The resulting precipitate was then collected on a medium-porosity filter funnel and dried *in vacuo* to give **14B** (36.0 mg, 0.0507 mmol, 80%) as a brown powder. ^{1}H NMR (acetone-d_6, ambient temperature, 300 MHz, δ): 8.97 (1H, d, Tp), 8.23 (1H, d, Tp), 7.96 (1H, d, Tp), 7.92 (1H, d, Tp), 7.67 (1H, d, Tp), 7.59 (1H, d, Tp), 7.17 (1H, d (J = 5.7), 7), 6.42 (1H, t, Tp), 6.27 (1H, t, Tp), 6.19 (1H, t, Tp), 3.91 (1H, dd (J = 5.7, 3.1 Hz), 3), 3.82 (3H, s, 11), 3.54 (3H, s, 12), 2.81 (1H, m, 4), 2.25 (3H, s, 10), 2.00 (1H, d (J = 13.9 Hz), 5), 1.30 (9H, d (J = 8.5 Hz), PMe_3). ^{13}C NMR (acetone-d_6, ambient temperature, 300 MHz, δ): 196.9 (s, 9), 169.2 (s, 2), 159.4 (s, 6), 150.0 (s, Tp), 145.1 (s, Tp), 144.0 (s, 7), 142.3 (s, Tp), 137.8 (s, Tp), 136.9 (s, Tp), 135.5 (s, Tp), 107.2 (s, Tp), 106.7 (s, Tp), 105.8 (s, Tp), 104.3 (s, 6), 65.5 (s, 5), 64.3 (d (J = 18.4 Hz), 4), 54.7 (s, 11), 53.5 (s, 12), 49.0 (s, 3), 28.9 (s, 10), 13.5 (d (J = 28.7 Hz), PMe_3). ^{31}P NMR: −12.08 (satellite d (J^{PW} = 257 Hz), PMe_3). IR: ν(NO) = 1575 cm^{-1}(vs), ν(CO) = 1700 cm^{-1} (s). CV: $E_{p,a}$ = +0.88 V. HRMS (UIUC) (*m*/*z*, obsd (%), calcd (%), error (ppm)): 709.1948 (82.53%), 709.1918 (83.4%), 4.2; 710.1973 (80.35%), 710.1948 (80.3%), 3.5; 711.1972 (100%), 711.1956 (100%), 2.2; 712.2103 (44.98), 712.1982 (44.2%), 4.4; 713.2004 (83.84%), 713.2007 (83.6%), 0.4.

1-Methoxy-3-oxo-2-azabicyclo[2.2.2]oct-5-ene-7-carbonitrile (15). A sample containing 0.099 g of **6** (1.33 × 10^{-4} mol) was dissolved with 0.792 g of CD_3CN and added to preweighed vial containing 0.059 g (2.66 × 10^{-4} mol, 2 equiv) of $CuBr_2$. The reaction turned green instantly and was allowed to react for 14 h at room temperature. The resulting solution was evaporated to a residue, redissolved with CH_2Cl_2, and purified via silica gel chromatography (elution with 15% acetone/ethyl acetate). Isolated yield was 29%. ^{1}H NMR ($CDCl_3$, ambient temperature, 300 MHz, δ): 7.90 (1H, br, H1), 6.67 (1H, dd, J = 8.2, 9.3 Hz, H5), 6.61 (1H, dd, J = 6.0, 8.2 Hz, H4), 3.64 (3H, s, H10), 3.44 (1H, m, H3), 3.17 (1H, dd, J = 4.1, 9.7 Hz, H8), 2.40 (1H, ddd, J = 2.4, 9.7, 12.8 Hz, H7′), 1.89 (1H, ddd, J = 3.1, 4.1, 13.0 Hz, H7). ^{13}C NMR ($CDCl_3$, ambient temperature, 300 MHz, δ): 174.2 (C2), 132.7 (C5), 132.4 (C4), 119.4 (C9), 89.4 (C6), 53.6 (C10), 43.0 (C3), 35.7 (C8), 28.9 (C7). IR: ν(CO) = 1688 cm^{-1} (vs), ν(amide) = 1611 cm^{-1} (m).

1,3-Dimethoxy-2-azabicyclo[2.2.2]octa-2,5-diene-7-carbonitrile (16). A sample containing 0.1025 g of **6** (1.47 × 10^{-4} mol) was dissolved with 0.881 g of CD_3CN and added to preweighed vial containing 0.097 g (2.95 × 10^{-4} mol, 2 equiv) of cerric(IV) ammonium nitrate. The reaction turned orange-brown instantly and was allowed to react for 14 h at room temperature. The resulting solution was evaporated to dryness and redissolved with 8 mL of CH_2Cl_2 and 2 mL of saturated $NaHCO_3$. The organic layer was extracted, while the aqueous layer was rewashed with 4 mL of CH_2Cl_2. The organic solution was dried over $MgSO_4$, filtered over a 30 mL fritted glass disk, and evaporated to a residue. The resulting residue was taken up in 2 mL of CH_2Cl_2 and purified via silica gel chromatography (elution with 75% Et_2O/hexanes). The isolated yield was 35%. ^{1}H NMR ($CDCl_3$, ambient temperature, 300 MHz, δ): 6.63 (1H, d, J =7.7 Hz, H5), 6.50 (1H, dd, J = 6.0, 7.7 Hz, H4), 3.70 (3H, s, H10), 3.66 (3H, s, H11), 3.54 (1H, m, H3), 2.80 (1H, dd, J = 4.8, 9.7, H8), 2.08 (1H, ddd, J = 2.8, 9.7, 12.4 Hz, H7′), 1.89 (1H, ddd, J = 2.5, 4.8 Hz, 12.4 H7). ^{13}C NMR ($CDCl_3$, ambient temperature, 300 MHz, δ): 172.3 (C2), 135.4 (C5), 130.8 (C4), 120.5 (C9), 94.0 (C6), 54.3 (C10), 51.9 (C11), 37.5 (C3), 32.3 (C8), 30.0 (C7). IR: ν(imidate) = 1643 cm^{-1} (s). HRMS (UIUC) (*m*/*z*, obsd (%), calcd (%), error (ppm)): 193.0969 (37.5%), 193.0977 (100%), 4.14; 194.1002 (4.7%), 194.1007 (11.8%), 2.57.

1,3-Dimethoxy-7-(phenylsulfonyl)-2-azabicyclo[2.2.2]octa-2,5-diene (17). A sample containing 0.1487 g of **7** (1.83 × 10^{-4} mol) was dissolved with 0.881 g of CD_3CN and added to preweighed vial containing 0.067 g (2.02 × 10^{-4} mol, 1.1 equiv) of cerric(IV) ammonium nitrate. The reaction turned orange-brown instantly and was allowed to react for 3 h at room temperature. The resulting solution was evaporated to dryness and redissolved with 8 mL of CH_2Cl_2 and 2 mL of saturated $NaHCO_3$. The organic layer was extracted, while the aqueous layer was rewashed with 4 mL of CH_2Cl_2. The organic solution was dried over $MgSO_4$, filtered over a 30 mL fritted glass disk, and evaporated to a residue. The resulting residue was taken up in 1 mL of CH_2Cl_2 and purified via silica gel chromatography (elution with 40% Et_2O/hexanes, R_f 0.45). Overall yield was 35%. ^{1}H NMR ($CDCl_3$, ambient temperature, 300 MHz, δ): 7.92 (2H, d, J = 7.3 Hz, H10, H14), 7.61 (H, t, J = 7.5,14.6 Hz, H12), 7.53 (2H, t, J = 7.8, 14.9 Hz, H11, H13), 6.52 (1H, d, J =7.6 Hz, H5), 6.44 (1H, dd, J = 6.1, 7.6 Hz, H4), 3.65 (3H, s, H15), 3.51 (1H, m, H8), 3.48 (1H, m, H3), 3.27 (3H, s, H16), 2.08 (1H, ddd, J= 3.1, 9.6, 12.8 Hz, H7), 1.89 (1H, ddd, J= 2.1, 5.7, 12.7 Hz; H7′). ^{13}C NMR ($CDCl_3$, ambient temperature, 300 MHz, δ): 173.4 (C2), 140.6 (C9), 134.8 (C5), 133.2 (C4), 129.8 (C12), 129.0 (C10, C14), 128.4 (C11, C13), 93.88 (C6), 77.0 ($CDCl_3$), 66.0 (C8), 54.3 (C15), 51.1 (C16), 38.0 (C3), 27.9 (C7). IR: ν(imidate) = 1641 cm^{-1} (s).

1-(2,6-Dimethoxypyridin-3-yl)pentan-3-one (18). 5 (0.084 g, 1.182 × 10^{-4} mol) was dissolved in 0.892 g of d_6-acetone and added to a preweighed vial containing 0.039 g of ceric(IV) ammonium nitrate (1.182 × 10^{-4} mol, 1 equiv). The reaction turned orange-brown instantly and was allowed to react for 14 h at room temperature. The resulting solution was evaporated to dryness and redissolved with 8 mL of CH_2Cl_2 and 2 mL of saturated $NaHCO_3$. The organic layer was extracted, while the aqueous layer was rewashed with 4 mL of CH_2Cl_2. The organic solution was dried

over $MgSO_4$, filtered over a 30 mL fritted glass disk, and evaporated to a residue. The resulting residue was taken up in 1 mL of CH_2Cl_2 and purified via silica gel chromatography (80% Et_2O/hexanes, R_f at 0.48). ^{1}H NMR ($CDCl_3$, ambient temperature, 300 MHz, δ): 7.33 (1H, dd, J =7.8 Hz, H5), 6.21 (1H, d, J = 7.8 Hz, H4), 3.91 (3H, s, H12), 3.87 (3H, s, H13), 2.75 (4H, m, H7, H7′ and H8, H8′), 2.43 (2H, q, J = 7.3, 14.6 Hz, H10), 1.05 (3H, t, J = 7.3, 14.6 Hz, H11). ^{13}C NMR ($CDCl_3$, ambient temperature, 300 MHz, δ): 211.2 (C9), 161.5 (C2), 160.3 (C6), 141.1 (C5), 114.0 (C3), 99.8 (C4), 53.5 (C12), 53.2 (C13), 41.8 (C8), 36.0 (C7), 23.6 (C10), 7.73 (C11). HRMS (UIUC) (*m*/*z*, obsd (%), calcd (%), error (ppm)): 224.1277 (100%), 224.1287 (100%), 4.46; 225.1323 (17.6%), 225.1319 (13.6%), 1.77.

[TpW(NO)(PMe$_3$)(4,5-η^2-(1,3-dimethoxy-7-(prop-1-en-2-yl)-2-azabicyclo[2.2.2]octa-2,5-diene))] (19). A 0.0994 g sample of **4B** was dissolved in 2 mL of THF (dried with basic alumina). The yellow, homogeneous solution was added to 0.143 g (2.513×10^{-4} mol, 2 equiv) of 0.5 M Tebbe's solution in toluene. The red-yellow reaction mixture was allowed to stir at room temperature for 12 h. The reaction was quenched with 20 drops of 1 M NaOH and diluted with 8 mL of CH_2Cl_2. The organic layer was extracted, dried with $MgSO_4$, and filtered over a 30 mL fine fritted glass disk. The filtrate was evaporated to a residue and redissolved with 1 mL of dry THF. The THF solution was added to a 125 mL flask containing 60 mL of pentanes. A tan precipitate was isolated from the pentanes solution over a 30 mL fine fritted glass disk, and the yellow filtrate was evaporated to a residue. The residue was resolvated with 1 mL of CH_2Cl_2 and purified with silica gel chromatography (R_f of 0.15, 10% acetone/Et_2O,). Overall yield was 25%. ^{1}H NMR ($CDCl_3$, ambient temperature, 300 MHz, δ): 8.79 (1H, Tp), 8.12 (1H, Tp), 7.69 (1H, J = 2.1 Hz, Tp), 7.64 (1H, J = 1.8 Hz Tp), 7.43 (1H, d, J = 1.8 Hz, Tp), 7.22 (1H, Tp), 6.27 (1H, t, Tp), 6.13 (1H, t, Tp), 6.07 (1H, t, Tp), 4.97 (1H, H11), 4.85 (1H, H12), 3.82 (3H, s, H14), 3.62 (3H, s, H15), 3.04 (1H, m, H3), 2.87 (1H, dd, J = 5.3, 10.4 Hz, H8), 2.36 (1H, ddd, J = 2.6, 10.2, 13.3 Hz, H4), 2.13 (1H, m, H7′), 1.85 (3H, s, H13), 1.82 (1H, dd, J = 2.3 Hz, 10.2 Hz, H5), 1.72 (1H, ddd, J = 1.0, 5.3, 12.1 Hz, H7) 1.26 (9H, d, J = 8.1 Hz, PMe_3). ^{13}C NMR ($CDCl_3$, ambient temperature, 300 MHz, δ): 166.3 (C2), 149.0 (Tp d), 146.8 (C9), 142.8 (Tp,d) 139.9 (Tp d), 136.2 (Tp d), 135.4 (Tp d), 134.1 (Tp d), 112.8 (C10), 106.1 (Tp t), 105.5 (Tp t), 105.1 (Tp t), 99.6 (C6), 77.0 ($CDCl_3$, t), 55.1 (C5), 55.0 (d, J = 15.3 Hz, C4), 53.1 (C14), 49.2 (C15), 48.5 (C8), 41.1 (C3), 37.7 (C7), 23.2 (C13), 13.6 (d, J = 27.8 Hz, PMe_3). IR: ν(NO) = 1562 cm^{-1} (vs), ν(imidate) = 1650 cm^{-1} (s). CV: $E_{p,a}$ +0.59 V.

[TpW(NO)(PMe$_3$)(4,5-η^2-(1-(1,3-dimethoxy-2-azabicyclo[2.2.2]octa-2,5-dien-7-yl)ethanol))] (20). A sample containing 0.112 g of **4B** dissolved with 1.561 mL of DME (dried over basic alumina) was prepared and added to a vial containing 0.012 g of $LiAlH_4$ (9.27×10^{-5} mol, 2 equiv). The dark, heterogeneous solution was allowed to stir at room temperature for 3 h. The resulting reaction mixture was diluted with 8 mL of CH_2Cl_2 and 1.5 mL of Rochelle's salt. The organic layer was extracted, while the aqueous layer was rewashed with 5 mL of CH_2Cl_2 and H_2O. Again, the organic layer was extracted, dried with $MgSO_4$, and filtered over a 30 mL fine fritted glass disk. The resulting filtrate was dried to a residue, taken up in minimal CH_2Cl_2, and purified with a SiO_2 column (R_f of 0.15, 10% acetone/Et_2O). Isolated yield of *exo* **20B** is 74% with a dr >10:1. ^{1}H NMR ($CDCl_3$, ambient temperature, 300 MHz, δ): 8.81 (1H, d, J = 1.8 Hz, Tp), 8.12 (1H, d, J = 1.8 Hz, Tp), 7.70 (1H, d, J = 2.4 Hz, Tp), 7.64 (1H, d, J = 2.3 Hz, Tp), 7.47 (1H, d, J = 2.4 Hz, Tp), 7.25 (1H, d, J = 2.0 Hz, Tp), 6.27 (1H, t, J = 2.1, 4.3 Hz, Tp), 6.10 (1H, t, J = 2.3, 4.4 Hz, Tp), 6.07 (1H, t, J = 2.3, 4.4 Hz, Tp), 5.38 (1H, s, H13), 3.89 (1H, m, H9), 3.81 (3H, s, H11), 3.68 (3H, s, H12), 2.96 (1H, m, H3), 2.24 (1H, ddd, J = 2.7, 10.4, 13.0 Hz, H4), 2.07 (3H, m, H7, H7′, H8) 1.82 (1H, dd, J= 2.6, 10.4 Hz, H5), 1.22 (9H, d, J = 8.2 Hz, PMe_3), 1.20 (3H, d, J = 4.6 Hz, H10). ^{13}C NMR ($CDCl_3$, ambient temperature, 300 MHz, δ): 166.3 (C2), 149.7 (Tp d), 142.7 (Tp d), 140.2 (Tp, d), 136.4 (Tp d), 135.4 (Tp d), 134.2 (Tp d), 106.1 (Tp t), 105.5 (Tp t), 104.9 (Tp t), 100.5 (C6), 72.4 (C9), 54.04 (C5), 53.9 (d, J = 15.6 Hz, C4), 53.3 (C11), 49.2 (C12), 45.8 (C8), 40.4 (C3), 36.1 (C7), 21.7 (C10), 13.6 (d, J = 27.8 Hz, PMe_3). IR: ν (NO) = 1561 cm^{-1} (vs), ν(imidate) = 1650 cm^{-1}(s), ν(OH) = 3480 cm^{-1} (b). CV: $E_{p,a}$ +0.62 V. HRMS (UIUC) (*m*/*z* obsd (%), calcd (%), error (ppm)): 713.2261 (82.53), 713.2263 (83.3), 0.3; 714.2286 (80.35), 714.2287 (80.3), 0.1; 715.2285 (100), 715.2279 (100), 0.8; 716.2325 (44.98), 716.2319 (44.3), 0.8; 717.2318 (83.84), 717.2318 (83.6), 0.0.

[TpW(NO)(PMe$_3$)(4,5-η^2-(1,3-dimethoxy-2-azabicyclo[2.2.2]octa-2,5-dien-7-yl)methanol)] (21). A sample containing 0.034 g of *exo* **8B** dissolved with 1.561 mL of DME (dried over basic alumina) was prepared and added to a vial containing 0.004 g of $LiAlH_4$ (9.27×10^{-5} mol, 2 equiv). The dark, heterogeneous solution was allowed to stir at room temperature for 3 h. The resulting reaction mixture was diluted with 8 mL of CH_2Cl_2 and 1.5 mL of Rochelle's salt. The organic layer was extracted, while the aqueous layer was rewashed with 5 mL of CH_2Cl_2 and H_2O. Again, the organic layer was extracted, dried with $MgSO_4$, and filtered over a 30 mL fine fritted glass disk. The resulting filtrate was dried to a residue and taken up in $CDCl_3$. Overall yield was 75% with a dr <2:1. ^{1}H NMR ($CDCl_3$, ambient temperature, 300 MHz, δ): 8.81 (1H, d, J = 1.6 Hz, Tp), 8.14 (1H, d, J = 1.6 Hz, Tp), 7.70 (1H, d, J = 2.2 Hz, Tp), 7.68 (1H, d, J = 2.0 Hz, Tp), 7.48 (1H, d, J = 2.0 Hz, Tp), 7.25 (1H, Tp), 6.28 (1H, t, J = 2.0, 4.1 Hz, Tp), 6.15 (1H, t, J = 2.0, 4.1 Hz, Tp), 6.10 (1H, t, J = 2.0, 4.1 Hz, Tp), 3.90 (1H, H9), 3.83 (3H, s, H11), 3.67 (3H, s, H12), 3.64 (1H, buried, H9′), 2.97 (1H, m, H3), 2.40 (1H, m, H8), 2.21 (1H, ddd, J = 2.6, 10.4, 13.0 Hz, H4), 2.04 (1H, ddd, J = 2.6, 12.3 Hz, H7′) 1.77 (1H, dd, J = 2.5, 10.4 Hz, H5), 1.23 (9H, d, J = 8.2 Hz, PMe_3), 1.07 (1H, ddd, J = 2.2, 4.1, 11.0 Hz, H7). ^{13}C NMR ($CDCl_3$, ambient temperature, 300 MHz, δ): 166.3 (C2), 149.1 (Tp d), 142.7 (Tp d), 140.1 (Tp, d), 136.5 (Tp d), 135.4 (Tp d), 134.3 (Tp d), 106.2 (Tp t), 105.5 (Tp t), 104.9 (Tp t), 100.0 (C6), 67.1 (C9), 53.8 (C5), 53.7 (d, J = 12.2 Hz, C4), 53.3 (C11), 49.2 (C12), 40.5 (C8), 40.1 (C3), 34.7 (C7), 13.6 (d, J = 27.8 Hz, PMe_3). IR: ν(NO) = 1561 cm^{-1} (vs), ν(imidate) = 1650 cm^{-1}(s), ν OH = 3410 cm^{-1} (b). CV: $E_{p,a}$ +0.61 V. HRMS (*m*/*z* obsd (%), calcd (%), error (ppm)): 699.2104 (82.61), 699.2111 (83.9), 1.0; 700.2130 (80.00), 700.2136 (80.1), 0.9; 701.2128 (100), 701.2132 (100), 0.6; 702.2169 (44.35), 702.2188 (43.6), 2.7; 703.2161 (83.91), 703.2167 (83.8), 0.9.

(1-(1,3-Dimethoxy-2-azabicyclo[2.2.2]octa-2,5-dien-7-yl)ethanol) (22). A sample containing 0.142 g of **20** (1.988×10^{-4} mol) was dissolved with 0.792 g of $CDCl_3$ and added to preweighed vial containing 0.068 g (3.396×10^{-4} mol, 2 equiv) of recrystallized *m*-CPBA. The reaction turned orange-brown instantly and was allowed to react for 14 h at room temperature. The resulting solution was evaporated to dryness, and resolvated with 8 mL of CH_2Cl_2 and 2 mL of saturated $NaHCO_3$. The organic layer was extracted, while the aqueous layer was rewashed with 4 mL of CH_2Cl_2. The organic solution was dried over $MgSO_4$, filtered over a 30 mL fritted glass disk, and evaporated to a residue. The resulting residue was taken up in 1 mL of CH_2Cl_2 and purified via silica gel chromatography (elution with 70% Et_2O/hexanes). Overall yield was 31%. ^{1}H NMR ($CDCl_3$, ambient temperature, 300 MHz, δ): 6.52 (1H, d, J = 7.8 Hz, H5), 6.37 (1H, dd, J= 6.0, 7.8 Hz, H4), 3.71 (3H, s, H11), 3.64 (3H, s, H12), 3.36 (3H, m, H3, H9, H9′), 2.10 (1H, m, H8), 1.83 (1H, ddd, J = 3.1, 9.6, 12.4 Hz, H7′), 0.62 (1H, ddd, J = 2.1, 5.2, 12.0 Hz, H7). ^{13}C NMR ($CDCl_3$, ambient temperature, 300 MHz, δ): 171.4 (C2), 133.8 (C5), 130.5 (C4), 98.1 (C6), 66.5 (C9), 54.0 (C11), 52.1 (C12), 43.6 (C8), 38.2 (C3), 27.8 (C7: IR: ν(imidate) = 1643 cm^{-1} (s). HRMS (UIUC) (*m*/*z* obsd (%), calcd (%), error (ppm)): 234.11045 (100), 234.11006 (100), 1.7; 235.10982 (11.8), 235.11329 (0.5), 14.8.

(1,3-Dimethoxy-2-azabicyclo[2.2.2]octa-2,5-dien-7-yl)methanol)] (23). A sample containing 0.119 g of **21** (1.698×10^{-4} mol) was dissolved with 0.792 g of $CDCl_3$ and added to preweighed vial containing 0.049 g (1.698×10^{-4} mol, 1 equiv) of cerric(IV) ammonium nitrate. The reaction turned orange-brown instantly and was allowed to react for 14 h at room temperature. The resulting solution was evaporated to dryness and resolvated with 8 mL of CH_2Cl_2 and 2 mL of saturated $NaHCO_3$. The organic layer was extracted, while the aqueous layer was rewashed with 4 mL of CH_2Cl_2. The organic solution was dried over $MgSO_4$, filtered over a 30 mL fritted glass disk, and evaporated to a residue. The resulting residue was taken up in 1 mL of CH_2Cl_2 and purified via silica gel chromatography (elution with 70% Et_2O/hexanes). Overall yield was 51%, with a dr <2:1. ^{1}H NMR ($CDCl_3$, ambient temperature, 300 MHz, δ): **23** *exo* 6.52 (1H, d, $J = 7.8$ Hz, H5), 6.37 (1H, dd, $J = 6.0$, 7.8 Hz, H4), 3.71 (3H, s, H11), 3.64 (3H, s, H12), 3.36 (3H, m, H3,H9, H9′), 2.10 (1H, m, H8), 1.83 (1H, ddd, $J = 3.1$, 9.6, 12.4 Hz, H7′), 0.62 (1H, ddd, $J = 2.1$, 5.2, 12.1 Hz, H7). ^{13}C NMR: 171.4 (C2), 133.8 (C5), 130.5 (C4), 98.1 (C6), 66.5 (C9), 54.0 (C11), 52.1 (C12), 43.6 (C8), 38.2 (C3), 27.8 (C7). IR: ν(imidate) = 1643 cm^{-1} (s).

Methyl-3-acetyl-4-methoxybenzimidate (24). A sample containing 0.101 g of **14B** (1.422×10^{-4} mol, 1 equiv) was added to a preweighed vial containing 0.072 g (2.845×10^{-4}, 2 equiv) of AgOTf. The two solids were dissolved with 0.960 g of d_6-acetone, and the solution was stirred for 20 h at room temperature. The resulting brown, heterogeneous mixture was extracted with 10 mL of CH_2Cl_2 and concentrated to a residue. The residue was redissolved in 1 mL of CH_2Cl_2 and purified with SiO_2 chromatography (R_f 0.45 in 50% ethyl acetate/Et_2O). Isolated yield was 37%. ^{1}H NMR ($CDCl_3$, ambient temperature, 300 MHz, δ): 8.15 (1H, $J = 2.2$ Hz, H3), 7.93 (1H, dd, $J = 2.2$, 8.8 Hz, H5), 7.02 (1H, d, $J = 8.8$ Hz, H6), 3.97 (3H, s, H8), 3.92 (3H, s, H10), 2.63 (3H, s, H12), 1.28 (hexanes). ^{13}C NMR ($CDCl_3$, ambient temperature, 300 MHz, δ): 197.8 (C11), 172.2 (C7), 164.6 (C1), 135.4 (C5), 132.9 (C3), 129.0 (C4), 116.9 (C2), 113.1 (C6), 60.0 (C8), 56.9 (C10), 31.9 (C11). IR: ν(CO) = 1677 cm^{-1}, ν(imidate) =1637 cm^{-1}. LRMS: (ESI^+) 208.1 (M + 1).

3-Acetyl-4-methoxybenzamide (25). ^{1}H NMR ($CDCl_3$, ambient temperature, 300 MHz, δ): 8.12 (1H, s, H3), 8.11 (1H, dd, $J = 2.2$, 9.4 Hz, H5), 7.08 (1H, d, $J = 9.4$ Hz, H6), 3.99 (3H, s, H8), 2.64 (3H, s, H10), 1.58 (H_2O), 1.26 (m, hexanes), 0.88 (m, hexanes). LRMS (ESI^+): found 194.0 (M + 1).

Methyl 5-methoxy-1,3-dioxoisoindoline-4-carboxylate (26). A sample containing 0.089 g (1.160×10^{-4} mol) of **13B** was added to a preweighed vial containing 0.059 g (2.320×10^{-4} mol, 2 equiv) of AgOTf. The two solids were dissolved with 0.882 g of d_6-acetone, and the solution was stirred for 20 h at room temperature. The resulting brown, heterogeneous mixture was extracted with 10 mL of CH_2Cl_2 and concentrated to a residue. The residue was redissolved in 1 mL of CH_2Cl_2 and purified with SiO_2 chromatography (R_f 0.71 in 75% Et_2O/hexanes). The product is also UV active at 354 nm. Overall yield was 33%. ^{1}H NMR ($CDCl_3$, ambient temperature, 300 MHz, δ): 7.88 (1H, d, $J = 8.4$ Hz, H5), 7.68 (1H, br, H9), 7.24 (1H, d, $J = 8.4$ Hz, H6), 4.09 (3H, s, H12), 3.97 (3H, s, H10), 1.24 (hexanes). ^{13}C NMR ($CDCl_3$, ambient temperature, 300 MHz, δ): 166.6 (C7 or C9), 165.7 (C7 or C9), 164.6 (C12), 160.7 (C1), 126.4 (C5), 124.2 (C4 and C2), 120.1 (C3), 115.8 (C6), 56.8 (C12), 53.2 (C10), 29.7 (hexanes). IR: ν(phthalimide) = 1762 cm^{-1} (m), ν(CO_2Me) = 1732 cm^{-1}. LRMS (ESI^+): 236.1 (M + 1).

TpW(NO)(PMe_3)(4,5-η^2-6-Methylpyridine-2-carboxylic acid ethyl ester) (28). A solution of TpW(NO)(PMe3)(4,5-η^2-2,6-lutidine)[16] (49.7 mg, 0.0815 mmol) in DME (6 mL) was added to a test tube and placed in a cold bath at −10 °C. Ethyl cyanoformate (45.0 mg, 0.454 mmol, 5 equiv) and DME (1 mL) were added to a second test tube, which was also placed in the cold bath. After 5 min the contents of the cyanoformate test tube were added to the one containing TpW(NO)(PMe3)(4,5-η^2-2,6-lutidine). The reaction was then left at −10 °C for 3 days. The reaction mixture was then added to pentane (50 mL), and the resulting precipitate was collected on a medium-porosity glass filter and dried *in vacuo* to yield **28** (23.4 mg, 0.0350 mmol, 43%) as a yellow powder. ^{1}H NMR (acetone-d_6, ambient temperature, 300 MHz, δ): 8.24 (1H, d, Tp), 8.02, (1H, d, Tp), 7.98 (1H, d, Tp), 7.96 (1H, d, Tp), 7.80 (1H, d, Tp), 7.53 (1H, d, Tp), 6.37 (1H, t, Tp), 6.34 (1H, t, Tp), 6.19 (1H, t, Tp), 5.56 (1H, d ($J = 4.3$), 3), 4.01 (2H, q ($J = 7.0$), 7), 3.48 (1H, ddd ($J = 4.3$, 9.8, 13.7), 4), 2.21 (3H, s, 9), 1.75 (1H, d ($J = 9.8$), 5), 1.26 (9H, d ($J = 8.5$), PMe3), 1.16 (3H, t ($J = 7.0$), 8). ^{13}C NMR (acetone-d_6, ambient temperature, 300 MHz, δ): 144.4 (s, Tp), 143.6 (s, Tp), 140.8 (s, Tp), 137.0 (s,Tp), 136.5 (s, Tp), 136.0 (s, Tp), 106.8 (s, 3), 106.5 (s, Tp), 105.5 (s, Tp), 104.6 (s, Tp), 57.6 (d ($J = 10.9$), 4), 57.0 (s, 7), 53.0 (s, 5), 17.3 (s, 9), 14.5 (s, 8), 12.4 (d ($J = 9.2$), PMe_3).

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Supporting Information Available: Crystallographic details for compounds *exo*-**5B**, *exo*-**6B**, *exo*-**7B**, *exo*-**8B**, *exo*-**11B**, and *endo*-**12B** and spectra for selected compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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