Furan [3 + 2] Dipolar Cycloadditions Promoted by a π-Basic Tungsten Metal Fragment

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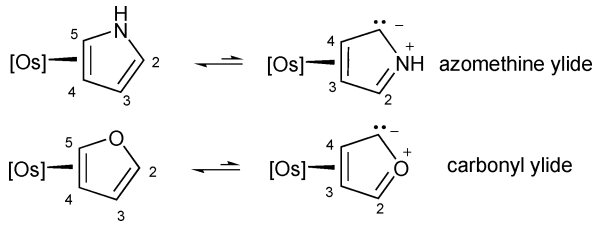
Reactions are reported for the TpW(NO)(PMe_3) complex of either 2-methylfuran or 2,5-dimethylfuran with various dipolarophiles (*N*-methylmaleimide, *N*-phenylmaleimide, acrylonitrile). The resulting 7-oxanorbornene complexes are thought to be formed from a two-step reaction sequence. The first step involves the metal shifting the coordination site from C4−C5 to C3−C4, an action that renders the furan similar to a carbonyl ylide. This is followed by a 1,3-dipolar cycloaddition. In the case of the maleimides, a high preference (>10:1) for exo stereochemistry is observed. For acrylonitrile, the preference for exo is only modest (2:1). Attempts to liberate the intact 7-oxanorbornene were unsuccessful. Two crystal structures are presented that support the stereochemical assignments of the complexed cycloadducts.

Introduction

Diels−Alder cycloaddition reactions remain one of the most useful and widely studied processes in synthetic chemistry.[1] While, in principle, aromatic heterocycles are a rich source of dienes for these reactions, their participation is hampered by the accompanying loss of aromatic stabilization.[2] Transition metals can facilitate these reactions,[3−5] typically by lowering the energy of the LUMO of the dienophile. However, in certain cases, the metal can promote cycloadditions by disrupting the aromaticity of the heterocycle itself. An example of this is the use of $[Os(NH_3)_5]^{2+}$ to promote cycloaddition reactions with pyrroles.[6] When coordinated across C3 and C4, the heterocycle is rendered as an azamethine ylide and readily reacts with dipolarophiles under mild conditions. The analogous furan complex can be readily prepared,[7] but complexation actually *inhibits* cycloaddition relative to the native furan. This difference in reactivity is attributed to the thermodynamic instability of the carbonyl ylide (3,4-η^2) relative to its 4,5-η^2 linkage isomer.



The rhenium dearomatization agent {TpRe(CO)(MeIm)} (where Tp = hydridotris(pyrazolyl)borate and MeIm = 1-methylimidazole) is more electron-rich than its osmium predecessor,[8,9] and the corresponding 2,5-dimethylfuran complex has been shown to undergo a 1,3-dipolar cycloaddition reaction with TCNE (tetracyanoethylene).[10] However, cycloaddition was not observed for more pedestrian alkenes. The complex {TpW(NO)(PMe_3)},[9] an analogue of the aforementioned rhenium system, shows even greater π-basic properties, and our hope was that this system was sufficiently electron-donating that the carbonyl ylide isomer would be more thermodynamically accessible.

Results and Discussion

Furan complexes **1**−**3** were prepared by the direct reduction of TpW(NO)(PMe_3)(Br)[9] with sodium metal, in the presence of an excess of furan (**1**), 2-methylfuran (**2**), or 2,5-dimethylfuran (**3**). These complexes were isolated in yields ranging from 26 to 44%, as a mixture of three stereoisomers (**A**−**C**; Figure 1).

All of the complexes were characterized using ^{1}H, ^{13}C, and ^{31}P NMR, along with HSQC, HMBC, cyclic voltammetric, and infrared data.[11] We initially focused on the 2,5-dimethylfuran complex **3**. This complex was expected to have the largest equilibrium ratio of 3,4-η^2 to 4,5-η^2 isomers (**3Y**:**3A**), owing to the steric interaction for the latter linkage isomer between the C5 methyl group and the {TpW(NO)(PMe_3)} fragment (Scheme 1).

Conventional Diels−Alder reaction conditions for furans[2] require high temperatures or pressures,[12,13] microwave heating,[4]

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(11) It is possible to separate the two diastereomers of **3** with preparatory TLC. **3B** could be isolated and recrystallized. When **3B** was allowed to stand in deuterated solvent, **3C** reappeared, eventually reaching its equilibrium ratio.

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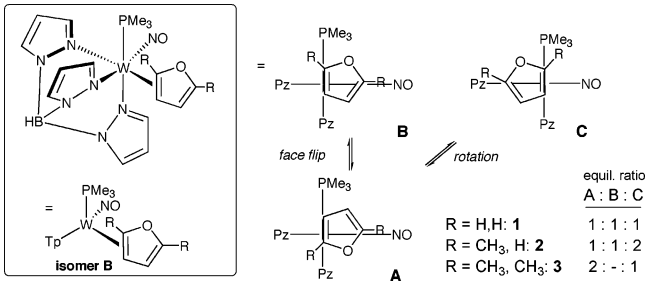
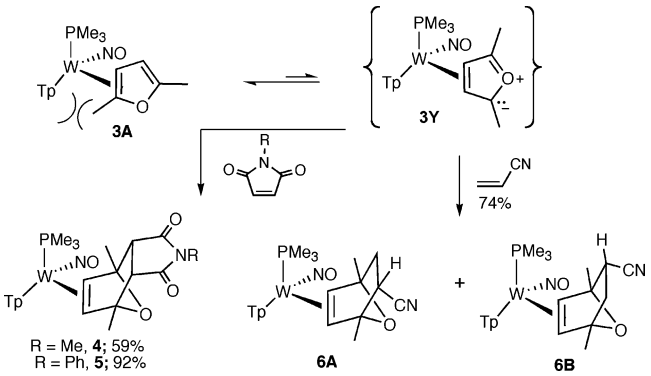


Figure 1. Stereoisomers of furan complexes **1**−**3**.

Scheme 1



ultrasonic irradiation,[14] ionic liquids,[15] or Lewis acids.[3−5] These methods usually afford cycloadducts as mixtures of diastereomers.[2] In contrast, complex **3** was found to undergo a [3 + 2] dipolar cycloaddition reaction with *N*-methylmaleimide, *N*-phenylmaleimide, or acrylonitrile at room temperature, under neutral conditions (Scheme 1). In the case of both *N*-methylmaleimide (**4**) and *N*-phenylmaleimide (**5**) the exo cycloadduct is formed as the dominant product (dr > 10:1). An ORTEP diagram was obtained, which confirms the stereochemistry of cycloadduct **4** (Figure 2). For comparison, a solution was prepared of uncoordinated 2,5-dimethylfuran and *N*-phenylmaleimide at concentrations similar to those used in the preparation of **5**. After 12 days, no reaction had occurred.

When the 2,5-dimethylfuran complex **3** is allowed to react with neat acrylonitrile over the course of 6 days, a mixture of three diastereomers, **6A**−**C** (A:B:C = 1:3:2), is isolated in 74% yield. Figure 3 shows an ORTEP diagram of **6A**, one of the diastereomers produced in this reaction. NOE data suggest that two diastereomers (**A** and **B**) possess the same exo ring stereochemistry but are coordination diastereomers, while the isomer **6C** is thought to be an endo isomer. The overall exo:endo ratio by ^{1}H NMR is 2:1. By comparison, Diels−Alder reactions described in the literature between 2,5-dimethylfuran and acrylonitrile require the use of Lewis acids and are moderately selective for the endo isomer.[4] The reaction of furan with acrylonitrile at room temperature takes 5 weeks to give a 39% yield.[16] Cycloaddition reactions were also attempted unsuccessfully with itaconic and citraconic anhydrides and maleate, fumarate, and acrylate methyl esters.

7-Oxabicyclo[2.2.1]heptenes are useful synthetic intermediates for carbohydrates and prostaglandins,[17] and oxanorbornenes

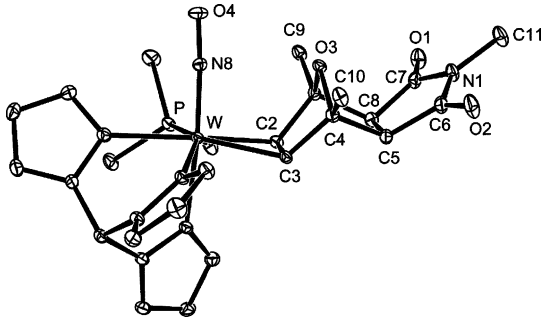


Figure 2. ORTEP diagram for cycloadduct **4** (30% ellipsoids).

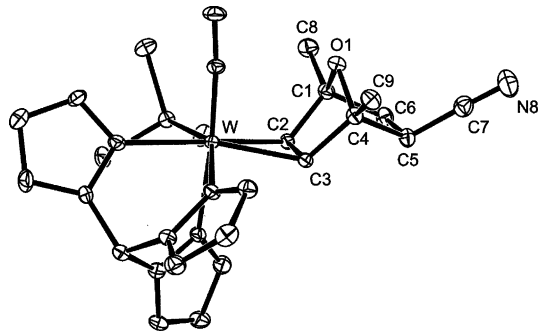
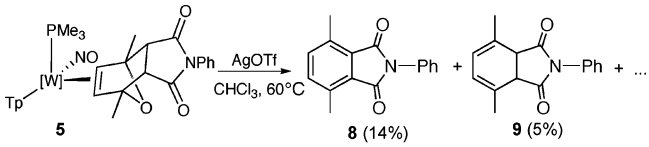
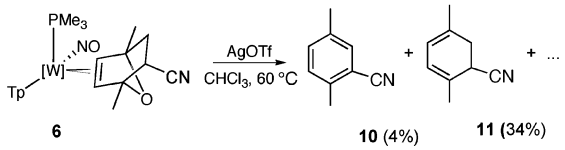


Figure 3. ORTEP diagram for cycloadduct **6A** (30% ellipsoids).

such as those found as ligands in the complexes **4**−**6** are currently of interest as potential antifungal agents,[18,19] Notably, the bridgehead methyl groups have been shown to enhance the potency of these antifungals relative to compounds derived from furan. Unfortunately, all attempts to decomplex cycloadducts **4**−**6** by metal oxidation with silver triflate and mild heating were unsuccessful. Instead, a complex mixture of products was produced from which only small amounts of purified organic samples could be isolated (eqs 1 and 2). These include the



(1)



(2)

phthalimide **8** and the benzonitrile **10**, both of which are products of double elimination. In addition, two compounds (**9** and **11**) were isolated that appear to be the dihydro analogues of **8** and **10**, respectively. Although the small quantities of these materials (typically 1−3 mg) were insufficient to obtain their full characterization, NMR data for **9** and **11** rule out the possibility of intact 7-oxabicyclo[2.2.1]heptenes.[4] Rather, NMR data for these compounds suggest a cyclohexadiene motif.[20] Such a structure could result from an oxygen atom transfer from

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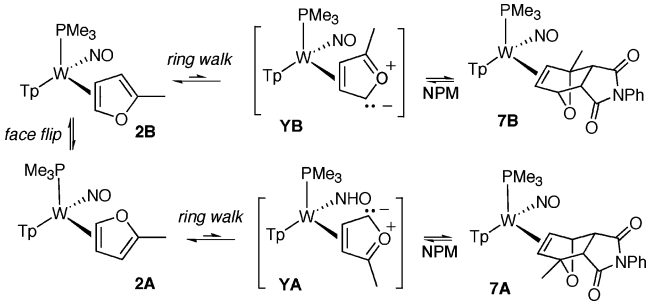
Scheme 2



the oxanorbornene ligand to the tungsten, and a similar reaction has been reported by Mayer et al., in which a tungsten(II) complex extracts an oxygen atom from a coordinated 2,5-dihydrofuran to generate a diene.[21]

The 2-methylfuran complex **2** reacts with *N*-phenylmaleimide in a fashion similar to that for **3** to give exo cycloadducts. Consistent with the notion that reactivity occurs through the 3,4-η^2 isomer, this reaction is slower (1 week; cf. 12 h) than that of the 2,5-dimethylfuran complex due to the increased stability of the 4,5-η^2 isomers (Scheme 2, **2A** and **2B**) compared to the ylides (**YA** and **YB**). Two coordination diastereomers are initially observed in the ^{1}H NMR spectrum of the product (**7A**, **7B**). At first, **7B** is the major isomer, but over several days or upon heating, this complex converts to its more stable isomer, **7A**. Presumably, isomerization occurs through a reaction pathway involving a retrocycloaddition and an interfacial isomerization (face flip) of **2**, as depicted in Scheme 2. However, the available data cannot rule out an alternative mechanism involving epimerization at the metal.

In summary, this study demonstrates an unconventional approach for promoting a cycloaddition reaction between furans and electron-deficient olefins. Instead of using a Lewis acid to activate the diene, the reaction is promoted by disrupting the aromatic stabilization of the heterocycle. The reaction is most facile for 2,5-dialkylated furans, as such a substitution pattern increases the equilibrium concentration of the reactive carbonyl ylide isomer. Attempts to remove the cycloadduct from the tungsten by metal oxidation failed to return the intact cycloadducts. This failure, along with the limited scope of dienophiles, may limit the synthetic value of the present system, but this study demonstrates the potential of a cycloaddition strategy in which furans are converted into carbonyl ylides via their η^2 coordination.

Experimental Section

General Methods. The {TpW(NO)(PMe$_3$)} fragment was prepared according to literature procedures.[9] NMR spectra were obtained on a 300 or 500 MHz Varian INOVA spectrometer or a Bruker 300 or 500 MHz Avance instrument. All chemical shifts are reported in ppm and are referenced to tetramethylsilane (TMS) using residual ^{1}H or ^{13}C signals of the deuterated solvents as internal standards. Coupling constants (*J*) are reported in hertz (Hz). Deuterated solvents were used as received from Cambridge Isotopes. 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 voltammetric (CV) data were taken at ambient temperature at 100 mV/s 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 tetrabutylammonium hexafluorophosphate (TBAH) electrolyte (~0.5 M). All potentials are reported versus NHE (normal hydrogen electrode) using cobaltocenium hexafluorophosphate ($E_{1/2}$ = −780 mV) or ferrocene ($E_{1/2}$ = +550 mV) as an internal standard. Elemental analysis was obtained from Atlantic Microlabs or with a Perkin-Elmer 2400 Series II CHNS/O analyzer. Mass spectra were obtained on a JEOL JMS600 instrument using FAB+ or a Shumadzu CSMS QP5050 by direct inlet; no counterions were observed. The isotopic mixture for the parent ion matches that calculated on the basis of natural abundances. Unless otherwise noted, all synthetic reactions and electrochemical experiments were performed under a dry nitrogen atmosphere. THF (tetrahydrofuran), benzene, and methylene chloride were purged with nitrogen and purified by passage through a column packed with activated alumina. Other solvents and liquid reagents were purged with nitrogen prior to use. Other reagents were used as received.

TpW(NO)(PMe$_3$)((4,5-η^2)-furan) (1A, 1B, and 1C). TpW(NO)(PMe$_3$)(Br) (509 mg, 1.01 mmol) was added to 30 mL of THF and stirred until homogeneous, and then furan (4.0 mL, 54 mmol) was added. Then a sodium dispersion (3.35 g, 0.43 mmol) was added and the reaction mixture was stirred for 3 days. The reaction mixture was filtered through 1 in. of Celite in a 15 mL medium-porosity glass filter over a 125 mL filter flask. The solvent was evaporated under reduced pressure to dryness, and then the residue was redissolved in methylene chloride and the solution chromatographed on a 2.5 in. silica column in a 150 mL medium-porosity glass filter. The yellow band was eluted with a 1:1 solvent mixture of diethyl ether and THF. The solvent was evaporated under reduced pressure to 5.0 mL and then diluted to 45 mL with pentane. The precipitate was collected on a 15 mL medium-porosity glass filter over a 125 mL filter flask. The precipitate was dried under reduced pressure. A 151 mg amount (0.26 mmol, 26%) of a yellow solid was isolated that contained three diastereomers, **1A**, **1B**, and **1C**, in a 1:1:1 ratio. ^{1}H NMR (chloroform-*d*): δ 8.53 (1H, d, J = 1.5, Tp), 8.34 (1H, d, J = 1.9, Tp), 8.32 (1H, d, J = 1.9, Tp), 8.02 (1H, d, J = 1.9, Tp), 7.98 (2H, dd, J = 1.9, 3.8, Tp), 7.73 (1H, d, J = 2.3, Tp), 7.71 (1H, d, J = 2.3, Tp), 7.65 (3H, t, J = 2.7, Tp), 7.61 (1H, d, J = 2.3, Tp), 7.58 (2H, t, J = 2.7, Tp), 7.56 (1H, d, J = 1.9, Tp), 7.45 (1H, dd, J = 5.4, 13.7, 5-H **C**), 7.35 (1H, dd, J = 5.8, 14.2, 5-H **B**), 7.18 (1H, d, J = 1.9, Tp), 7.04 (1H, d, J = 1.9, Tp), 7.00 (1H, d, J = 1.9, Tp), 6.47 (1H, d, J = 2.3, 2-H **A**), 6.40 (1H, d, J = 2.3, 2-H **B**), 6.27 (5H, m, Tp), 6.11 (3H, m, 3-H **B**, Tp), 5.98 (1H, t, J = 2.1, Tp), 5.91 (1H, d, J = 2.3, 2-H **C**), 5.81 (1H, dd, J = 4.2, 5.4, 5-H **A**), 5.77 (1H, t, J = 2.3, 3-H **A**), 5.09 (1H, t, J = 2.7, 2.3, 3-H **C**), 4.61 (1H, dt, J = 2.7, 5.4, 5.0, 4-H **C**), 4.26 (1H, ddd, J = 2.3, 5.4, 12.3, 4-H **A**), 2.81 (1H, dt, J = 2.7, 5.8, 5.8, 4-H **B**), 1.44 (9H, J = 8.1, PMe$_3$), 1.41 (9H, J = 8.4, PMe$_3$), 1.38 (9H, J = 8.1, PMe$_3$). ^{13}C NMR (acetone-d_6): 146.1 (s, Tp), 145.8 (s, Tp), 144.9 (s, Tp), 144.5 (s, Tp), 144.0 (s, Tp), 143.4 (s, Tp), 143.2 (s, Tp), 142.8 (s, Tp), 140.5 (s, Tp), 138.5 (s, Tp), 138.3 (s, Tp), 137.8 (s, Tp), 137.7 (s, Tp), 137.0 (s, Tp), 136.7 (s, Tp), 111.9 (s, Tp), 111.6 (s, 3-C **B**), 110.6 (s, 3-C **C**), 109.4 (s, 3-C **A**), 107.8 (s, 2-C **A**), 107.6 (s, 2-C **B**), 107.5 (s, 5-C **A**), 107.4 (s, 2-C **C**), 107.1 (s, Tp), 107.0 (s, Tp), 106.7 (s, 5-C **B**), 105.4 (s, Tp), 105.3 (s, 5-C **C**), 58.1 (s, 4-C **C**), 57.6 (s, 4-C **B**), 56.3 (s, 4-C **A**),15.5−14.7 (m, PMe$_3$). IR: $\nu_{N\equiv O}$ 1561 cm^{-1}. CV: $E_{p,a}$ = +32 mV. Purity estimated to be >90% according to ^{1}H NMR and electrochemical data.

TpW(NO)(PMe$_3$)((4,5-η^2)-2-methylfuran) (2A, 2B, and 2C). This compound was prepared using the same procedure as for **1**. The yellow product was isolated in 44% yield (4.4 mmol, 2.6 g) as a 1:1:2 mixture of **2A**, **2B**, and **2C**, respectively. ^{1}H NMR (chloroform-*d*): δ 8.60 (1H, d, J = 1.7, Tp), 8.34 (1H, d, J = 1.7, Tp), 8.32 (1H, d, J = 1.9, Tp), 8.01 (1H, d, J = 1.9, Tp), 7.94

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(2H, broad, Tp), 7.71 (1H, d, $J = 2.3$, Tp), 7.70 (1H, d, $J = 2.3$, Tp), 7.64 (2H, broad, Tp), 7.58 (4H, broad, Tp), 7.45 (1H, dd, $J =$ 5.4, 13.0, 5-H **C**), 7.29 (1H, dd, $J = 5.7$, 14.5, 5-H **B**), 7.16 (1H, d, $J = 1.9$, Tp), 7.02 (1H, d, $J = 2.1$, Tp), 6.97 (1H, d, $J = 1.9$, Tp), 6.26 (4H, m, Tp), 6.11 (1H, t, $J = 2.3$, Tp), 6.09 (1H, t, $J =$ 2.3, Tp), 5.99 (1H, t, $J = 2.3$, Tp), 5.80 (1H, dd, $J = 1.1$, 2.2, 3-H **B**), 5.74 (1H, dd, $J = 4.3$, 5.5, 5-H **A**), 5.46 (1H, s, broad, 3-H **A**), 4.70 (1H, dd, broad, 3-H **C**), 4.62 (1H, dtd, $J = 0.9$, 2.6, 5.4, 4.3, 4-H **C**), 4.22 (1H, dddd, $J = 1.0$, 2.3, 5.7, 12.6, 4-H **A**), 2.76 (1H, m, broad, 4-H **B**), 2.21 (6H, d, $J = 0.9$, Me (**A** and **B**)), 1.74 (3H, s, broad, Me (**C**)), 1.50 (9H, d, $J = 8.3$, PMe_3 (minor)), 1.46 (9H, d, $J = 8.1$, PMe_3 (major)), 1.43 (9H, d, $J = 8.1$, PMe_3 (minor)). ^{13}C NMR (chloroform-*d*): δ 149.9 (s, Tp), 142.9 (s, Tp), 142.8 (s, Tp), 142.7 (s, Tp), 141.7 (s, Tp), 140.8 (s, Tp), 140.5 (s, Tp), 136.3 (s, Tp), 136.1 (s, Tp), 135.7 (s, Tp), 134.9 (s, Tp), 134.5 (s, Tp), 107.3 (s, 5-C **A**), 107.1 (s, 3-C **B**), 106.3 (s, 3-C **A**), 106.3 (s, Tp), 106.0 (s, Tp), 105.9 (s, Tp), 105.8 (s, Tp), 105.7 (s, Tp), 105.5 (s, Tp), 105.4 (s, Tp), 105.2 (s, 3-C **C**), 104.8 (d, $J = 16.1$, 5-C **B**), 104.1 (s, Tp), 103.9 (d, $J = 14.4$, 5-C **C**), 58.72 (s, 4-C **C**), 57.6 (s, 4-C **B**), 56.3 (s, 4-C **A**), 14.7 (d, $J = 27.6$, PMe_3 minor), 14.4 (d, $J = 27.6$, PMe_3 minor), 14.2 (d, $J = 27.6$, PMe_3 major), 13.6 (s, Me major), 12.4 (s, Me minor), 12.2 (s, Me minor). CV: $E_{p,a} =$ +43 mV. IR: $\nu_{N\equiv O}$ 1561 cm^{-1}. LRMS: calcd, 585; found, 585. Purity estimated to be >90% according to ^{1}H NMR and electrochemical data.

TpW(NO)(PMe_3)((4,5-η^2)-2,5-dimethylfuran) (3A and 3C). TpW(NO)(PMe_3)Br (5 g, 8.5 mmol) is reacted with 2,5-dimethylfuran (50 equiv) in the same manner as for **1**. The yellow product was isolated in 43% yield (2.26 g, 3.7 mmol) as a 2:1 mixture of **3A** and **3C**. ^{1}H NMR (chloroform-*d*): δ 8.49 (1H, d, $J = 1.5$, Tp), 8.27 (1H, d, $J = 1.5$, Tp), 7.99 (1H, d, $J = 1.5$, Tp), 7.89 (1H, d, $J = 1.5$, Tp), 7.66 (1H, d, $J = 1.5$, Tp), 7.58 (4H, m, Tp), 7.16 (1H, d, $J = 1.9$, Tp), 7.11 (1H, d, $J = 1.7$, Tp), 6.26 (3H, m, Tp), 6.22 (1H, t, $J = 2.0$, Tp), 6.13 (1H, t, $J = 2.0$, Tp), 6.02 (1H, t, $J =$ 2.1, Tp), 5.46 (1H, s, 3-H **A**), 4.56 (1H, s, 4-H **C**), 4.31 (1H, s, 3-H **C**), 3.60 (1H, dd, $J = 0.9$, 12.1, 4-H **A**), 2.38 (3H, s, 2-H **C** (Me)), 2.20 (3H, s, 2-H **A** (Me)), 1.75 (3H, s, 5-H **C** (Me)), 1.36 (9H, d, $J = 7.7$, PMe_3), 1.28 (9H, d, $J = 8.1$, PMe_3), 1.03 (3H, d, $J = 1.3$, 5-H **A** (Me)). ^{13}C NMR (chloroform-*d*): δ 144.1 (s, Tp), 143.9 (s, Tp), 142.6 (s, Tp), 142.5 (s, Tp), 141.2 (s, Tp), 140.9 (s, Tp), 136.1 (s, Tp), 135.8 (s, Tp), 135.4 (s, Tp), 135.1 (s, Tp), 134.9 (s, Tp), 134.7 (s, Tp), 107.5 (s, 3A), 106.3 (s, Tp), 106.0 (s, Tp), 105.9 (s, Tp), 105.8 (s, 4-C **C**), 105.6 (s, Tp), 105.2 (s, Tp), 104.3 (s, Tp), 64.9 (s, 3-C **C**), 58.9 (s, 4-C **A**), 28.6 (s, 2-C **C** (Me)), 22.1 (s, 5-C **A** (Me)), 14.7 (d, PMe_3), 14.0 (s, 5-C **C** (Me)), 13.9 (d, PMe_3), 12.4 (s, 2A (Me)). CV: $E_{p,a} = -19$ mV. IR: $\nu_{N\equiv O}$ 1557 cm^{-1}. LRMS: calcd M$^+$, 599; found, 599. Purity estimated to be >90% according to ^{1}H NMR and electrochemical data. Anal. Calcd for $C_{18}H_{27}BN_7O_2PW$: C, 36.09; H, 4.54; N, 16.37. Found: C, 36.38; H, 4.55; N, 16.37.

TpW(NO)(PMe_3)((8,9-η^2)-1,4,7-trimethyl-10-oxa-4-azatricyclo-[5.2.1.0^{2,6}]dec-8-ene-3,5-dione) (4). TpW(NO)(PMe_3)((4,5-η^2)-2,5-dimethylfuran) (160 mg, 0.26 mmol) was dissolved in 2.0 g of CH_2Cl_2. *N*-Methylmaleimide (59 mg, 0.53 mmol) was dissolved in 2.0 g of THF. The solutions were combined and stirred at room temperature for 5 days. The solution was then diluted to 30 mL with pentane, and the product precipitated. The solid was collected on a 15 mL medium-porosity glass filter. The precipitate was dried under reduced pressure. A 59% yield (110 mg, 0.15 mmol) of a pale yellow precipitate was isolated. ^{1}H NMR (chloroform-*d*): δ 8.42 (1H, d, $J = 1.7$, Tp), 8.20 (1H, d, $J = 1.9$, Tp), 7.74 (1H, d, $J = 2.3$, Tp), 7.69 (1H, d, $J = 2.1$, Tp), 7.52 (1H, d, $J = 2.3$, Tp), 7.30 (1H, d, $J = 1.7$, Tp), 6.31 (1H, t, $J = 2.3$, Tp), 6.19 (1H, t, $J =$ 2.2, Tp), 6.14 (1H, t, $J = 2.3$, Tp), 3.22 (1H, d, $J = 6.6$, 2-H), 3.14 (1H, d, $J = 6.6$, 6-H), 2.90 (3H, s, Me, N-bound), 2.56 (1H, dd, $J = 8.2$, 10.9, 8-H), 1.96 (3H, s, 7-Me), 1.71 (3H, s, 1-Me), 1.62 (1H, dd, $J = 2.8$, 8.2), 0.99 (9H, d, $J = 8.3$, PMe_3). ^{13}C NMR (chloroform-*d*): δ 177.3 (s, CO), 177.1 (s, CO), 146.8 (s, Tp), 143.2 (s, Tp), 140.7 (s, Tp), 137.0 (s, Tp), 136.4 (s, Tp), 135.7 (s, Tp), 107.1 (s, Tp), 106.1 (s, Tp), 105.6 (s, Tp), 69.7 (d, $J = 15$, 8-C), 66.4 (s, 9-C), 60.1 (s, 6-C), 59.9 (s, 2-C), 24.8 (s, Me, N-bound), 20.7 (s, 1-Me), 20.4 (s, 7-Me), 13.6 (d, $J = 28.2$, PMe_3). CV: +722 mV. IR: $\nu_{C=O}$ 1690 cm^{-1}, $\nu_{N\equiv O}$ 1561 cm^{-1}. Purity estimated to be >90% according to ^{1}H NMR and electrochemical data.

TpW(NO)(PMe_3)((8,9-η^2)-1,7-Dimethyl-4-phenyl-10-oxa-4-azatricyclo[5.2.1.0^{2,6}]dec-8-ene-3,5-dione) (5). TpW(NO)(PMe_3)-((4,5-η^2)-2,5-dimethylfuran) (525 mg, 0.88 mmol) was dissolved in 3 mL of CH_2Cl_2. *N*-Phenylmaleimide (152 mg, 0.88 mmol) was dissolved in 1.5 mL of CH_2Cl_2. The solutions were combined and stirred at room temperature for 2 days. The solution was then diluted to approximately 30 mL with hexanes, and the product precipitated out. The solid was collected on a 15 mL medium-porosity glass filter dried under reduced pressure. 92% (622 mg, 0.81 mmol) of a pale yellow precipitate was isolated. ^{1}H NMR (chloroform-*d*): δ 8.46 (1H, d, $J = 1.9$, Tp), 8.24 (1H, d, $J = 1.9$, Tp), 7.75 (1H, d, $J = 2.3$, Tp), 7.72 (1H, d, $J = 2.3$, Tp), 7.54 (1H, d, $J = 2.3$, Tp), 7.44−7.29 (6H, m, Tp and phenyl), 6.33 (1H, t, $J = 2.2$, Tp), 6.22 (1H, t, $J = 2.2$, Tp), 6.17 (1H, t, $J = 2.2$, Tp), 3.41 (1H, d, $J =$ 6.9, 6-H), 3.31 (1H, d, $J = 6.9$, 2-H), 2.61 (1H, dd, $J = 8.3$, 10.9, 8-H), 2.04 (3H, s, 1-Me), 1.79 (3H, s, 7-Me), 1.69 (1H, dd, $J =$ 2.8, 8.3, 9-H), 1.03 (9H, d, $J = 8.3$, PMe_3). ^{13}C NMR (chloroform-*d*): δ 176.3 (s, CO), 176.1 (s, CO), 146.9 (s, Tp), 143.2 (s, Tp), 140.7 (s, Tp), 137.4 (s, Tp), 135.7 (s, Tp), 132.6 (s, Tp), 129.1 (s, phenyl), 128.4 (s, phenyl), 127.0 (s, phenyl), 90.6 (s, bridgehead-1), 90.2 (s, bridgehead-7), 107.2 (s, Tp), 106.2 (s, Tp), 105.7 (s, Tp), 70.0 (d, $J = 15.0$, 8-C), 66.7 (s, 9-C), 60.1 (s, 6-C), 60.0 (s, 2-C), 20.9 (s, Me-1), 20.5 (s, Me-7), 13.6 (d, $J = 28.2$, PMe_3). Purity estimated to be >90% according to ^{1}H NMR and electrochemical data. CV: $E_{p,a} = +699$ mV. IR: $\nu_{C=O}$ 1697 cm^{-1}, $\nu_{N\equiv O}$ 1548 cm^{-1}. LRMS: 772 (M$^+$).

TpW(NO)(PMe_3)((5,6-η^2)-1,4-Dimethyl-7-oxabicyclo[2.2.1]-hept-5-ene-2-carbonitrile) (6). TpW(NO)(PMe_3)(4,5-η^2-2,5-dimethylfuran) (53 mg, 0.088 mmol) was dissolved in acrylonitrile (2.54 g, 47 mmol) and stirred for 6 days at room temperature. The reaction mixture was diluted with 75 mL of stirred hexanes, and the product precipitated out of solution as an oil. The solvent was evaporated, and the oil was redissolved in a minimum amount of methylene chloride. The methylene chloride solution was added slowly to stirring hexanes, and a white solid was collected on a 15 mL medium-porosity glass filter. The cycloadduct was isolated as a mixture of isomers **A**, **B**, and **C** in a 1:3:2 ratio and in 74% yield (402 mg, 616 mmol). ^{1}H NMR (acetonitrile-d_3): δ 8.38 (1H, d, $J =$ 1.9, Tp), 8.35 (1H, d, $J = 1.9$, Tp), 8.34 (1H, d, $J = 2.1$, Tp), 8.14 (1H, d, $J = 1.9$, Tp, 7.92 (2H, broad, Tp), 7.85 (1H, d, $J =$ 2.4, Tp), 7.83 (2H, d, $J = 2.3$, Tp), 7.72 (1H, d, $J = 2.3$, Tp), 7.69 (1H, d, $J = 2.5$, Tp), 7.56 (1H, d, $J = 2.3$, Tp), 7.48 (1H, d, $J =$ 2.1, Tp), 7.45 (1H, d, $J = 1.5$, Tp), 7.43 (1H, d, $J = 2.1$, Tp), 7.38 (1H, d, $J = 1.9$, Tp), 7.28 (1H, d, $J = 1.5$, Tp), 6.43 (2H, t, $J =$ 2.2, Tp), 6.28 (1H, t, $J = 2.3$, Tp), 6.25 (3H, m, Tp), 6.05 (1H, t, $J = 1.3$, Tp), 3.15 (1H, dd, $J = 4.5$, 8.9, 3-H **A**), 3.01 (1H, dd, $J =$ 4.7, 8.9, 2-H **B**), 2.90 (1H, dd, $J = 4.9$, 10.5, 2-H **C**), 2.70 (1H, dd, $J = 8.5$, 12.1, 5-H **C**), 2.63 (1H, dd, $J = 8.5$, 11.5, 5-H **B**), 2.52 (2H, dd, $J = 8.9$, 11.3, 5-H **A** and 3-H **B** trans to CN), 2.39 (1H, dd, $J = 9.0$, 11.5, 2-H **A** trans to CN), 2.29 (1H, t, $J = 10.9$, 3-H **C** trans to CN), 2.22 (1H, dd, 4.7, 11.3, 3-H **C** cis to CN), 2.03 (1H, dd, $J = 4.5$, 11.3, 3-H **B** cis to CN), 1.96 (1H, buried, 2-H **A** cis to CN), 1.92 (3H, s, Me-1 **B**), 1.84 (3H, s, Me-4 **C**), 1.78 (3H, s, Me-1 **A**), 1.71 (3H, s, Me-4 **A**), 1.67 (1H, dd, $J = 3.0$, 8.5, 6-H **C**), 1.58 (3H, s, Me-4 **B**), 1.54 (3H, s, Me-1 **C**), 1.28 (2H, broad, 6-H **A** and **B**), 0.98 (9H, d, $J = 8.5$, PMe_3), 0.97 (9H, d, $J = 8.5$, PMe_3). ^{13}C NMR (acetonitrile-d_3): δ 147.1 (s, Tp), 147.0 (s, Tp), 143.6 (s, Tp), 143.5 (s, Tp), 142.2 (s, Tp), 142.1 (s, Tp), 140.3 (s, Tp), 138.2 (s, Tp), 137.5 (s, Tp), 136.9 (s, Tp), 135.3 (s, Tp), 123.8 (s, CN A and B), 123.5 (s, CN C), 108.0 (s, Tp),

107.0 (s, Tp), 106.9 (s, Tp), 106.7 (s, Tp), 106.5 (s, Tp), 103.8 (s, Tp), 90.4 (s, 4-C **C**), 90.0 (s, 4-C **A**, 1-C **C**), 89.9 (s, 1-C **B**), 89.0 (s, 1-C **A**, 4-C **B**), 68.3 (s, 5-C **C**), 68.2 (s, 5-C **B**), 68.1 (s, 5-C **A**), 64.9 (s, 6-C **A** and **B**), 60.9 (s, 6-C **C**), 49.6 (s, 5-C **A**, 3-C **B**), 49.0 (s, 3-C **C**), 43.7 (s, 3-C **A**), 43.5 (s, 2-C **B**, 2-C **C**), 32.2 (s, 6-C **A**, 6-C **B**), 23.4 (s, Me-1 **C**), 23.3 (s, Me-4 **B**), 23.2 (s, Me-1 **A**, Me-1 **B**), 22.8 (s, Me-4 **C**), 21.3 (s, Me-4 **A**), 13.4 (d, $J = 1.7$, PMe_3), 13.0 (d, $J = 1.7$, PMe_3). CV: +648 mV. IR: $\nu_{N\equiv O}$ 1561 cm^{-1}, $\nu_{C\equiv N}$ 2231 cm^{-1}. Anal. Calcd for $C_{21}H_{30}BN_8O_2PW\cdot 0.5CH_2Cl_2$ (CH_2Cl_2 is present in the crystal structure): C, 37.18; H, 4.50; N, 16.13. Found: C, 37.36; H, 4.61; N, 16.30. LRMS: calcd, 653; found, 653.

TpW(NO)(PMe_3)((8,9-η^2)-1-methyl-4-phenyl-10-oxa-4-azatricyclo[5.2.1.0^{2,6}]dec-8-ene-3,5-dione) (7). TpW(NO)(PMe_3)(4,5-η^2-2,5-dimethylfuran) (50 mg, 0.085 mmol) was dissolved in 1.03 g of *N*,*N*-dimethylformamide-d_7. *N*-Phenylmaleimide (29.5 mg, 0.17 mmol) was added to the DMF-d_7 solution. The solution was transferred to an NMR tube and placed in an oil bath at 65 °C for 2 days. A 45% conversion was observed with an A:B ratio of 5.5:1. ^{1}H NMR data were collected from a sample that was isolated from a preparatory TLC plate previously. ^{1}H NMR (acetone-d_6): δ 8.49 (1H, d, $J = 2.3$, Tp **A**), 8.25 (1H, d, $J = 1.8$, Tp **A**), 8.17 (1H, d, $J = 2.1$, Tp **B**), 8.16 (1H, d, $J = 1.5$, Tp **B**), 8.02 (1H, d, $J = 2.1$, Tp **B**), 7.99 (1H, d, $J = 2.4$, Tp **A**), 7.96 (1H, d, $J = 1.8$, Tp **B**), 7.94 (1H, d, $J = 2.4$, Tp **A**), 7.82 (1H, d, $J = 2.4$, Tp **A**), 7.77 (2H, d, $J = 2.1$, Tp **A** and **B**), 7.50−7.14 (10H, m, phenyl **A** and **B**), 6.45 (1H, t, $J = 2.1$, Tp **B**), 6.39 (1H, t, $J = 2.3$, Tp **B**), 6.38 (1H, t, $J = 2.3$, Tp **A**), 6.32 (1H, t, $J = 1.8$, Tp **B**), 6.31 (1H, t, $J = 1.8$, Tp **A**), 6.13 (1H, t, $J = 2.3$, Tp **A**), 5.0 (1H, s, bridgehead **B**), 4.88 (1H, s, bridgehead **A**), 3.58 (1H, d, $J = 6.5$, 6-H **A**), 3.48 (1H, d, $J = 6.9$, 2-H **B**), 3.37 (1H, d, $J = 6.9$, 6-H **B**), 3.20 (1H, d, $J = 6.5$, 2-H **A**), 3.10 (1H, dd, $J = 8.1$, 10.8, 9-H **B**), 2.98 (3H, s, Me **B**), 2.79 (1H, dd, $J = 8.3$, 17.3, 8-H **A**), 1.96 (3H, s, Me **A**), 1.60 (1H, dd, $J = 3.5$, 8.3, 9-H **A**), 1.36 (1H, dd, $J = 2.7$, 8.1, 8-H **B**), 1.29 (9H, d, $J = 8.5$, PMe_3 **A**), 1.21 (9H, d, $J = 8.5$, PMe_3 **B**). Other NMR data were collected in the presence of starting material, and the following are ^{13}C NMR data of just cycloadduct peaks of isomer **A**. ^{13}C NMR (*N*,*N*-dimethylformamide-d_7): δ 177.5 (s, CO), 176.3 (s, CO), 91.5 (s, 1-C), 84.9 (s, bridgehead), 64.2 (s, 8-C), 62.9 (s, 9-C), 57.8 (s, 2-C), 57.6 (s, 6-C), 19.8 (s, Me), 12.7 (d, $J = 28.2$, PMe_3).

3,6-Dimethyl-*N*-phenylphthalimide (8).[22] ^{1}H NMR (acetone-d_6): δ 2.65 (s, 6H), 7.52 (s, 2H), 7.4−7.5 (5H, Ph). ^{13}C NMR (acetone-d_6): δ 17.4, 127.5, 127.9, 128.9, 135.6, 136.6, 168.0 (C_{ipso} not observed). IR (HATR): $\nu_{C\equiv O}$ 1764 (w), 1720 (s) cm^{-1}. Yield: 14% from **5**.

1,2-Dihydro-3,6-dimethyl-*N*-phenylphthalimide. ^{1}H NMR (CD_3Cl): δ 2.03 (s, 6-H, Me), 3.72 (s, 2H, 1-H, 2-H), 5.73 (s, 2H, 4-H, 5-H), 7.25−7.47 (m, 5H, Ph). ^{13}C NMR (acetone-d_6): δ 22.1 (Me), 46.7 (1-C, 2-C), 121.0 (4-C, 5-C), 126.4 (Ph), 126.6 (3-C, 6-C), 128.5 (Ph), 129.1 (Ph). IR (HATR): $\nu_{C\equiv O}$ 1764 (w), 1720 (s) cm^{-1}. Yield: 5% from **5**. LRMS: 253 (M^+).

1,2-Dihydro-3,6-dimethylbenzonitrile. ^{1}H NMR ($CDCl_3$): δ 1.82 (s, 3H), 1.91 (s, 3H), 3.02 (d, 2H), 3.24 (t, 1H), 5.70 (d, $J = 5.6$), 5.77 ($J = 5.6$). Yield: 34% from **6**.

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Supporting Information Available: CIF files giving crystallographic data for compounds **4** and **6A**. This material is available free of charge via the Internet at http://pubs.acs.org.

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