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Cycloaddition Reactions of Dihapto-Coordinated Furans

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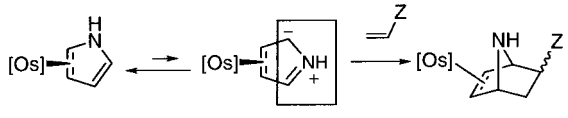
Abstract: Complexes of the type [TpRe(CO)(L)(η^2-furan)], where Tp = hydridotris(pyrazolyl)borate and L = PMe_3 (**1**) or ^{t}BuNC (**2**), undergo dipolar cycloadditions with TCNE (tetracyanoethylene) to afford 7-oxabicycloheptene complexes **3** and **4**, respectively. The corresponding 2-methylfuran complexes (**5** and **7**) for these L ligands give similar methyloxabicycloheptene complexes (**6** and **8**), with a diastereomer ratio >20:1 for **8**. For L = *N*-methylimidazole (MeIm, **9**), TCNE oxidizes the complex, but cycloadditions can be achieved with DMAD (dimethyl acetylenedicarboxylate) as the electrophile. Three complexes are observed: one in which DMAD undergoes a cycloaddition with the carbonyl ylide form of the complex (**10C**), and two complexes that are coordination diastereomers where DMAD has undergone a formal [2+2] cycloaddition with the uncoordinated double bond of the 4,5-η^2-furan ligand (**10B** and **10A**). With the imidazole complex of 2-methylfuran (**11**), only the [2+2] products (**12B** and **12A**) are observed. In the case of the 2,5-dimethylfuran complex (L = MeIm, **13**), which is formed as a single coordination diastereomer, only one [2+2] product is observed (**14**), the structure of which was confirmed by X-ray crystallography. Oxidative decomplexation of **14** results in liberation of the free oxabicyclo[3.2.0]heptadiene **15**, which can be thermally converted to the corresponding oxepin **16** in 70% yield.

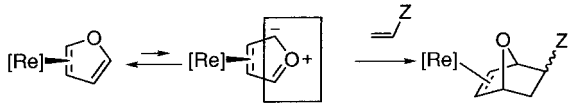
Introduction

Furans undergo [4+2] cycloaddition reactions (Diels−Alder) with a variety of dienophiles to generate the oxabicycloheptene core.[1] However, the aromaticity of furan as well as the strain of the resulting [2.2.1] bicyclic ring system often require the use of high pressures and/or temperatures to allow such reactions to proceed at appreciable rates.[2] For pyrroles, [4+2] cycloaddition is even more difficult than for furan owing to the increased aromatic character of the heterocycle.[3] In 1989, Taube et al. discovered that η^2-coordination of pyrrole by the π base pentaammineosmium(II) dramatically increased the rate of the cycloaddition reaction between pyrrole and maleic anhydride.[4] This surprising observation was proposed to occur by way of a transient intermediate in which the metal bound the pyrrole across C3 and C4, rendering the uncoordinated portion of the heterocycle similar to an azomethine ylide. This [3+2] cycloaddition reaction has been utilized in the efficient synthesis of several 7-azanorbornenes.[3,5] In contrast, the furan complex of pentaammineosmium(II) shows no reactivity with maleic anhydride over a 10 day period (20 °C), an observation that was ascribed to the decreased stability of the corresponding carbonyl ylide complex.[4]



azomethine ylide

We recently reported a detailed study on the rates and mechanisms of linkage isomerization processes in rhenium(I) η^2-aromatic complexes,[6] in which we observed intrafacial migration (ring walk) of the {TpRe(CO)(L)} fragment (L = ^{t}BuNC, PMe_3, pyridine, or *N*-methylimidazole (abbreviated MeIm)) coordinated to furan and *N*-methylpyrrole (L = MeIm only). We demonstrated that this process occurred through a transient intermediate in which the metal was bound 3,4-η^2, similar to that observed for the pentaammineosmium(II) system.[7] A recent communication from our group demonstrated that the cycloaddition of dimethyl fumarate with the {TpRe(CO)(MeIm)} complex of *N*-methylpyrrole occurs at a rate significantly faster than that observed for osmium(II).[8] This increase in rate is consistent with {TpRe(CO)(L)} fragments being more electron rich than the similar $\{Os(NH_3)_5\}^{2+}$ fragment. We postulated that the more electron-rich rhenium systems could raise the energy of the HOMO for the putative 3,4-η^2-furan intermediate, a carbonyl ylide, to such an extent that a dipolar cycloaddition reaction would become accessible.



carbonyl ylide

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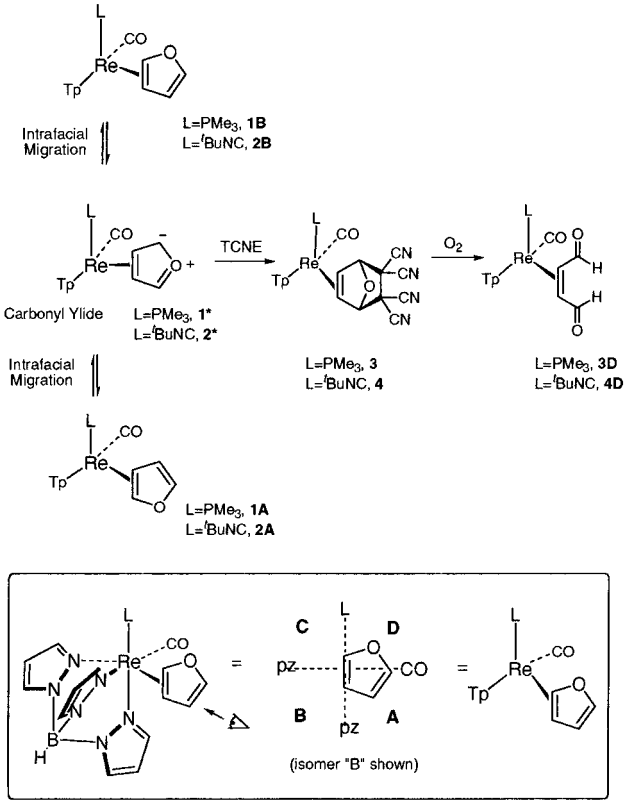
(1) Kappe, C. O.; Murphree, S. S.; Padwa, A. *Tetrahedron* **1997**, *53*, 14179.
(2) Moore, J. A.; Partain, E. M., III *J. Org. Chem.* **1983**, *48*, 1105.
(3) Chen, Z.; Trudell, M. L. *Chem. Rev.* **1996**, *96*, 1179.
(4) Cordone, R.; Harman, W. D.; Taube, H. *J. Am. Chem. Soc.* **1989**, *111*, 5969.
(5) Gonzalez, J.; Koontz, J. I.; Myers, W. H.; Hodges, L. M.; Sabat, M.; Nilsson, K. R.; Neely, L. K.; Harman, W. D. *J. Am. Chem. Soc.* **1995**, *117*, 3405.

10.1021/ja020137k CCC: $22.00

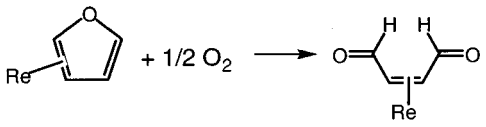
Scheme 1. Syntheses of 7-Oxabicyclo[2.2.1]heptene Complexes and Their Oxidation to Enedials



Results

The complexes [TpRe(CO)(L)(2,3-η^2-furan)] (L = PMe_3 (**1**), ^{t}BuNC (**2**)) were found to undergo [3+2] cycloaddition reactions with tetracyanoethylene (TCNE) to generate oxabicycloheptene complexes **3** (73%) and **4** (66%), respectively (Scheme 1). The reactions proceed quickly, with no starting material present after the reaction is allowed to proceed for less than 5 min ([Re] = [TCNE] = ~20 mM). These complexes show infrared absorptions at 1845 (**3**) and 1869 (**4**) cm^{-1} and Re(II)/(I) reduction potentials at $E_{1/2}$ = 0.92 (**3**) and 0.94 (**4**) V (NHE), consistent with Re(I)-alkene complexes that are more electron deficient than ethylene complexes of the same metal fragments.[9] Although the nitrile stretching absorptions are too weak to be observed in the infrared spectrum of **3**, the nitriles are accounted for in the ^{13}C NMR spectrum by signals near 129 ppm, in addition to bridgehead carbons near 95 ppm. For **4**, bridgehead carbons appear near 94 and 93 ppm, but nitrile carbon signals are too weak to be readily observed. For comparison purposes, the cycloaddition reaction was repeated with TCNE and free furan at four times the concentrations used with rhenium. No cycloadduct was observed after 2 days, even after heating to 80 °C. To our knowledge, the uncomplexed [2.2.1]oxabicycloheptene, resulting from a Diels−Alder reaction between furan and TCNE, has not been reported in the literature.

In contrast to simple alkene complexes of {TpRe(CO)(L)} systems, the tetranitrile cycloadducts **3** and **4** are extremely air sensitive. Upon brief exposure to air, these cycloadducts convert into the corresponding *C,C*-η^2-(Z)-2-butenedial complexes **3D** and **4D**, whether in solution or solid state. Key features of the oxidized products include two aldehyde signals in both the ^{13}C and ^{1}H NMR spectra. The structure of complex **4D** was confirmed by growing a single crystal from an acetone solution of the complex layered over water (Figure 1). The structure shows that the alkene is orthogonal to the Re−CO bond, and the two aldehydes are held in a nearly coplanar arrangement (O=C−C=C dihedral angles are 162 and 168°). The C=O bonds have been lengthened and the C−C bonds shortened by about 0.02 Å each, relative to those values expected for the uncomplexed dial.[10] These structural changes in **4D**, along with the observations that the rhenium CO stretching frequency (1864 cm^{-1}) and the Re(II)/(I) reduction potential ($E_{1/2}$ = 1.16 V) for **4D** are significantly higher than those values for [TpRe(CO)(^{t}BuNC)(η^2-ethylene)],[9] indicate a greater degree of metal−ligand π back-bonding in this complex. While the stoichiometry and mechanism of the formation of **4D** are unclear, the overall process of treating the bound furan with TCNE followed by exposure to air is to oxidize the bound furan ligand, presumably by the following relationship:



(1)

Monitoring the conversion of **3** to **3D** by ^{1}H NMR with an internal standard indicates that the conversion is virtually quantitative. The oxidation of furan to butenedial is well-known for a variety of different oxidants, including $KMnO_4$, H_2O_2, and more recently dimethyldioxirane.[11]

With use of the 2-methylfuran complexes of the PMe_3 and ^{t}BuNC systems (complexes **5** and **7**, respectively), cycloadducts resulting from the [3+2] cycloaddition with TCNE are also observed (**6** and **8**, Scheme 2). Because the methyl group originating from the furan differentiates the bridgehead carbons,

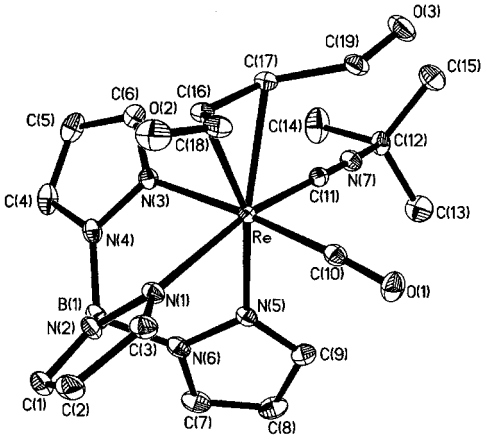
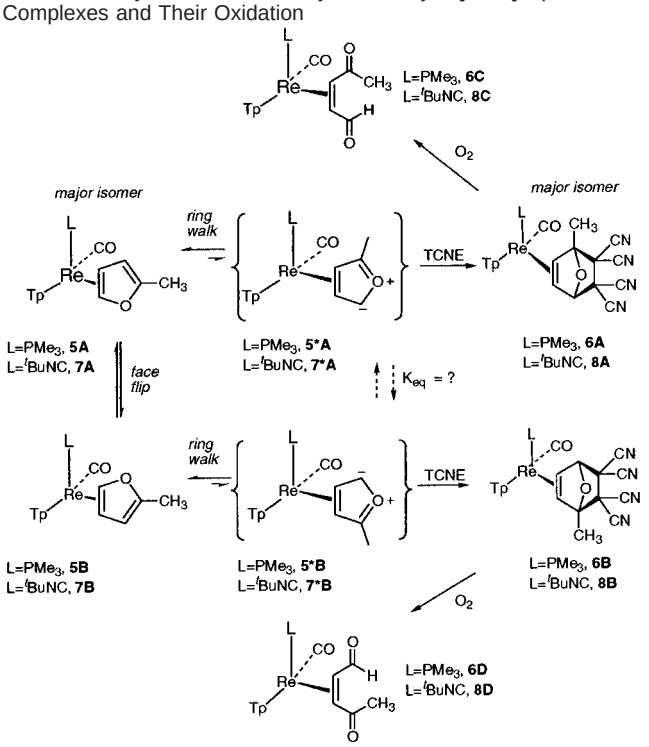


Figure 1. ORTEP diagram of enedial complex **4D** (30% probability ellipsoids shown). Selected bond distances (Å): Re−C(16) 2.202(2), Re−C(17) 2.205(2), C(16)−C(17) 1.445(3), C(17)−C(19) 1.465(3), C(16)−C(18) 1.451(3), O(3)−C(19) 1.216(3), O(2)−C(18) 1.219(3).

(6) Brooks, B. C.; Meiere, S. H.; Friedman, L. A.; Carrig, E. H.; Gunnoe, T. B.; Harman, W. D. *J. Am. Chem. Soc.* **2001**, *123*, 3541.
(7) Chen, H. C. *Activation of Olefins and Dearomatization of Furans with Pentaammineosmium(II)*; University of Virginia, 1997.
(8) Chordia, M. D.; Smith, P. L.; Meiere, S. H.; Sabat, M.; Harman, W. D. *J. Am. Chem. Soc.* **2001**, *123*, 10756.
(9) Friedman, L. A.; Meiere, S. H.; Brooks, B. C.; Harman, W. D. *Organometallics* **2001**, *20*, 1699.
(10) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, *12*, S1.
(11) Adger, B. J.; Barrett, C.; Brennan, J.; McGuigan, P.; McKervey, M. A.; Tarbit, B. *J. Chem. Soc., Chem. Commun.* **1993**, *15*, 1220.

Scheme 2. Syntheses of 1-Methyl-7-oxabicyclo[2.2.1]heptene Complexes and Their Oxidation



two diastereomers of the cycloadduct complex are observed for both **5** and **7** when each is reacted with TCNE.

For L = PMe_3, the furan complex (**5**) exists in a 2.1:1 equilibrium ratio of coordination diastereomers (**5A**:**5B**), where the major isomer has the oxygen in quadrant A (see Scheme 1). Both **5A** and **5B** react with TCNE (~20 mM of each) to generate methyloxabicycloheptene complexes **6A** and **6B** in a ratio of 1.8:1. These products differ in the location of the bridgehead methyl group with respect to the ligand configuration about the metal. NOE data indicate that complex **6A** has the methyl group oriented toward the PMe_3 ligand (quadrant D),[9] while complex **6B** has the methyl group oriented away from the PMe_3 ligand (quadrant A). The same ratio of **6A**:**6B** (1.8:1) is observed if the reaction is repeated at −40 °C or if it is carried out under more dilute conditions ([**5**] = [TCNE] = ~1.7 mM).

Combining complexes **6A** and **6B** (in a 1.8:1 ratio) with an equivalent amount of the furan complex **1** (~20 mM) for 24 h (25 °C) results in a ratio of ~12.5:1 for (**6A**+**6B**):**3**, the ratio of **6A** and **6B** remaining approximately constant (1.9:1). This observation indicates that a retrocycloaddition is operative and that its half-life at 25 °C is on the order of 200 h. Allowing the 2-methylfuran complex **5** to react with 0.4 equiv of TCNE gives the same ratio of **6A**:**6B** as when 1 equiv of TCNE is used. When an equimolar mixture of the PMe_3 furan (**1**) and 2-methylfuran (**5**) complexes was treated with 0.25 equiv of TCNE, a 1:1.1 ratio of cycloadducts (**6A**+**6B**):**3** was observed, indicating that the rate of cycloaddition is similar for furan and 2-methylfuran complexes.

For L = ^{t}BuNC, the 2-methylfuran complex **7** exists as a 4.9:1 ratio of coordination diastereomers (**7A**:**7B**), where the major diastereomer has the oxygen in quadrant A (see Scheme 1).[6] Complex **7** reacts with TCNE ([Re] = [TCNE] = ~32 mM) to generate methyloxabicycloheptene complexes **8A** and **8B** (Scheme 2), which differ solely in the placement of the bridgehead methyl group relative to the ligand set about the metal. However, in contrast (vide supra) to **6A** and **6B**, the ratio observed for **8A**:**8B** is 27:1. Similar to the phosphine complexes described above, the ratio of **8A**:**8B** is unchanged when the reaction is performed at −40 °C. However, repeating this reaction at 6 mM TCNE (still 1 equiv) resulted in a ratio of 43:1 of **8A**:**8B**, and repeating this reaction with 20 mM rhenium and 0.44 equiv of TCNE increases the ratio of **8A**:**8B** to 75:1. NOE data indicate that the major isomer (**8A**) has the methyl group oriented toward the isonitrile ligand.

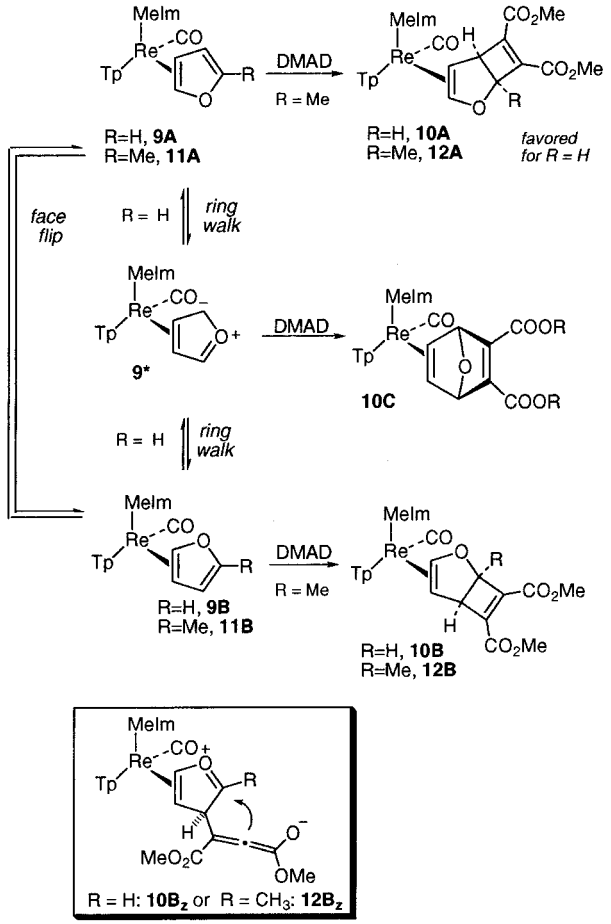
When an equimolar mixture of the isonitrile furan (**2**) and 2-methylfuran (**7**) complexes was treated with 0.25 equiv of TCNE, a 1.4:1 ratio of cycloadducts (**8A**+**8B**):**4** was observed, indicating that the rate of cycloaddition is similar for furan and 2-methylfuran complexes. When a solution of **8A** and **8B** is mixed with **2** (~20 mM each) and allowed to stir for 24 h, the ratio of (**8A**+**8B**):**4** is found to be ~130:1, indicating that the half-life for the retrocycloaddition is about 1600 h. Thus, for the ^{t}BuNC/2-methylfuran system, a large kinetic bias exists for the coordination diastereomer with the methyl group oriented *toward* the ^{t}BuNC ligand (**8A**).

To better establish the role that the electronic properties of the metal play in the cycloaddition reaction, an equimolar mixture of the furan complex **1** (L = PMe_3) and furan complex **2** (L = ^{t}BuNC) was treated with 0.22 equiv of TCNE. The ratio of **3**:**4** was found to be 6.2:1. Thus, under identical reaction conditions, phosphine complex **1** reacted with TCNE at a rate approximately 6 times faster than did the isonitrile analogue **2**. Like their des-methyl counterparts, cycloadducts **6** and **8** are readily oxidized in air to give oxoenal complexes **6C** and **6D**, and **8C** and **8D**, respectively.

Complexes **1** and **2** were found to be unreactive toward cycloaddition with dipolarophiles that are less reactive than TCNE (e.g., *N*-methylmaleimide, maleic anhydride, DMAD (dimethyl acetylenedicarboxylate)). However, we were pleased to find that the more electron-rich furan complex [TpRe(CO)(MeIm)(η^2-furan)] (**9**) does react with DMAD (Scheme 3). While the reaction was slow at 25 °C ([Re] = 20 mM, [DMAD] = 80 mM), heating an acetonitrile solution of **9** and DMAD at 55 °C for 30 h resulted in the formation of three products, in a ratio of 18:1:10 (**10C**:**10B**:**10A**). Repeating this reaction at 100 °C does not significantly change this ratio, but repeating it at 55 °C with 10 mM LiOTf resulted in a ratio of **10C**:(**10A**+**10B**) of 1.3:1. The major product **10C** is a 7-oxabicyclo[2.2.1]-heptadiene, the product of the desired dipolar cycloaddition reaction. Through a variety of NMR experiments, the minor products **10B** and **10A** were found to be the result of a formal [2+2] cycloaddition between DMAD and the uncoordinated double bond of the 4,5-η^2-furan ligand of **9**. The two 2-oxabicyclo[3.2.0]hepta-3,6-diene products are coordination diastereomers, differing only by which face of the vinyl ether is bound by the rhenium.

Heating an equimolar mixture of complex **9** and free furan at 55−65 °C (each ~10 mM) with 0.5 equiv of DMAD reveals a ratio of **10C** to the uncomplexed furan/DMAD cycloadduct of 40:1 (along with **10B** and **10A**) at 13 h and again at 30 h. Further heating resulted in the disappearance of the organic cycloadduct, presumably due to a retrocycloaddition at these elevated temperatures.

Scheme 3. The Reaction of the Furan-Imidazole Complexes **9** and **11** with DMAD



Using [TpRe(CO)(MeIm)(4,5-η^2-2-methylfuran)] (**11**) instead of the furan complex **9** under the same concentrations as in the synthesis of **10** results exclusively in the formation of [3.2.0] cycloadducts **12B** and **12A** in a 1:1 ratio (Scheme 3). No dipolar cycloadducts are observed. In addition, the reaction involving **11** proceeds under milder conditions than the similar reaction of **9**. Whereas the reaction between DMAD and **9** has a half-life of approximately 7 h at 55−60 °C, the reaction between DMAD and **11** has a half-life of less than 1 h at 20 °C ([Re] = 20 mM).

The complex [TpRe(CO)(MeIm)(4,5-η^2-2,5-dimethylfuran)] (**13**) was prepared by a method analogous to that used in the synthesis of **11**. In contrast to the corresponding furan and 2-methylfuran complexes, **13** is present as a single coordination diastereomer in solution. The absent coordination diastereomer would have to place a methyl group in quadrant C, where it is expected to have a destabilizing steric interaction with the pyrazolyl ring trans to the CO.[12] To confirm the coordination stereochemistry of **13**, a crystal structure determination was carried out, and the ORTEP drawing is presented in Figure 2. As expected, the C5 methyl group projects into quadrant B. Like its pentaammineosmium(II) analogue, **13** has a shorter metal−carbon bond length for the bound α carbon (Re−C(2) in Figure 2, 2.216(2) Å) than for the bound β carbon (2.188(2) Å), and it has an unbound C═C bond length (1.333(3) Å) that is shorter than that for the free ligand.[10] Also of note, the

(12) Meiere, S. H.; Harman, W. D. *Organometallics* **2001**, *20*, 3876.

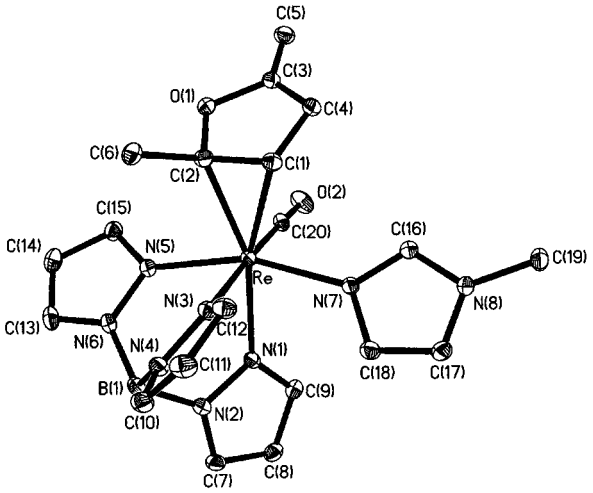
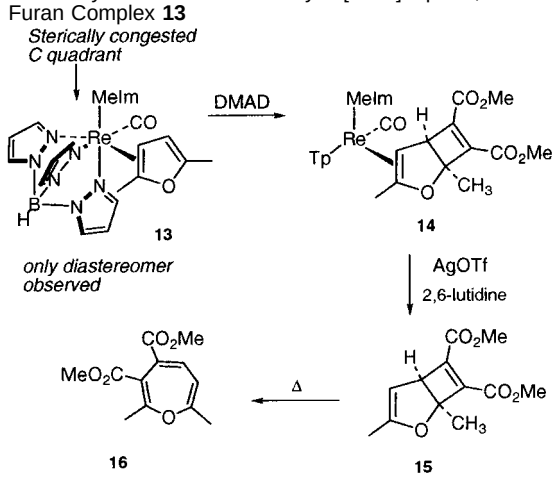


Figure 2. ORTEP diagram of 2,5-dimethylfuran complex **13** (30% probability ellipsoids shown). Selected bond distances (Å): Re−C(1) 2.216(2) Re−C(2) 2.188(2), C(1)−C(2) 1.432(3), C(1)−C(4) 1.462(3), C(3)−C(4) 1.333(3), O(1)−C(3): 1.386(3), O(1)−C(2) 1.440(3).

Scheme 4. Synthesis of a 2-Oxabicyclo[3.2.0]hepta-3,6-diene from Furan Complex **13**



imidazole ring, which typically is nearly coplanar with the rhenium and CO ligand, is somewhat canted in the 2,5-dimethylfuran structure, with a OC−Re−N(7)−C(16) dihedral angle of 40°.

The 2,5-dimethylfuran complex **13** reacts with DMAD in a manner similar to that of **11** to generate one diastereomer of the [3.2.0] cycloadduct complex (**14**, Scheme 4). A single crystal of this complex was grown by layering an acetone solution over water. X-ray analysis of the resulting crystal confirmed the identity of **14**, the ORTEP of which appears in Figure 3. As expected, the rhenium is bound to the *exo* face of the bicylic structure, with the oxygen oriented toward quadrant A. The C5−C6 bond length of 1.338 Å in the cyclobutene ring is consistent with that of a double bond.[10]

Allowing complex **14** to stir in CH_3CN with 2 equiv each of AgOTf and 2,6-lutidine resulted in decomplexation of the organic ligand, **15** (isolated yield: 43%). Although the 2-oxabicyclo[3.2.0]hepta-3,6-diene is stable at 25 °C, heating an NMR solution of **15** at 80 °C for 4 days resulted in the formation of oxepin **16** (70%).

Discussion

Cycloaddition reactions involving electron deficient alkenes are often promoted by Lewis acidic transition metal complexes,

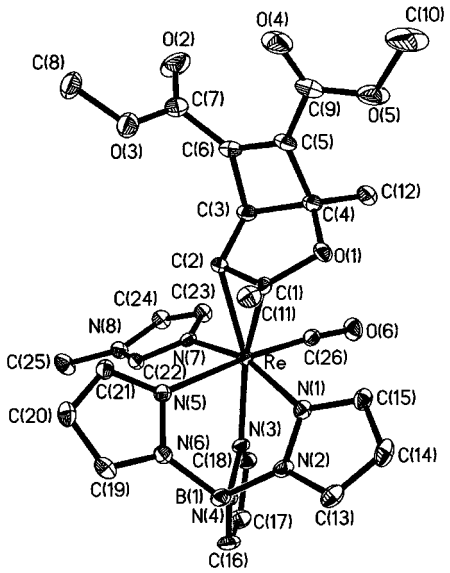


Figure 3. ORTEP diagram of 2-oxabicyclo[3.2.0]hepta-3,6-diene complex **14** (30% probability ellipsoids shown). Selected bond distances (Å): Re−C(1) 2.182(4), Re−C(2) 2.162(4) C(1)−C(2) 1.425(5), C(5)−C(6) 1.338(5), O(1)−C(4) 1.430(5), O(1)−C(1) 1.444(4).

in which the metal serves to lower the energy of the alkene LUMO.[13,14] For the reactions described herein, the metal is an electron donor. By disrupting the aromatic character of furan through π back-bonding,[15,16] the rhenium transforms furan into either a vinyl ether or a carbonyl ylide. Directly comparing the reactivity of these rhenium furan complexes with organic furans or dihydrofurans illustrates this effect. The rhenium furan and 2-methylfuran complexes (**1**, **2**, **5**, and **7**) undergo cycloadditions with TCNE that are essentially complete in <5 min (20 mM; 25 °C). The analogous reaction with furan shows no sign of any product after 48 h at 80 °C. Similarly, a competition experiment shows that the reaction of DMAD and the rhenium furan complex **9** to form the 7-oxabicyclo[2.2.1]heptene **10C** proceeds at a rate that is >40 times faster than the cycloaddition of DMAD with furan itself (60 ± 5 °C).

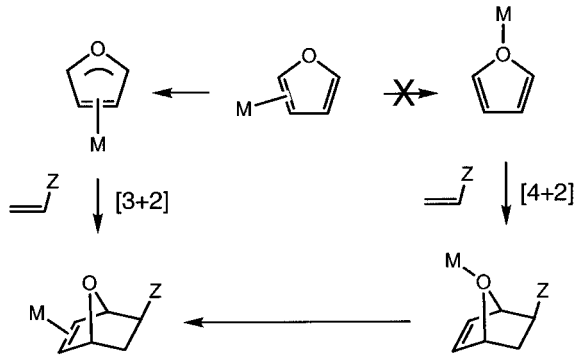
We believe that the [2+2] cycloaddition reaction between DMAD and 2,3-η^2-furan complexes occurs through a stepwise mechanism in which the furan complex first adds to DMAD in a Michael fashion, followed by closure of the enolate on C2 of the 3H-furanium intermediate to generate the cyclobutene ring. This reaction does not occur without the metal, as it is preempted by a [4+2] cycloaddition reaction. Comparison of the reactivity of the rhenium−furan complexes **9**, **11**, and **13** with various dihydrofurans proves to be useful. Whereas the [2+2] cycloaddition reaction with furan complex **9** and DMAD occurs at 55 °C (80 mM DMAD, 30 h, 38%), the reaction with 2,3-dihydrofuran requires refluxing toluene (110 °C, 1 h, 39%).[17] Similarly, while the reaction of the 2-methylfuran complex **11** and DMAD was complete after 4 h at 25 °C (20 mM, 50%), the same reaction with 4,5-dihydro-2-methylfuran required 60 °C (41%) (concentrations for these organic reactions were not published, but are likely to be higher than those used herein).

(13) Carey, F. A.; Sundberg, R. J. *Advanced Organic Chemistry Part A: Structure and Mechanism*; Plenum Press: New York, 1990.
(14) Miesch, M.; Wendling, F. *Eur. J. Org. Chem.* **2000**, 3381.
(15) Friedman, L. A.; Harman, W. D. *J. Am. Chem. Soc.* **2001**, *123*, 8697.
(16) Gunnoe, T. B.; Sabat, M.; Harman, W. D. *Organometallics* **2000**, *19*, 728.
(17) Nicolaou, K. C.; Hwang, C.-K.; Duggan, M. E.; Reddy, B. *Tetrahedron Lett.* **1987**, *28*, 1501.

The closest analogy to the reactivity of the rhenium furan complex **9** may be silyl ketene acetals, which undergo [2+2] cycloadditions with DMAD at 25 °C over a period of hours.[14] In this regard, the η^2-bound rhenium (where L = MeIm) has a π donating ability roughly equivalent to a siloxy group.

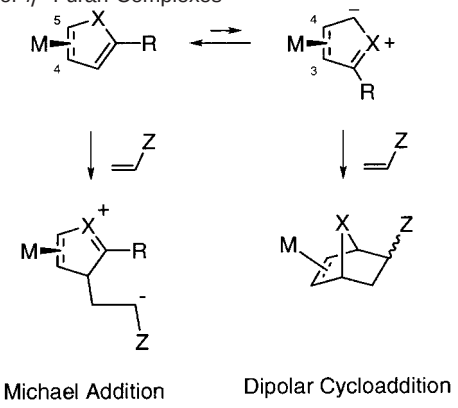
Adjusting the auxiliary ligand (L) of the [TpRe(CO)(L)(η^2-furan)] systems from ^{t}BuNC to MeIm renders the metal more reducing by about 0.5 V. Employing a more electron-rich metal has the predicted effect of increasing the rate of both the [2+2] and [3+2] cycloaddition reactions of the bound furan. For the reaction with TCNE, replacing the ^{t}BuNC ligand of **2** with PMe_3 (**1**) results in a 6-fold increase in the rate of [3+2] cycloaddition. Such a reaction is not observed with DMAD unless L = MeIm. In this same vein, the [2+2] cycloaddition reaction with DMAD is not observed for the less electron-rich phosphine and isonitrile systems (**1**, **2**, **5**, and **7**). Of note, neither a [2+2] nor a [3+2] cycloaddition product is formed between DMAD and the pentaammineosmium(II) complex of furan at 25 °C or at 80 °C (15 h; decomposition). This observation supports the notion that the {TpRe(CO)(MeIm)} system is more electron donating than its osmium(II) predecessor.

We have extensively investigated the rates and mechanisms of the isomerization of aromatic molecules bound to the {TpRe(CO)(L)} fragment (L = ^{t}BuNC, PMe_3, pyridine, or *N*-methylimidazole).[6] Intrafacial isomerizations (ring walks) were observed in which the metal fragment remained coordinated to the same face of an aromatic ligand but migrated to the uncoordinated double bond. These linkage isomerizations occur in furans, thiophenes, naphthalenes, and other η^2-bound aromatic molecules. In the case of furan, migration of the metal fragment from the 2,3-position to the 3,4-position would render the uncoordinated portion of the ring a carbonyl ylide, although we have never been able to spectroscopically observe such a species. In that study, however, hydrogenation of [TpRe(CO)(PMe_3)(η^2-furan)] over Pd/C yielded significant amounts of the 2,5-dihydrofuran complex, our first clue to the fact that carbonyl ylides may be kinetically accessible under typical reaction conditions. Although the observations reported herein strongly support a mechanism involving 1,3-dipolar cycloaddition of the 3,4-η^2 furan isomer with dipolarophiles, an alternative explanation involving an oxygen-bound intermediate may also be considered. By inductive arguments, the σ-withdrawing rhenium could lower the aromatic character of the furan and activate it toward a [4+2] cycloaddition.



Although this mechanism cannot be categorically eliminated, we point out that while ^{1}H NMR spin transfer data support the presence of a 3,4-η^2 intermediate along the intrafacial isomer-

Scheme 5. Michael Addition/1,3-Dipolar Cycloaddition Reaction Manifold for η^2-Furan Complexes



ization pathway for furan complexes, the type of spin transfer associated with a transient Re−O-bound furan species was not observed.[6] Furthermore, activation of furan through oxygen coordination would likely be enhanced by the more electron-deficient metal systems, but the opposite trend is observed.

The reactions of DMAD with the imidazole−furan complexes (**9**, **11**, and **13**) provide information concerning the [2+2] and [3+2] reaction manifold. This manifold can be viewed as a competition between a dipolar cycloaddition of a 3,4-η^2 furan complex and a Michael reaction of the more stable but less reactive 2,3-η^2 isomer (Scheme 5). We have extensively investigated this reaction manifold for osmium(II) pyrrole complexes and shown that the Michael addition pathway was favored by stabilizing the zwitterionic intermediate, either through solvent interactions, Lewis acids, or functional group effects.[5] In contrast, the [3+2] cycloaddition was favored by increasing the stability of the 3,4-η^2 isomer relative to the 4,5-η^2 isomer, which could be achieved by placing methyl groups at both the 2 and 5 positions of the heterocycle. Indeed, when the reaction of the furan complex **9** (L = MeIm) and DMAD is carried out in the presence of lithium triflate, the ratio of [2+2] to [3+2] cycloaddition products increases. Equally significant, the presence of a methyl group at C2 apparently sufficiently stabilizes the zwitterionic intermediate (**12B$_z$**, Scheme 3) through hyperconjugation so that the dipolar cycloaddition pathway is completely pre-empted by the Michael addition. Apparently this stabilization is so great that destabilizing the 4,5-η^2 isomer with a second methyl group does not change the reaction outcome.

When the furan ligand is asymmetrically substituted, two coordination diastereomers are possible for the [3+2] cycloaddition reaction. The oxabicyclo[2.2.1]heptene complexes formed from 2-methylfuran complexes and TCNE (**6** and **8**) can have the methyl group (i.e., in **13**) oriented toward (quadrant D) or away from (quadrant A) the auxiliary ligand (see Scheme 1). Referring to Scheme 2, the final stereochemistry of the cycloadduct is determined by the orientation of the methyl group for the carbonyl ylide intermediate. The only way for these ylides to interconvert is to undergo an interfacial isomerization (face flip), either directly or via their 4,5-η^2 isomers. The coordination diastereomer ratios for the products (**6A**:**6B** or **8A**:**8B**) will be related to the ratio of the carbonyl ylides (**5*A**:**5*B** or **7*A**:**7*B**) and to the relative rates of cycloaddition of these intermediates with TCNE. For L = PMe_3 and ^{t}BuNC, the major ylide diastereomer is that in which the methyl group is oriented toward the auxiliary ligand (L), and in both cases, the major isomer for the furan precursor (**5A**, **7A**) is related to this major intermediate (**5*A**, **7*A**) by an intrafacial isomerization. However, whereas the ratio for L = PMe_3 cycloadducts (**6A**:**6B** = 1.8:1) is approximately equal to that of the starting furan complex, this ratio for L = ^{t}BuNC (**8A**:**8B**) is 27:1 and this increases to 43:1 if the concentration of TCNE is lowered. The following discussion offers a possible explanation consistent with these observations.

Competition experiments indicate that k_{obs} for cycloaddition is about 6 times faster for L = PMe_3 (**1**) than for L = ^{t}BuNC (**2**). The rate of retrocycloaddition of **6** is about 8 times faster than that for **8** ($t_{1/2}$ = 200 h; cf., 1600 h). Thus, $K_{eq}(PMe_3) \sim 0.75K_{eq}(^t\text{BuNC})$, and there is practically no difference in $\Delta G°$ for these two reactions as a function of L (at 25 °C). However, the free energy of activation for the 2,3-η^2 to 4,5-η^2 intrafacial isomerization (ring walk) is about 3.5 kcal/mol higher for L = PMe_3 compared to L = ^{t}BuNC, assuming that there is not a strong temperature dependence on $\Delta G^{\ddagger}$,[6] and this barrier is taken to be essentially the same for the 4,5-η^2 to 3,4-η^2 isomerization. While formation of the carbonyl ylide is slower for L = PMe_3 than for L = ^{t}BuNC, the cycloaddition step is expected to be faster, on the grounds that the rhenium−phosphine system is more electron-rich. When L = PMe_3, it is likely that intrafacial isomerization to the carbonyl ylide is the rate-limiting step. If the rates of ylide formation and cycloaddition are similar (vide infra), the diastereomer ratio for furan coordination (2.1:1) would be similar to the cycloadduct dr (1.8:1). For L = ^{t}BuNC, this condition apparently does not hold. Now both intra- and interfacial (face flip) linkage isomerizations are faster,[6] and the cycloaddition of the carbonyl ylide is expected to be slower, perhaps becoming rate limiting. The two carbonyl ylides can now equilibrate with each other and their more stable 4,5-η^2 isomers. For L = PMe_3, formation of either carbonyl ylide isomer (**5*A** or **5*B**) is expected to result in steric strain between the furan methyl group and either the PMe_3 ligand or the pyrazole ring trans to it. However, when L = ^{t}BuNC, conversion of **7A** to **7*A** requires moving the methyl group into quadrant D which, in contrast to the PMe_3 complex **5**, does not result in a significant steric strain.[6] Thus, not only is **7A** favored over **7B**, but its conversion to **7*A** is expected to be much faster than the intrafacial isomerization of **7B** to **7*B**. If cycloaddition is sufficiently slow such that the carbonyl ylides are able to equilibrate, then the ratio of furan complexes **7A** and **7B** would be irrelevant and the ratio of **7*A** to **7*B**, which is expected to heavily favor **7*A**, would determine the ratio of the cycloadducts. Recall that lowering the concentration of TCNE from 32 to 6 mM increased the ratio of the cycloadducts from 27:1 to 43:1 (**7A**:**7B**), and using less than 1 equiv increased the ratio to 75:1.

Regarding the stereochemistry of the [2+2] cycloaddition, an interesting comparison can be made between the ratios of the oxabicyclo[3.2.0]heptadiene complexes **10B** and **10A** and that of their methylated analogues (**12B** and **12A**, Scheme 3). Whereas the cycloaddition takes place with high stereocontrol (**10A**:**10B** = 10:1) for the furan complex **9**, the 2-methylfuran complex **11** reacts much faster, and with complete loss of stereocontrol (**12A**:**12B** =1:1). Two scenarios could explain this. Previous studies have shown that a substituent in a vicinal relationship to a bound alkene has a significant steric interaction with the pyrazolyl ring trans to the auxiliary ligand (quadrant

A).[6,12] Thus, assuming that the Michael addition step forming the zwitterion is endothermic, by the Hammond postulate, the specific rate of the Michael reaction for isomer **10A** is expected to be faster than that for isomer **10B**, which reflects the differences in stability of the zwitterionic intermediates $\mathbf{10B_z}$ and $\mathbf{10A_z}$ (Scheme 3). Addition of a methyl group is expected to stabilize the zwitterionic intermediate ($\mathbf{12B_z}$ or $\mathbf{12A_z}$) via hyperconjugation, making the Michael addition much faster to **11** than to **9**, as is observed. With an interfacial isomerization (face flip) barrier of ~23 kcal/mol, it is possible that the rate of face flipping for **11** becomes slower than the rate of the Michael addition under experimental conditions. Since the system cannot respond to the depletion of furan isomer **11A**, the coordination diastereomers (**12B** and **12A)** are formed in approximately the same ratio as their 2-methylfuran precursors **11B** and **11A**. Alternatively, it is possible that the C2 methyl group of **11** stabilizes the Michael addition to the point where the reaction is close to thermoneutral and the Hammond postulate no longer applies. In other words, there is not enough character of $\mathbf{12B_z}$ or $\mathbf{12A_z}$ in the transition state to provide good discrimination between products. To differentiate these two scenarios, the reaction of **11** with DMAD was repeated under identical reaction conditions to those reported above, but with only 0.3 equiv of DMAD. Under these conditions, the ratio of **12A** to **12B** improves to 1.9:1, indicating that **11A** is more reactive than **11B**.

The 2,5-dimethylfuran complex **13** exists as one diastereomer due to the propensity for the metal fragment to coordinate trisubstituted olefins diastereoselectively.[12] Consequently, one product (**14**) is formed from reaction with DMAD (Scheme 4). Spectroscopic features of **14** are very similar to **12A**, consistent with a formal [2+2] cycloaddition between DMAD and the uncoordinated portion of the 2,3-η^2-furan ligand. The structure of **14** was confirmed by X-ray crystallography to be the formal [2+2] cycloadduct (Figure 3). Oxidative decomplexation of the organic ligand (**15**) was achieved by using AgOTf and 2,6-lutidine in CH_3CN. Proton and carbon spectra of **15** were consistent with the proposed structure. Demonstration of this decomplexation is significant in that 2-oxabicyclo[3.2.0]hepta-3,6-dienes are readily converted to functionalized oxepins,[18] which are of interest to both synthetic and physical chemists.[17,19] Indeed, heating **15** results in its conversion to oxepin **16** (Scheme 4). There is no method presently available to form oxepins directly from furans, except under photochemical conditions, where irradiation experiments typically require longer times than those used herein and result in lower yields.[20]

One final point should be raised. TCNE is a powerful one-electron oxidant, and its role as a redox catalyst for linkage isomerizations or a reaction through a radical-based mechanism should not be dismissed. The reduction potential for the phosphine complex (**1**) is $E_{p,a} = 0.30$ V (NHE), while that of the isonitrile complex is 0.47 V.[21] The $E_{1/2}$ for the 0/−1 reduction potential for TCNE is 0.40 V in CH_3CN. This suggests that outer-sphere electron transfer could easily occur, especially with the more electron-rich PMe_3 system. For L = MeIm, rapid oxidation of the rhenium occurs and no cycloadduct is observed. In studies with η^2-aromatic complexes of pentaammineosmium(II), rapid increases in linkage isomerization rates upon one-electron oxidation of the metal were observed.[22] It is therefore possible that the linkage isomerization rate for rhenium−η^2-furan complexes in the presence of TCNE is much faster than what we have observed in the absence of a one-electron oxidant.

Conclusions

The complexation of furans or alkylated furans with an electron-rich rhenium complex of the form {TpRe(CO)(L)} (L = ^{t}BuNC, PMe_3, or *N*-methylimidazole) activates the heterocycles to either [2+2] or [3+2] cycloaddition reactions, depending on the position of the ring that is coordinated. When the metal binds across C4 and C5, the uncoordinated ring resembles a vinyl ether and undergoes [2+2] cyclizations with DMAD. However, when the metal binds the 3,4-positions of the furan, the uncoordinated portion of the ring reacts like a carbonyl ylide and undergoes [3+2] cycloaddition. For both modes of reactivity, the metal accelerates the reaction compared to that of organic analogues. Moderate to high degrees of selectivity can be achieved provided that reaction conditions are chosen such that equilibration between intrafacial and interfacial linkage isomers is maintained.

Experimental Section

General. All reactions were performed in a Vacuum Atmospheres Co. glovebox. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Inova-300, Varian Inova-500, or GN-300 spectrometer at room temperature unless otherwise noted. Chemical shifts are reported in ppm relative to TMS (tetramethylsilane) with residual protonated solvent (acetonitrile-$d_2 = \delta$ 1.94 ppm) as an internal standard. Two-dimensional NMR experiments (gDQCOSY, gHSQC, nOe) were recorded on a Varian Inova-300 or a Varian Inova-500 spectrometer. Electrochemical experiments were performed under nitrogen with a PAR model 362 potentiostat driven by a PAR model 175 universal programmer. Cyclic voltammograms were recorded (Kipp & Zonen BD90 XY recorder) in a standard three-electrode cell from +1.7 to −1.7 V utilizing a glassy carbon electrode. All potentials are reported versus NHE and, unless otherwise noted, were determined in CH_3CN (~0.5 M tetrabutylammonium hexafluorophosphate) at a scan rate of 100 mV/s with colbaltocenium hexafluorophosphate ($E_{1/2} = -0.78$ V) in situ as a calibration standard. Infrared spectra were recorded on a MIDAC Prospect (Model PRS) spectrometer as a glaze using a Horizontal Attenuated Total Reflectance Accessory (HATR, Pike Industries). High Resolution Mass Spectrometry (HRMS) was performed by the UIUC (University of Illinois at Urbana−Champaign) School of Chemical Science. Elemental analyses were obtained on a Perkin-Elmer PE-2400 Series II CHN analyzer or by Atlantic Microlabs (Norcross, GA). Due to the rapid conversion of TCNE cycloadducts to their corresponding dial or aldehyde ketone complexes, we were unable to obtain satisfactory elemental analyses on some compounds. This was further frustrated by not knowing all of the decomposition products (particularly with respect to the TCNE portion). Samples isolated as cycloadducts routinely gave analysis results consistent with the spectroscopically observed decomposition product.

Solvents and Reagents. All solvents were purified via distillation under nitrogen or passage through an activated alumina column under inert atmosphere and degassed prior to use.[23] Acetonitrile-d_3 (Cambridge Isotope Labs) was distilled over CaH_2 under an inert atmosphere prior to use. 2,5-Dimethylfuran was purchased from Acros Organics and

(18) Vogel, E.; Günther, H. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 385.
(19) Christl, M.; Leininger, H.; Kemmer, P. *Chem. Ber.* **1984**, *117*, 2963.
(20) Muramatsu, H.; Shibita, K.; Masaki, M. *J. Heterocycl. Chem.* **1992**, *29*, 113.
(21) Meiere, S. H.; Brooks, B. C.; Gunnoe, T. B.; Carrig, E. H.; Sabat, M.; Harman, W. D. *Organometallics* **2001**, *20*, 3661.
(22) Hodges, L. M.; Spera, M. L.; Moody, M.; Harman, W. D. *J. Am. Chem. Soc.* **1996**, *118*, 7117.
(23) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.

filtered through an activated alumina plug immediately prior to use. The syntheses of complexes **1**, **2**, **7**, **9**, and [TpRe(CO)(MeIm)-(η^2-benzene)][16,21,24,25] have been previously reported.

[TpRe(CO)(PMe$_3$)(5,6-η^2-7-oxa-bicyclo[2.2.1]hept-5-ene-2,2,3,3-tetracarbonitrile)] (3). [TpRe(CO)(PMe$_3$)(4,5-η^2-furan)] (**1**, 0.105 g, 0.184 mmol) was dissolved in 3 mL of THF. Tetracyanoethylene (0.024 g, 0.190 mmol, 1.03 equiv) in 0.5 mL of THF was added, and the resulting solution was stirred for 5 min. The reaction mixture was added to 50 mL of hexanes, and the slurry was filtered through a fine frit. The solid was washed with hexanes and dried in vacuo to afford 93 mg (73%) of a green solid. ^{1}H NMR (CD$_3$CN): δ 8.08 (d, J = 1.8 Hz, 1H, TpH), 8.06 (d, J = 1.8 Hz, 1H, TpH), 7.86 (d, J = 2.4 Hz, 1H, TpH), 7.82 (d, J = 2.2 Hz, 1H, TpH), 7.69 (d, J = 2.4 Hz, 1H, TpH), 7.31 (d, J = 1.8 Hz, 1H, TpH), 6.33 (t, J = 2.2 Hz, 1H, TpH), 6.30 (t, J = 2.2 Hz, 1H, TpH), 6.25 (t, J = 2.2 Hz, 1H, TpH), 5.79 (d, J = 1.3 Hz, 1H, H1), 5.59 (s, 1H, C4), 2.91 (dd, J = 11.4, 7.0 Hz, 1H, H5), 1.82 (dd, J = 6.9, 2.8 Hz, 1H, H6), 1.29 ppm (d, J = 9.7 Hz, 9H, PMe$_3$). ^{13}C NMR (CD$_3$CN): δ 197.6 (C≡O), 147.8, 146.1, 140.4, 138.1, 137.5, 136.5 (Tp 3 and 5 positions), 107.9, 107.3, 107.2 (Tp 3 and 5 positions), 129.9 (2C), 129.2 (2C) (C≡N), 107.61, 107.51, 107.06 (Tp 4 positions), 94.8 (C4), 94.5 (C1), 47.3 (C6), 46.6 (d, J = 17.4 Hz, C5), 16.2 ppm (d, J = 33.9 Hz) (C2, C3 not seen). $E_{1/2}$ = 0.92 V. IR (HATR): 1845 ($\nu_{C\equiv O}$), 2487 cm^{-1} (ν_{BH}). Anal. Calcd for $C_{23}H_{23}N_{10}BO_2PRe$: C, 39.49; H, 3.31; N, 20.02. Found: C, 39.0; H, 3.48; N, 19.77.

[TpRe(CO)(PMe$_3$)(2,3-η^2-(Z)-but-2-enedial)] (3D). An NMR solution (CD$_3$CN) of **3** was exposed to air. After a few days, the solution was found to consist entirely of complex **3D**. ^{1}H NMR (CD$_3$CN): δ 9.57 (d, J = 8.4 Hz, 1H, CHO), 9.49 (d, J = 8.4 Hz, 1H, CHO), 8.16 (d, J = 2.2 Hz, 1H, TpH), 7.89 (d, J = 2.4 Hz, 2H, TpH), 7.68 (d, J = 2.6 Hz, 1H, TpH), 7.51 (d, J = 2.2 Hz, 1H, TpH), 7.50 (d, J = 2.2 Hz, 1H, TpH), 6.37 (t, J = 2.4 Hz, 1H, TpH), 6.35 (t, J = 2.4 Hz, 1H, TpH), 6.13 (t, J = 2.2 Hz, 1H, TpH), 3.99 (ddd, J = 9.7, 8.6, 8.6 Hz, 1H, H2), 2.76 (ddd, J = 8.6, 8.6, 1.5 Hz, 1H, H3), 1.13 ppm (d, J = 9.7 Hz, 9H, PMe$_3$). ^{13}C NMR (CD$_3$CN): δ 199.7 (d, J = 3.7 Hz, CHO), 199.6 (CHO), 147.8, 146.1, 141.5, 138.7, 137.8, 137.5 (Tp 3 and 5 positions), 108.4, 107.5, 106.8 (Tp 3 and 5 positions), 65.5 (C3), 63.3 (d, J = 8.4 Hz, C2), 13.7 ppm (d, J = 34.8 Hz) (C2, C3, C≡O not seen). $E_{1/2}$ = 1.05 V. IR (HATR): 1653 ($\nu_{C=O}$), 1839 ($\nu_{C\equiv O}$), 2491 cm^{-1} (ν_{BH}).

[TpRe(CO)(^{t}BuNC)(5,6-η^2-7-oxa-bicyclo[2.2.1]hept-5-ene-2,2,3,3-tetracarbonitrile)] (4). [TpRe(CO)(^{t}BuNC)(4,5-η^2-furan)] (**2**, 0.098 g, 0.170 mmol) was dissolved in 3 mL of THF. Tetracyanoethylene (0.023 g, 0.181 mmol, 1.06 equiv) in 0.5 mL of THF was added, and the resulting solution was stirred for 5 min. The reaction mixture was added to 50 mL of hexanes, and the slurry was filtered through a fine frit. The solid was washed with hexanes and dried in vacuo to afford 79 mg (66%) of a green solid. ^{1}H NMR (CD$_3$CN): δ 8.18 (d, J = 1.8 Hz, 1H, TpH), 8.04 (d, J = 2.0 Hz, 1H, TpH), 7.81 (dd, J = 2.4, 0.4 Hz, 1H, TpH), 7.78 (dd, J = 2.2, 0.4 Hz, 1H, TpH), 7.76 (dd, J = 2.4, 0.4 Hz, 1H, TpH), 7.46 (d, J = 2.0 Hz, 1H, TpH), 6.37 (t, J = 2.2 Hz, 1H, TpH), 6.33 (t, J = 2.2 Hz, 1H, TpH), 6.26 (t, J = 2.2 Hz, 1H, TpH), 5.82 (d, J = 0.4 Hz, 1H, H1), 5.52 (s, 1H, C4), 3.39 (d, J = 6.6 Hz, 1H, H5), 2.06 (d, J = 6.6 Hz, 1H, H6), 1.51 ppm (s, 9H, ^{t}Bu). ^{13}C NMR (CD$_3$CN): δ 146.3 (2C), 141.0, 137.1, 136.6 (2C) (Tp 3 and 5 positions), 113.07 (4C, C≡N), 107.61, 107.51, 107.06 (Tp 4 positions), 93.88 (C4), 93.32 (C1), 49.68 (C6), 47.24 (C5), 31.02 ppm (C(CH_3)$_3$ (C≡O, C≡N, C2, C3, C(CH_3)$_3$ not seen). $E_{1/2}$ = 0.94 V (quasi-reversible). IR (HATR): 1869 ($\nu_{C\equiv O}$), 2138 (($\nu_{C\equiv N}$), 2489 cm^{-1} (ν_{BH}).

[TpRe(CO)(^{t}BuNC)(2,3-η^2-(Z)-but-2-enedial)] (4D). An NMR solution (CD$_3$CN) of **4** was exposed to air. After a few days, the solution was found to consist primarily of complex **4D**. ^{1}H NMR (CD$_3$CN): δ 9.48 (d, J = 8.1 Hz, 1H, CHO), 9.30 (d, J = 7.7 Hz, 1H, CHO), 8.14 (d, J = 2.0 Hz, 1H, TpH), 7.81 (m, 3H, TpH), 7.65 (d, J = 2.2 Hz, 1H, TpH), 7.60 (d, J = 2.0 Hz, 1H, TpH), 6.34 (t, J = 2.2 Hz, 1H, TpH), 6.28 (t, J = 2.4 Hz, 1H, TpH), 6.28 (t, J = 2.2 Hz, 1H, TpH), 4.05 (dd, J = 8.8, 7.9 Hz, 1H, H2), 2.80 (dd, J = 8.6, 8.4 Hz, 1H, H3), 1.42 ppm (s, 9H, ^{t}BuNC). ^{13}C NMR (CD$_3$CN): δ 197.9 (CHO), 196.2 (C≡O), 196.1 (CHO), 147.0, 146.0, 142.1, 137.7, 137.4, 137.1 (Tp 3 and 5 positions), 108.0, 107.4 (2C) (Tp 3 and 5 positions), 65.0 (C3), 62.3 (C2), 30.7 ppm (^{t}Bu) (C2, C3, C≡N) not seen). $E_{1/2}$ = 1.16 V. IR (HATR): 1657 ($\nu_{C=O}$), 1864 ($\nu_{C\equiv O}$), 2492 cm^{-1} (ν_{BH}), 2164 ($\nu_{C\equiv N}$). Anal. Calcd for $C_{19}H_{23}N_7BO_3Re$: C, 38.39; H, 3.90; N, 16.49. Found: C, 38.16; H, 3.90; N, 16.49.

[TpRe(CO)(PMe$_3$)(4,5-η^2-2-methylfuran)] (5). This complex was synthesized by using a previously published procedure,[24] except that 2-methylfuran was substituted for furan. Two diastereomers were isolated in a 2.1:1 ratio, with the major diastereomer having the oxygen of the heterocycle oriented toward the CO/pyrazole quadrant (see Scheme 1). Yield: 66%. ^{1}H NMR (CD$_3$CN): δ 8.6−7.2 (m, 12H, Tp 3 and 5 positions), 7.17 (dd, J = 15.2, 4.4 Hz, 1H, minor HC5), 6.4−6.2 (m, 6H, Tp 4 positions), 5.99 (dd, J = 2.0, 1.1 Hz, 1H, major HC3), 5.87 (dd, J = 4.4, 1.3 Hz, 1H, major HC5), 5.63 (m, 1H, minor HC3), 4.41 (ddd, J = 10.7, 4.3, 2.2 Hz, 1H, major HC4), 2.97 (m, 1H, minor HC4), 2.05 (s, 3H, major CH_3), 2.05 (s, 3H, minor CH_3), 1.42 (d, J = 8.6 Hz, 9H, minor PMe$_3$), 1.38 ppm (d, J = 8.6 Hz, 9H, major PMe$_3$). ^{13}C NMR (CD$_3$CN): δ 150−135 (m, 12C, Tp 3 and 5 positions), 107−105 (m, 6C, Tp 4 positions), 151.4 (minor C2), 148.0 (major C2), 111.4 (minor C3), 111.1 (major C3), 102.2 (major C5), 99.1 (m, minor C5), 53.3 (minor C4), 50.9 (d, J = 8.8 Hz, major C4), 17.1 (d, J = 32.2 Hz, major PMe$_3$), 16.8 ppm (d, J = 32.2 Hz, minor PMe$_3$), 15.6 (minor CH_3), 13.3 (major CH_3) (C≡O not seen). $E_{p,a}$ =1.19V, $E_{1/2}$ = 0.29 V (quasi-reversible). IR (HATR): 1823 ($\nu_{C=O}$), 2479 cm^{-1} (ν_{BH}). Anal. Calcd for $C_{18}H_{25}N_6BO_2PRe$: C, 36.93; H, 4.30; N, 14.36. Found: C, 37.22; H, 4.22; N, 14.16.

[TpRe(CO)(PMe$_3$)(5,6-η^2-4-methyl-7-oxa-bicyclo[2.2.1]hept-5-ene-2,2,3,3-tetracarbonitrile)] (6A and 6B). To a solution of **5** (0.057 g, 0.097 mmol) in 1 g of THF was added TCNE (0.013 g, 0.105 mmol, 1.08 equiv) in 0.5 g of THF. The resulting solution was stirred for 5 min and then added to 50 mL of stirring hexanes. The slurry was filtered through a fine frit and the resulting blue solid washed with hexanes and dried in vacuo. Yield: 46 mg (67%). Two diastereomers were observed in a 1.8:1 (**6A**:**6B**) ratio (major has methyl toward PMe$_3$). **6A**: ^{1}H NMR (CD$_3$CN): δ 8.07 (d, J = 1.9 Hz, 1H, TpH), 7.94 (d, J = 1.5 Hz, 1H, TpH), 7.89 (d, J = 2.2 Hz, 1H, TpH), 7.84 (d, J = 2.3 Hz, 1H, TpH), 7.73 (d, J = 2.7 Hz, 1H, TpH), 7.12 (d, J = 1.9 Hz, 1H, TpH), 6.36 (t, J = 2.3 Hz, 1H, TpH), 6.31 (t, J = 1.9 Hz, 1H, TpH), 6.25 (t, J = 1.9 Hz, 1H, TpH), 5.64 (d, J = 1.2 Hz, 1H, HC1), 3.02 (dd, J = 13.1, 6.7 Hz, 1H, HC5), 2.05 (s, 3H, Me), 1.93 (dd, J = 6.7, 2.8 Hz, 1H, HC6), 1.21 ppm (d, J = 8.9 Hz, 9H, PMe$_3$). ^{13}C NMR (CD$_3$CN): δ 198.6 (C≡O), 146.6, 146.2, 139.9, 138.4, 137.4, 138.8 (Tp 3 and 6 positions), 113.0 (4 C≡N), 108.2, 107.7, 107.3 (Tp 4 positions), 101.67 (C4), 92.91 (C1), 52.0 (C6), 49.8 (d, J = 14.6 Hz, C5), 19.7 (CH_3), 15.6 ppm (d, J = 34.0 Hz, PMe$_3$) (C2 and C3 not seen). **6B**: ^{1}H NMR (CD$_3$CN): δ 8.23 (d, J = 1.6 Hz, 1H, TpH), 8.16 (d, J = 1.9 Hz, 1H, TpH), 7.87 (d, J = 2.7 Hz, 1H, TpH), 7.83 (d, J = 2.7 Hz, 1H, TpH), 7.66 (d, J = 2.7 Hz, 1H, TpH), 7.51 (d, J = 1.9 Hz, 1H, TpH), 6.35 (m, 1H, TpH), 6.32 (m, 1H, TpH), 6.24 (m 1H, TpH), 5.47 (s, 1H, HC1), 3.14 (dd, J = 9.2, 6.9 Hz, 1H, HC5), 2.28 (s, 3H, CH_3), 2.12 (dd, J = 7.0, 3.0 Hz, 1H, HC6), 1.13 ppm (d, J = 8.9 Hz, 9H, PMe$_3$). ^{13}C NMR (CD$_3$CN): δ 198.4 (C≡O), 148.4, 147.4, 140.6, 138.1, 138.0, 136.8 (Tp 3 and 5 positions), 1136 (4 C≡N), 108.2, 107.7, 107.3 (Tp 4 positions), 101.7 (C1), 93.5 (C4), 50.2 (d, J = 17.0 Hz, C5), 48.4 (C6), 19.4 (CH_3), 15.6 ppm (d, J = 34.0 Hz, PMe$_3$). **Data for 6A and 6B**: $E_{1/2}$ = 0.91 V. IR (HATR): 1845 ($\nu_{C\equiv O}$), 2489 cm^{-1} (ν_{BH}). Anal. Calcd for $C_{24}H_{25}BN_{10}O_2PRe$: C, 40.40; H, 3.53; N, 19.63. Found: C, 40.41; H, 3.81; N, 19.21.

(24) Gunnoe, T. B.; Sabat, M.; Harman, W. D. *J. Am. Chem. Soc.* **1999**, *121*, 6499.
(25) Meiere, S. H.; Brooks, B. C.; Gunnoe, T. B.; Sabat, M.; Harman, W. D. *Organometallics* **2001**, *20*, 1038.

[TpRe(CO)(PMe$_3$)(2,3-η^2-(Z)-4-oxo-pent-2-eneal)] (6C and 6D). An NMR solution of complexes **6A** and **6B** was exposed to air and allowed to stand for several days. Two diastereomers were observed in a 3.2:1 (**6C**:**6D**) ratio (major has ketone toward PMe$_3$). **6C**: ^{1}H NMR (CD$_3$CN): δ 8.87 (d, J = 8.1 Hz, 1H, CHO), 8.18 (d, J = 2.2 Hz, 1H, TpH), 7.85 (d, J = 2.4 Hz, 2H, TpH), 7.68 (d, J = 1.8 Hz, 1H, TpH), 7.65 (d, J = 2.4 Hz, 1H, TpH), 7.60 (d, J = 2.0 Hz, 1H, TpH), 6.35 (t, J = 2.4 Hz, 1H, TpH), 6.35 (t, J = 2.4 Hz, 1H, TpH), 6.12 (t, J = 2.2 Hz, 1H, TpH), 4.32 (dd, J = 9.9, 8.8 Hz, 1H, HC3), 2.53 (s, 3H, CH$_3$), 2.48 (ddd, J = 10.1, 8.1, 2.0 Hz, 1H, HC2), 1.12 ppm (d, J = 9.2 Hz, 1H, TpH). **6D (selected resonances)**: ^{1}H NMR (CD$_3$CN): δ 9.92 (d, J = 7.7 Hz, 1H, CHO), 1.40 ppm (d, J = 13.2 Hz, 9H, PMe$_3$). **Data for 6C and 6D**: $E_{1/2}$ = 0.84 V (quasireversible). IR (HATR): 1847 ($\nu_{C\equiv O}$), 2494 cm^{-1} (ν_{BH}).

[TpRe(CO)(^{t}BuNC)(5,6-η^2-4-methyl-7-oxa-bicyclo[2.2.1]hept-5-ene-2,2,3,3-tetracarbonitrile)] (8A and 8B). [TpRe(CO)(^{t}BuNC)(4,5-η^2-2-methylfuran)] (**7**, 0.050 g, 0.084 mmol) was dissolved in 1 g of THF. To this solution was added TCNE (0.012 g, 0.092 mmol, 1.1 equiv) in approximately 0.5 g of THF. The solution was allowed to stir for 5 min and added to 50 mL of stirring hexanes. The slurry was filtered through a fine frit, washed with hexanes, and dried in vacuo. Yield: 41 mg (67%). Two diastereomers were observed by NMR in a 27:1 (**8A**:**8B**) ratio. **8A** has bridgehead methyl toward isonitrile. **8A**: ^{1}H NMR (CD$_3$CN): δ 8.08 (d, J = 2.0 Hz, 1H, TpH), 8.03 (d, J = 1.5 Hz, 1H, TpH), 7.83 (d, J = 2.0 Hz, 1H, TpH), 7.79 (d, J = 2.2 Hz, 1H, TpH), 7.77 (d, J = 2.2 Hz, 1H, TpH), 7.32 (d, J = 1.8 Hz, 1H, TpH), 6.36 (t, J = 2.2 Hz, 1H, TpH), 6.33 (t, J = 2.2 Hz, 1H, TpH), 6.26 (t, J = 2.2 Hz, 1H, TpH), 5.70 (s, 1H, HC1), 3.40 (d, J = 6.6 Hz, 1H, HC5), 2.11 (s, 3H, CH$_3$), 2.04 (d, J = 6.8 Hz, 1H, HC6), 1.45 ppm (s, 9H, ^{t}Bu). ^{13}C NMR (CD$_3$CN): δ 197.4 (C≡O), 146.4, 146.2, 140.8, 137.2, 136.9, 136.9 (Tp 3 and 5 positions), 112.8 (4 C≡N), 107.7, 107.3 (2C) (Tp 4 positions), 101.4 (C4), 92.5 (C1), 52.8 (C6), 50.57 (C5), 31.8 (C3), 30.7 (tBu), 18.2 ppm (CH$_3$) (C2 not seen). **8B** (selected peaks): ^{1}H NMR (CD$_3$CN): δ 5.39 ppm (s, 1H, HC4), 3.59 (d, J = 6.4 Hz, 1H, HC5), 1.49 ppm (s, 9H, ^{t}Bu). **Data for 8A and 8B**: $E_{1/2}$ = 1.03 V. IR (HATR): 1866 ($\nu_{C\equiv O}$), 2145 ($\nu_{C\equiv N}$), 2486 cm^{-1} (ν_{BH}).

[TpRe(CO)(^{t}BuNC)(2,3-η^2-4-oxo-pent-2-eneal)] (8C and 8D). An NMR solution of complexes **8A** and **8B** was exposed to air and allowed to stand for several days. Two diastereomers were observed in a 5.5:1 (**8C**:**8D**) ratio (major has ketone toward isonitrile). **8C**: ^{1}H NMR (CD$_3$CN): δ 9.91 (d, J = 7.7 Hz, 1H, CHO), 8.13 (d, J = 1.6 Hz, 1H, TpH), 7.79 (d, J = 1.9 Hz, 1H, TpH), 7.77 (d, J = 2.3 Hz, 2H, TpH), 7.73 (d, J = 1.9 Hz, 1H, TpH), 7.71 (d, J = 1.9 Hz, 1H, TpH), 7.65 (d, J = 1.9 Hz, 1H, TpH), 6.33 (d, J = 1.9 Hz, 1H, TpH), 6.30 (d, J = 2.2 Hz, 1H, TpH), 6.25 (d, J = 2.2 Hz, 1H, TpH), 4.39 (d, J = 8.7 Hz, 1H, HC3), 2.59 (dd, J = 8.7, 7.7 Hz, 1H, HC2), 2.40 (s, 3H, CH$_3$), 1.40 ppm (s, 9H, tBu). **8D (selected resonances)**: ^{1}H NMR (CD$_3$CN): δ 9.71 (d, J = 7.7 Hz, 1H, CHO), 2.76 (dd, J = 8.7, 7.9 Hz, 1H, HC2), 1.37 (s, 9H, tBu). **Data for 8C and 8D**: $E_{1/2}$ = 0.98 V. IR (HATR): 1868 ($\nu_{C\equiv O}$), 2149 ($\nu_{C\equiv N}$), 2492 cm^{-1} (ν_{BH}).

[TpRe(CO)(MeIm)(2,3-η^2-dimethyl-7-oxanorbornadiene-4,5-dicarboxylate)] (10C) and [TpRe(CO)(MeIm)(3,4-η^2-2-oxabicyclo-[3.2.0]hepta-3,6-diene-6,7-dicarboxylic acid dimethyl ester)] (10B and 10A). In a glovebox, [TpRe(CO)(MeIm)(4,5-η^2-furan)] (**9**, 0.050 g, 0.087 mmol) was dissolved in 1 g of CH$_3$CN. Dimethyl acetylene dicarboxylate (0.051 g, 0.359 mmol, 4.13 equiv) was added, and the solution was transferred to a pressure tube. The tube was sealed and heated at 55 °C for 30 h. The solvent was removed via nitrogen purge under vacuum. The resulting oil was dissolved in 3 mL of THF, and this solution was added to 50 mL of stirring hexanes. The resulting solution was filtered through a fine frit and washed with hexanes. The solid was dried in vacuo. Yield: 60 mg (96%). Three diastereomers were observed in a 18:1:10 ratio (**10C**:**10B**:**10A**). **10C**: ^{1}H NMR (CD$_3$CN): δ 7.90 (d, J = 1.3 Hz, 1H, TpH), 7.84 (d, J = 2.3 Hz, 1H, TpH), 7.72 (m, 2H, TpH), 7.49 (d, J = 1.9 Hz, 1H, TpH), 7.46 (s, br, 1H, ImH), 7.28 (d, J = 1.9 Hz, 1H, TpH), 6.87 (t, J = 1.6 Hz, 1H, ImH), 6.40 (t, J = 1.3 Hz, 1H, ImH), 6.30 (t, J = 2.3 Hz, 1H, Tp), 6.24 (t, J = 2.2 Hz, 1H, TpH), 6.13 (d, J = 2.3 Hz, 1H, TpH), 5.18 (s, 1H, HC4), 5.10 (s, 1H, HC1), 3.71 (s, 3H, NMe), 3.65 (s, 3H, CO$_2$-Me), 3.64 (s, 3H, CO$_2$Me), 2.94 (d, J = 7.1 Hz, 1H, HC5), 2.35 ppm (d, J = 7.1 Hz, 1H, HC6). ^{13}C NMR (CD$_3$CN): δ 162.3 (2 × C═O), 152.4 (C2 and C3), 147−122 (6 Tp 3 and 5 positions, 3 MeIm peaks), 107.0, 106.8, 106.7 (Tp 4 positions), 87.8 (C4), 87.6 (C1), 64.8 (C5), 63.5 (C6), 52.5 (OMe), 52.3 (OMe), 34.7 ppm (NMe) (C≡O not seen). **10B (selected resonances)**: ^{1}H NMR (CD$_3$CN): δ ∼6.3 (located by gHSQC, 1H, HC3), 4.49 (d, J = 3.2 Hz, 1H, HC1), 2.56 ppm (d, J = 5.5 Hz, 1H, HC4). ^{13}C NMR (CD$_3$CN): 108.7 ppm (C3). **10A**: ^{1}H NMR (CD$_3$CN): δ 8.21 (s, br, TpH), 7.81 (d, J = 1.9 Hz, 1H, TpH), 7.72 (m, br, 2H, ImH and TpH), 7.65 (s, br, 1H, TpH), 7.38 (s, br, 1H, TpH), 7.34 (s, br, 1H, TpH), 6.91 (t, br, J = 1.3 Hz, 1H, ImH), 6.63 (s, br, 1H, ImH), 6.27 (t, J = 2.2 Hz, 1H, TpH), 6.23 (t, J = 2.2 Hz, 1H, TpH), 6.13 (t, J = 2.2 Hz, 1H, TpH), 5.30 (d, J = 4.5 Hz, 1H, HC3), 5.06 (d, J = 3.5 Hz, 1H, HC1), 4.26 (d, J = 3.5 Hz, 1H, HC5), 3.75 (s, 3H, NMe), 3.73 (s, br, 3H, CO$_2$Me), 3.66 (s, br, 3H, CO$_2$Me), 3.10 ppm (d, J = 4.5 Hz, 1H, HC4). ^{13}C NMR (CD$_3$CN): δ 162.3 (2 × C═O), 152.4 (C6 and C7), 147−122 (6 Tp 3 and 5 positions, 3 MeIm peaks), 108.7 (C3), 107.3, 107.2, 106.8 (Tp 4 positions), 79.9 (C1), 57.1 (C5), 52.5 (OMe), 52.3 (OMe), 47.6 (C4), 34.7 ppm (NMe) (C≡O not seen). **Data for 10C, 10B and 10A**: $E_{p,a}$ = 0.41 (br), 1.33 V. IR (HATR): 1730 ($\nu_{C=O}$), 1815 ($\nu_{C\equiv O}$), 2488 cm^{-1} (ν_{BH}).

[TpRe(CO)(MeIm)(4,5-η^2-2-methylfuran)] (11). To a solution of [TpRe(CO)(MeIm)(η^2-benzene)] (1.06 g, 1.81 mmol) in 10 mL of THF was added neat 2-methylfuran (7.40 g, 90.3 mmol, 50 equiv). The resulting solution was stirred for 16 h. Hexanes (250 mL) were added, and the slurry was filtered through a medium frit. The tan precipitate was washed with hexanes and dried in vacuo. Yield: 0.724 g (70%). Two diastereomers were observed in a 1.2:1 ratio, with the major having the oxygen of the heterocycle toward the pyrazole/CO quadrant (see Scheme 1). ^{1}H NMR (CD$_3$CN): δ 8.38 (d, J = 1.54 Hz, 1H, TpH), 8.17 (d, J = 1.8 Hz, 1H, TpH), 7.84 (m, 3H, TpH), 7.78 (m, 4H, TpH), 7.63 (s, br, 1H, minor ImH), 7.60 (s, br, 1H, major ImH), 7.26 (d, J = 2.0 Hz, 1H, TpH), 7.16 (d, J = 2.0 Hz, 1H, TpH), 7.11 (d, J = 2.0 Hz, 1H, TpH), 7.05 (t, J = 1.5 Hz, 1H, major ImH), 7.03 (t, J = 1.5 Hz, minor ImH), 6.95 (d, J = 4.4 Hz, 1H, HC5 minor), 6.60 (t, J = 1.1 Hz, 1H, ImH major), 6.52 (t, J = 1.3 Hz, ImH minor), 6.33 (d, J = 3.7 Hz, 1H, HC5 major), 6.25 (m, 4H, TpH), 6.10 (t, J = 2.4 Hz, 1H, TpH), 6.09 (t, J = 2.2 Hz, 1H, TpH), 5.91 (m, br, 1H, HC3 minor), 5.76 (s, br, 1H, HC3 major), 4.06 (s, br, 1H, HC4 major), 3.83 (s, 2 × 3H, NMe major and minor), 3.37 (m, br, 1H, HC4 minor), 2.17 (s, 3H, CH$_3$ major), 2.17 ppm (s, 3H, CH$_3$ minor). ^{13}C NMR (CD$_3$CN): δ 198.4 (C≡O minor), 198.2 (C≡O major), 150.7 (C2 minor), 150.4 (C2 major), 144.7, 144.3, 143.7, 141.4, 140.3, 140.3, 136.1, 135.8, 135.3, 134.9, 134.8 (Tp 3 and 5 positions), 132.1 (2C), 132.05 (2C) (Im), 129.55, 128.93, 128.8 (Tp 3 and 5 positions), 122.0, 121.7 (Im), 111.4 (C5 minor), 111.2 (C5 major), 109.1 (C3 minor), 108.0 (C3 major), 106.4 (2C), 106.2 (2C), 106.1 (2C) (Tp 4 positions), 58.0 (C4 major), 57.4 (C4 minor), 34.3 (2C) (NMe major and minor), 13.7 (Me minor), 13.6 ppm (Me major). $E_{1/2}$ = −0.07, 0.91 (quasireversible) V. IR (HATR): 1800 ($\nu_{C\equiv O}$), 2480 cm^{-1} (ν_{BH}).

[TpRe(CO)(MeIm)(3,4-η^2-1-methyl-2-oxa-bicyclo[3.2.0]hepta-3,6-diene-6,7-dicarboxylic acid dimethyl ester)] (12B and 12A). To a solution of **11** (0.052 g, 0.088 mmol) in 1 g of THF was added dimethyl acetylenedicarboxylate (0.074 g, 0.523 mmol, 5.96 equiv). The solution was stirred for 4 h, then added to 50 mL of stirring hexanes. The slurry was filtered through a fine frit and washed with hexanes. The tan solid was dried in vacuo. Yield: 32 mg (50%). Two diastereomers were observed in a 1:1 ratio. ^{1}H NMR (CD$_3$CN): δ 8.20 (d, J = 2.0 Hz, 1H, TpH), 8.09 (d, J = 1.8 Hz, 1H, TpH), 7.81 (dd, J = 2.4, 0.4 Hz, 2H, TpH), 7.80 (dd, J = 2.2, 0.4 Hz, 2H, TpH), 7.75 (m, 6H, TpH), 7.73 (dd, J = 2.42, 0.7 Hz, 2H, TpH), 7.57 (s, br, ImH), 7.52 (s, br, ImH), 7.31 (d, J = 2.0 Hz, 1H, TpH), 7.29 (d, J = 2.0 Hz, 1H, TpH),

7.26 (d, J = 1.8 Hz, 1H, TpH), 7.22 (d, J = 2.2 Hz, 1H, TpH), 6.89 (t, J = 1.5 Hz, 1H, ImH), 6.84 (t, J = 1.5 Hz, 1H, ImH), 6.55 (t, J = 1.5 Hz, ImH), 6.34 (t, J = 1.3 Hz, 1H, ImH), 6.24 (m, 4H, TpH), 6.17 (t, J = 2.2 Hz, 1H, TpH), 6.15 (t, J = 2.2 Hz, 1H, TpH), 5.90 (d, J = 5.05 Hz, 1H, **12B**, HC3), 5.16 (d, J = 4.8 Hz, 1H, **12A**, HC3), 4.09 (s, 1H, HC5), 3.95 (s, 1H, HC5), 3.74 (s, NMe), 3.74 (s, NMe), 3.72 (s, CO_2Me), 3.67 (s, CO_2Me), 3.65 (s, CO_2Me), 3.65 (s, CO_2Me), 3.37 (d, J = 5.1 Hz, 1H, **12A**, HC4), 2.81 (d, J = 5.1 Hz, **12B**, HC4), 1.87 (s, 3H, Me), 1.86 ppm (s, 3H, Me). ^{1}H NMR (CD_3CN): δ 200.1 (2 C≡O), 163.6 (C═O), 163.4 (C═O), 162.5 (C═O), 162.5 (C═O), 150.6, 150.2, 147.4, 147.1 (C6 and C7 for **12B** and **12A**), 146.0, 145.4, 144.5, 143.3, 142.2, 142.0, 141.0, 140.1, 136.8, 136.5, 136.2 (Tp 3 and 5 positions), 135.7, 135.6 (Im), 132.1 (Tp), 132.0, 129.3, 122.5, 121.9 (Im), 108.6 (C3, **12B**), 107.8 (C3, **12A**), 107.2 (2C), 107.0, 106.8, 106.8, 106.6 (Tp 4 positions), 88.5 (C1), 88.4 (C1), 60.4 (C5), 60.3 (C5), 52.4 (OMe), 52.4 (OMe), 52.1 (2 OMe), 51.7 (C4, **12A**), 50.3 (C4, **12B**), 34.6 (2 NMe), 19.3 (Me), 19.2 ppm (Me). $E_{p,a}$ = 0.31, 1.42 V. IR (HATR): 1803 ($\nu_{C\equiv O}$), 1730 ($\nu_{C=O}$), 2488 cm^{-1} (ν_{BH}).

[TpRe(CO)(MeIm)(4,5-η^2-2,5-dimethylfuran)] (13). To a solution of [TpRe(CO)(MeIm)(η^2-benzene)] (0.308 g, 0.52 mmol) in approximately 5 mL of THF was added 2,5-dimethylfuran (2.56 g, 26.7 mmol, 50.9 equiv). The solution was allowed to stir for 17 h, at which point 300 mL of hexanes were added. The suspension was stirred for 15 min and filtered through a fine frit. The solid was washed with hexanes and dried in vacuo. Yield: 0.200 g (63%). ^{1}H NMR (CD_3CN): δ 8.25 (s, br, 1H, TpH), 7.81 (d, J = 1.8 Hz, 1H, TpH), 7.79 (d, J = 2.0 Hz, 1H, TpH), 7.70 (d, J = 2.2 Hz, 1H, TpH), 7.54 (s, br, 1H, ImH), 7.36 (s, br, 1H, TpH), 7.09 (s, br, 1H, TpH), 6.92 (t, J = 1.3 Hz, 1H, ImH), 6.64 (s, br, 1H, ImH), 6.31 (t, J = 2.0 Hz, 1H, TpH), 6.25 (t, J = 2.2 Hz, 1H, TpH), 6.08 (t, J = 2.2 Hz, 1H, TpH), 5.86 (s, br, 1H, HC4), 3.68 (s, 3H, NMe), 3.52 (s, br, 1H, HC3), 2.18 (s, 3H, CH_3), 0.88 ppm (s, 3H, CH_3). ^{13}C NMR: δ 199.0 (C≡O), 149.7 (C2), 144.6, 143.8, 141.6, 141.4, 136.4, 136.0 (Tp 3 and 5 positions), 135.3, 132.0, 122.2 (Im), 112.8 (C3), 112.0 (C5), 107.1, 106.8, 106.5 (Tp 4 positions), 58.9 (C4), 34.6 (NMe), 22.4 (CH_3), 13.5 ppm (Me). $E_{1/2}$ = −0.08, 0.95 V. IR (HATR): 1794 ($\nu_{C\equiv O}$), 2483 cm^{-1} (ν_{BH}). Anal. Calcd for $C_{20}H_{24}BN_8O_2Re$: C, 39.67; H, 4.00; N, 18.51. Found: C, 39.29; H, 3.99; N, 18.61.

[TpRe(CO)(MeIm)(3,4-η^2-1,3-dimethyl-2-oxabicyclo[3.2.0]hepta-3,6-diene-6,7-dicarboxylic acid dimethyl ester)] (14). To a solution of compound **13** (0.233 g, 0.385 mmol) in 4.0 mL of THF was added dimethylacetylene dicarboxylate (0.213 g, 1.50 mmol, 3.9 equiv). The solution was stirred for 5 h and precipitated into 60 mL of stirring hexanes. The slurry was stirred for 5 min and filtered through a fine frit. The solid was washed with hexanes and dried in vacuo. Yield: 0.269 g (94%). ^{1}H NMR (CD_3CN): δ 8.16 (d, J = 1.3 Hz, 1H, TpH), 7.80 (d, J = 2.0 Hz, 1H, TpH), 7.76 (dd, J = 2.4, 0.7 Hz, 1H, TpH), 7.70 (dd, J = 2.2, 0.4 Hz, 1H, TpH), 7.64 (s, br, 1H, ImH), 7.45 (d, J = 1.8 Hz, 1H, TpH), 7.21 (d, J = 1.5 Hz, 1H, TpH), 7.21 (d, J = 1.8 Hz, 1H, TpH), 6.91 (t, J = 1.5 Hz, 1H, ImH), 6.67 (t, J = 1.3 Hz, 1H, ImH), 6.27 (t, J = 2.2 Hz, 2H, TpH), 6.11 (t, J = 2.2 Hz, 1H, TpH), 3.87 (s, 1H, HC5), 3.73 (s, 3H, OMe), 3.72 (s, 3H, OMe), 3.66 (s, 3H, NMe), 2.99 (s, 1H, HC4), 1.83 (s, 3H, Me), 0.75 ppm (s, 3H, Me). ^{13}C NMR (CD_3CN): 200.1 (C≡O), 163.7 (C═O), 162.6 (C═O), 150.4, 148.2 (C6 and C7), 145.4, 143.1, 142.3, 141.3, 136.6, 136.2 (Tp 3 and 5 positions), 135.6, 132.2, 122.3 (Im), 112.0 (C3), 107.0, 106.8, 106.7 (Tp 4 positions), 87.8 (C1), 61.7 (C5), 53.2 (OMe), 52.4 (C4), 52.1 (OMe), 34.7 (NMe), 25.2 (Me), 19.0 ppm (Me). $E_{1/2}$ = 0.20 (quasireversible); $E_{p,a}$ = 1.02, 1.29 V. IR (HATR): 1730 ($\nu_{C=O}$), 1801 ($\nu_{C\equiv O}$), 2485 cm^{-1} (ν_{BH}). Anal. Calcd for $C_{24}H_{25}BN_{10}O_2PRe$: C, 41.77; H, 4.04; N, 14.99. Found: C, 41.92; H, 4.07; N, 14.63.

1,3-Dimethyl-2-oxa-bicyclo[3.2.0]hepta-3,6-diene-6,7-dicarboxylic Acid Dimethyl Ester (15). Compound **14** (0.170 g, 0.228 mmol) was dissolved in 4 g of CH_3CN. A solution of AgOTf (0.121 g, 0.470 mmol, 2.1 equiv) and 2,6-lutidine (0.053 g, 0.491 mmol, 2.2 equiv) in 2 g of CH_3CN was added. The resulting solution was stirred overnight and filtered through a fine frit. The CH_3CN was removed by rotary evaporation, and the oil was chromatographed on a 1000 μm silica gel preparatory TLC plate, which had been pretreated with NMe_3, using 1:1 EtOAc/hexanes as the eluent. The desired band was cut out, extracted with acetone, and rotary evaporated to dryness to afford 23 mg (43%) of **15**. ^{1}H NMR (CD_3CN): δ 4.84 (m, H4)), 3.75 (s, CO_2-Me), 3.74 (s, CO_2Me), 3.51 (m, H5), 1.73 (t, J = 1.1 Hz, CH_3), 1.62 ppm (s, CH_3). ^{13}C NMR (CD_3CN): δ 162.6 (C═O), 161.5 (C═O), 159.8 (C3), 150.4 (C7), 139.4 (C6), 98.2 (C4), 87.8 (C1), 55.9 (C5), 52.7 (OCH_3), 52.3 (OCH_3), 19.3 (CH_3), 14.8 ppm (CH_3). HRMS m/z Calcd for $C_{12}H_{15}O_5$: 239.0920. Found: 239.0920.

2,7-Dimethyloxepine-3,4-dicarboxylic Acid Dimethyl Ester (16). An NMR solution (CD_3CN) of complex **15** was heated at 80 °C for 100 h. During this time, the disappearance of **15** was observed, along with the appearance of peaks for compound **16**. The yield of **16** was 70% based on an internal NMR standard. ^{1}H NMR (CD_3CN): δ 7.18 (dd, J = 5.7, 0.9 Hz, 1H, H5), 5.78 (dd, J = 5.7, 1.1 Hz, 1H, H6), 3.68 (s, 3H, CO_2Me), 3.63 (s, 3H, CO_2Me), 2.20 (s, 3H, C2−CH_3), 2.01 ppm (t, J = 1.1 Hz, 3H, C7−CH_3). ^{13}C NMR (CD_3CN): δ 168.2, 167.5, 161.9, 161.0 (C2, C7, 2 CO_2Me), 137.22 (C5), 129.2, 119.4 (C3, C4), 112.8 (C6), 52.6, 52.5 (CO_2CH_3), 21.9, 20.5 (2 CH_3) ppm.

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Supporting Information Available: Details of X-ray diffraction data for **4D**, **13**, and **14**, including refinement data, bond lengths and angles, atomic coordinates, and anisotropic displacement parameters (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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