Rhenium(I) η^2-Coordinated Furan Complexes: Converting Furan into a 1,3-Carbon Dipole

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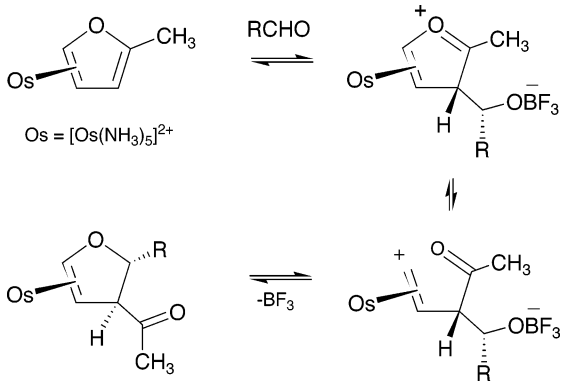
TpRe(CO)(MeIm)(η^2-2-methylfuran) (**1**; Tp = hydridotris(pyrazolyl)borate and MeIm = *N*-methylimidazole) and TpRe(CO)(MeIm)(η^2-2,5-dimethylfuran) (**9**) undergo Lewis acid promoted cyclopentannulation reactions with enones and enals to generate 3-acetylcyclopentene complexes. During the reaction, a rearrangement occurs such that the α- and β-carbons of the enone or enal are incorporated into the new carbocycle. The reactions are completely regioselective. Yields vary from 26 to 78%, depending on reaction conditions. Diastereomer ratios vary from 50:50 to >95:5. In a similar fashion, these furan complexes undergo reactions with aldehydes to form acetyldihydrofuran complexes, where a new dihydrofuran ring is generated from the aldehyde and C3−C5 of the original furan. These dihydrofuran complexes are readily converted into the corresponding trisubstituted furans via oxidative demetalation. Attempts to synthesize TpRe(CO)(MeIm)(η^2-2-methoxyfuran) for the synthesis of cyclopentene esters resulted in the formation of a novel rhenium carbene.

Introduction

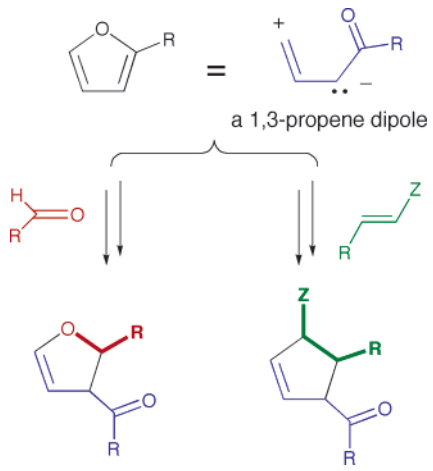
The assembly of five-membered rings is an integral part of the synthesis of many natural products,[1,2] and a variety of strategies, both organic-[3−12] and organometallic-based,[13,14] have been established for their syntheses. This paper describes a novel approach to [3 + 2] cycloaddition reactions using an η^2-coordinated furan that functions as a 1,3-propene dipole. The 1,3-dipole character of η^2-furan complexes was first reported for an unusual cyclization process between $[Os(NH_3)_5(\eta^2$-2-methylfuran$)]^{2+}$ and various aldehydes (Scheme 1).[15] In that reaction, the bound heterocycle reacted with an aldehyde in the presence of $BF_3{\cdot}OEt_2$ to form a 3*H*-furanium intermediate which then rearranged to form a new dihydrofuran ring.

In principle, by replacing the aldehyde with an electrophilic alkene (Scheme 2), a cyclopentene ring could be constructed in a similar manner. Unfortunately, this reaction was never realized for osmium furan complexes.[16] However, this novel cyclopentannu-

Scheme 1



Scheme 2



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(1) Corey, E. J.; Cheng, X. *The Logic of Chemical Synthesis*; Wiley: New York, 1989.
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(14) Ryter, K.; Livinghouse, T. *J. Am. Chem. Soc.* **1998**, *120*, 2658.
(15) Liu, R.; Chen, H.; Harman, W. D. *Organometallics* **1995**, *14*, 2861.

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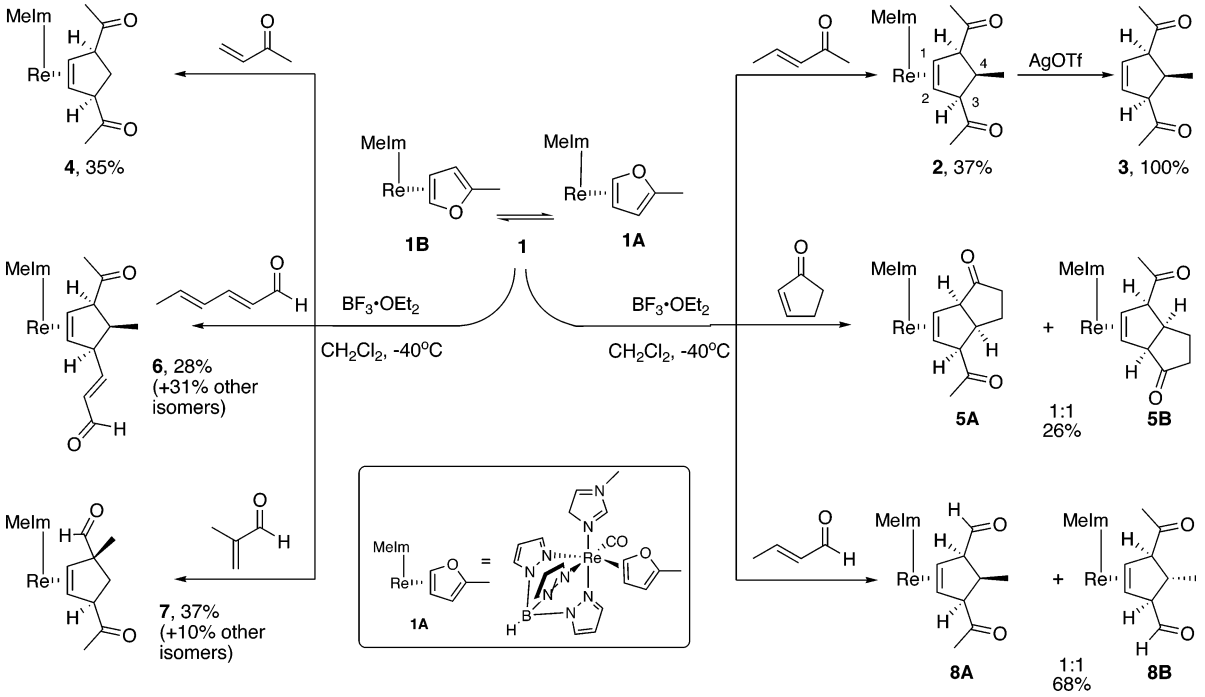
Scheme 3



lation reaction was ultimately demonstrated by utilizing the more electron-rich rhenium(I) fragment {TpRe(CO)(MeIm)}, and our preliminary findings to this effect were recently communicated.[17] Herein, we wish to report the full details of our investigation, which include examples of η^2-furan complexes reacting with both aldehydes and alkenes. Where possible, the resulting products have been oxidized to provide novel organic molecules.

Results and Discussion

When TpRe(CO)(MeIm)(η^2-2-methylfuran) (**1**), present as a mixture of coordination diastereomers,[18] was combined with various Michael acceptors in the presence of BF_3·OEt_2, cyclopentene complexes were generated and isolated in yields ranging from 26 to 68%. The following example was typical. The furan complex **1** was combined with 3-penten-2-one (BF_3·OEt_2/−40 °C) in CH_2Cl_2 for a period of 1 min. After treatment with pyridine, the reaction mixture was immediately chromatographed and cyclopentene complex **2** was isolated in 37% yield (Scheme 3). The constitution and stereochemistry of complex **2** was confirmed by a combination of ^{1}H, ^{13}C NMR, gDQCOSY, gHSQC, gHMBC, and 1D NOE spectra. Particularly noteworthy in the ^{1}H NMR spectrum of **2** is the isolated spin system for H1 and H2. Consequently, the gHMBC spectrum was instrumental in the full structural assignment of **2**. For instance, acetyl groups appear at δ 2.06 and 1.61 in the ^{1}H NMR spectrum, and these assignments are supported by gHMBC correlations to carbonyl groups at δ 212.3 and 213.5 in the ^{13}C NMR spectrum, respectively. Irradiation of the acetyl methyl at δ 2.06 revealed a 6.2% enhancement in H2 at δ 2.60 (away from MeIm). Additionally, irradiation of the acetyl methyl group at δ 1.61 revealed a 4.2% enhancement in H1 at δ 3.10 (toward MeIm). Taken together, these data are consistent with both acetyl groups being anti to the metal. To further support this stereochemical assignment, we note that, for the previously reported TpRe(CO)(L)(η^2-2-methoxy-2,3-dihydrofuran) complexes, protons associated with the bound carbons vicinally couple only to protons that are anti to the metal fragment.[19] Irradiation of the CH_3 group (on C4, δ 1.12) reveals enhancements of 9.5 and 12.3% in the peaks at δ 4.18 and δ 4.10, respectively. These enhancements first led us to believe that the methyl group at C4 was syn to the metal, but further analysis of the data is most consistent with the C4 methyl group being anti to the metal (vide infra). An argument can be made for either orientation of the C4 methyl group (syn or anti), depending on how the ring puckers. The bound carbons are expected to be coplanar with the α unbound carbons (i.e., the C(5)−C(1)−C(2)−C(3) dihedral angle is expected to be close to 0°); this notion is supported by the crystal structures of complex **10**,[17] **13**, and **14**. The cyclopentene ring could pucker such that C4 is toward or away from the metal. Molecular modeling suggests that either conformation may be consistent with the NOE enhancements observed. To resolve the issue, we were able to decomplex the cyclopentene ligand of **2** with AgOTf to give **3** in quantitative yield (Scheme 3). ^{1}H NMR spectral data are consistent with **3** containing an internal mirror plane, and H4 exhibits coupling constants and coupling patterns similar to those of **2** (cf. $J_{3,4}$ = 8.7 Hz vs 7.0 Hz), indicating that epimerization did not occur during the decomplexation process. Barba et al.[20] have synthesized a cyclopentene in which the saturated portion contains mutually trans substituents; the vicinal cou-

(16) Chen, H.; Liu, R.; Myers, W. H.; Harman, W. D. *J. Am. Chem. Soc.* **1998**, *120*, 509.
(17) Friedman, L. A.; You, F.; Sabat, M.; Harman, W. D. *J. Am. Chem. Soc.* **2003**, *125*, 14980.
(18) Friedman, L. A.; Sabat, M.; Harman, W. D. *J. Am. Chem. Soc.* **2002**, *124*, 7395.
(19) Friedman, L. A.; Harman, W. D. *J. Am. Chem. Soc.* **2001**, *123*, 8967.
(20) Barba, F.; de la Fuente, J. L. *J. Org. Chem.* **1993**, *58*, 7685.

pling constants are 3.6 Hz, which are inconsistent with observations for **2** and **3**. Furthermore, coupling constants for the CH_2 group of C4 in compound **4** support the assignment of **3** as that shown in Scheme 3.

Similar to the formation of **2**, the methylfuran complex **1** undergoes cyclopentannulation with methyl vinyl ketone to generate the diacetylcyclopentene complex **4** (Scheme 3). Again, NOE and coupling data indicate that both acetyl groups are anti to the metal. Irradiation of H3 or H5 reveals enhancements of 5.6 or 6.4% in the CH_2 proton at δ 2.49. No enhancement in the CH_2 proton at δ 2.38 was observed upon irradiation of H3 or H5. Thus, the proton at δ 2.49 was assigned as being syn to the metal, coupling to H3 and H5, each with J = 9.3 Hz. The CH_2 proton that is anti to the metal (δ 2.38) couples to H3 and H5, each with J = 2.9 Hz.

Cyclopentannulation of **1** with cyclopentenone gives pentalenone complexes **5A** and **5B** in a 1:1 ratio (Scheme 3), a ratio nearly identical to the diastereomer ratio of **1** (1:1.2). Chemical shifts of H1 and H2 and 2D NMR spectra were used to determine the identities of the coordination diastereomers. Although silica gel chromatography did not separate **5A** from **5B**, NOE data obtained from a 1:1 mixture of the complexes clearly identified the stereochemistry of the substituents about the uncoordinated portions of the coordinated ring as all anti to the metal.

The reaction of the furan complex **1** with 2,4-hexadienal resulted in multiple products. Chromatography provided the major product **6** in 93% purity and 28% yield (Scheme 3), but many other products, whose spectral features are consistent with other stereoisomers, were present in a combined 31% yield. Spectroscopic features for **6** are similar to those of **2** but also include olefinic signals at δ 7.21 (dd) and 5.91 (dd) with a mutual coupling constant of 15.4 Hz, indicating trans alkene stereochemistry. In addition, an aldehyde resonance at δ 9.41 is present. NOE data were used to determine the orientation of the cyclopentene ring. In a similar fashion, cyclopentannulation of **1** with methacrolein resulted in the synthesis of complex **7** (Scheme 3) in 37% yield. Four minor diastereomers were observed along with **7**, but these diastereomers comprised less than 10% of the total isolated yield.

Cyclopentannulation of **1** with crotonaldehyde yields complexes **8A** and **8B** (Scheme 3) in a total yield of 68% (the ratio of **8A** to **8B** is 1:1). Coupling constant and NOE data for **8A** are similar to those of **2**, supporting the assignment of the C4 methyl group of **8A** as being oriented toward the metal. In contrast, the signal corresponding to H4 of **8B** appears as a quartet (J = 7.7 Hz), indicating no significant coupling with protons other than the vicinal methyl group. The stereochemistry for that methyl group is therefore assigned as trans to the two carbonyl groups.

The poor diastereocontrol exhibited in many of the reactions in Scheme 3 is likely a direct result of the poor coordination stereoselectivity for the 2-methylfuran complex. To avoid these complications, we directed our attention to the reactivity of the 2,5-dimethylfuran complex TpRe(CO)(MeIm)(η^2-2,5-dimethylfuran) (**9**).[18] In contrast to the 2-methylfuran complex **1**, complex **9** is present in solution as a single diastereomer, owing to the steric interaction for the unobserved isomer

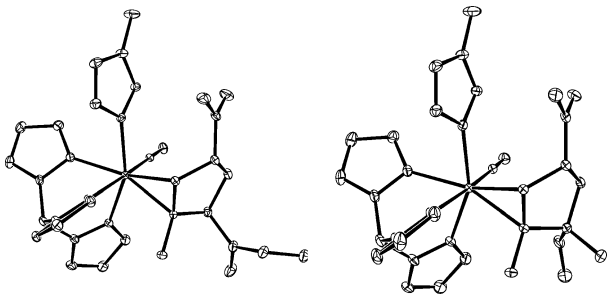
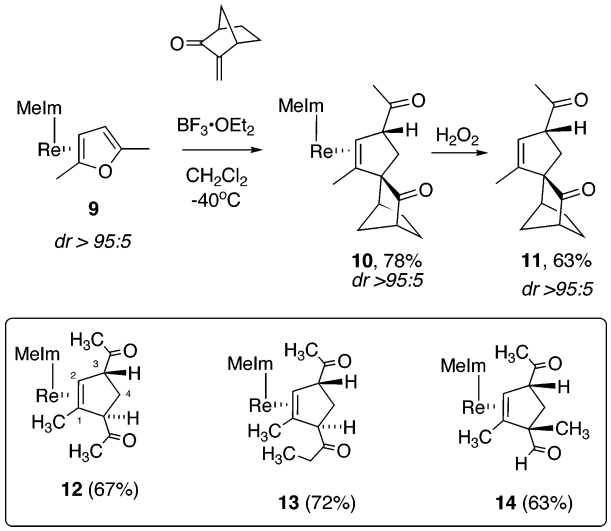


Figure 1. ORTEP diagrams (30% ellipsoids) of compounds **13** (left) and **14** (right).

Scheme 4

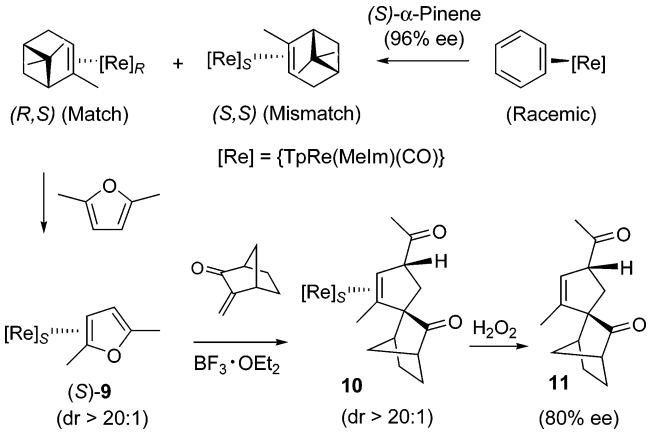


between the C5 methyl group of the furan and the pyrazole ring trans to the CO.[21] Whereas the cyclopentannulation of **1** with 3-methylene-2-norbornanone yields a complicated mixture of at least five inseparable diastereomers, cyclopentannulation of **9** with 3-methylene-2-norbornanone yields a single diastereomer (**10**, Scheme 4) in 78% yield. Full spectroscopic analysis, and ultimately a crystal structure analysis, confirmed the identity of **10** as the tricyclic undecene shown in Scheme 4.[17] In contrast to most of the other products observed, the acetyl group was found to be oriented syn to the metal, as evidenced by a coupling constant of 4.8 Hz between H1 and H5 and a 6.3% NOE between these two protons. Oxidative decomplexation of **10** (to yield **11**) was achieved using AgOTf, $Cu(OTf)_2$, or peroxides, although the last oxidant gave the best yield. Using procedures similar to the synthesis of **10**, complexes **12**–**14** were prepared by combining **9** with methyl vinyl ketone, ethyl vinyl ketone, and methacrolein, respectively, in yields ranging from 63 to 72% (see Scheme 4), and all were recovered in diastereomer ratios greater than 20:1.[17] Crystal structures were obtained for the last two compounds, and the corresponding ORTEP drawings are shown in Figure 1. Treatment of **12** and **13** with silver triflate liberated the organic cyclopentenes in yields >95% with dr > 20:1 (NMR).[17,22]

Numerous synthetic methodologies for cyclopentenes have been developed, as a result of the vast number of

(21) Meiere, S. H.; Harman, W. D. *Organometallics* **2001**, *20*, 3876.
(22) The cyclopentene ligands liberated from **12** and **13** are volatile; thus, accurate yields were determined by proton NMR using an internal integration standard.

Scheme 5

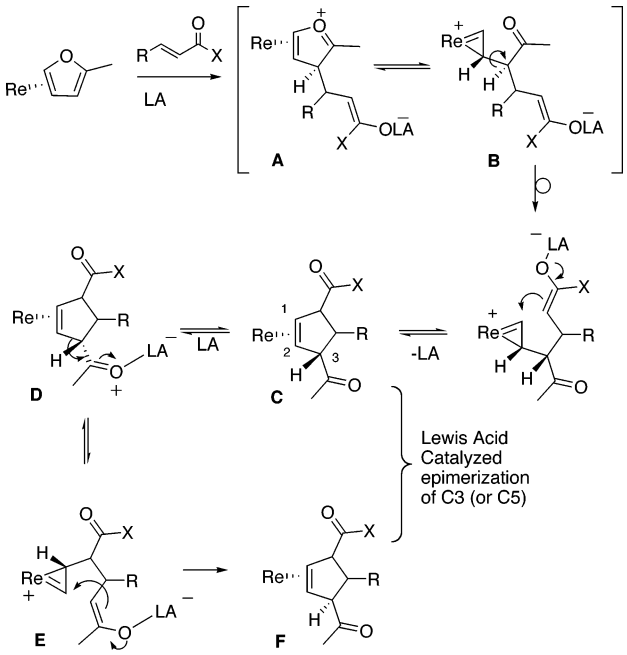


natural products containing this ring (e.g. steroids and prostaglandins). Perhaps the most sought after approach has been a [3 + 2] construction[23] akin to the Diels−Alder reaction for six-membered rings, as this approach offers the possibility of controlling multiple stereocenters.[3−12,24] Of these methodologies, most are considered to be "anionic", requiring basic reaction conditions to carry out the cyclization. In contrast, the approach presented herein is carried out under mildly acidic conditions. Further, since the 1,3-dipole is derived from a furan, an acyl group is installed at the 3-position, which is easily manipulated. However, the present system provides acceptable stereocontrol only in the case of 2,5-dimethylfuran, where coordination stereochemistry can be controlled. In our initial report,[17] the preparation of the tricyclic enedione complex **10** was ultimately carried out with a resolved form of the 2,5-dimethylfuran complex (*S*)-**9**, as prepared from (*S*)-α-pinene according to Scheme 5.[25] It is noteworthy that this reaction is carried out with a large excess of racemic methylenenorbornanone and yet only one diastereomer is isolated, with an ee of 80%.

The proposed mechanism for the cyclopentannulation reaction is presented in Scheme 6. The Lewis acid activates the electrophile by binding to the carbonyl, inducing addition at C3 of the furan ligand. The resulting 3*H*-furanium intermediate (**A**) is thought to be in equilibrium with its metallacyclopropene intermediate (**B**), a species that is equivalent to an η^2-vinyl cation.[19] The boron enolate of **B** next attacks the electrophilic η^2-vinyl group, forming the cyclopentene ring. In the presence of the Lewis acid, *either* carbonyl group can be reactivated, reversing this last step and thereby providing a means to epimerize either C3 or C5 (**C**−**F**). In contrast, compounds derived from 2,5-dimethylfuran apparently do not undergo this epimerization process. Consequently, both the stereochemistry of coordination and the configuration of the cyclopentene C3 are predictable and highly selective, and only one diastereomer for compounds **10**−**14** is observed (see Scheme 4).

Of note, when the reaction is performed in the presence of CD_3OD, no deuterium incorporation is

Scheme 6



observed at C3 or C5. This observation discounts any epimerization mechanism involving deprotonation at either of these carbons. Thus, these two stereocenters are likely formed under kinetic control. In contrast, the C4 stereocenter is formed as a result of the Michael reaction. In order for this carbon to epimerize, the Michael reaction must be reversible. While this is possible, when a sample of **2** was subjected to $BF_3{\cdot}OEt_2$ and an excess of cyclopentenone at −40 °C, pentalenone complexes **5A** and **5B** were not detected. This observation suggests that, in contrast to what is seen for aldehyde addition to furans (vide infra),[15,26] the Michael addition is irreversible, at least at −40 °C.

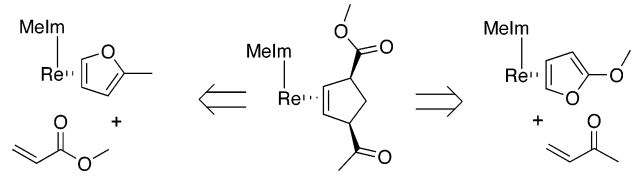
The cyclopentannulation reaction fails when the imidazole ligand is replaced by weaker σ-donating ligands such as PMe_3 and isocyanide. For comparison, the MeIm complex is 320 and 490 mV more reducing than the PMe_3 and *tert*-butyl isocyanide analogues, respectively.[27] Furthermore, a 2-alkyl substituent on the furan appears to be required. Both of these attributes are expected to enhance the stability of the purported 3*H*-furanium intermediate (e.g. **A**, Scheme 6).

In an attempt to prepare cyclopentenes functionalized with both a ketone and an ester, we tried to perform a cyclopentannulation of **1** with methyl acrylate. This reaction was unsuccessful, presumably due to the decreased electrophilicity of a carbomethoxy group relative to an aldehyde or ketone. However, we thought that we might be able to achieve the same result through TpRe(CO)(MeIm)(η^2-2-methoxyfuran), which is expected to be more nucleophilic at the β-carbon than is **1** (Scheme 7).

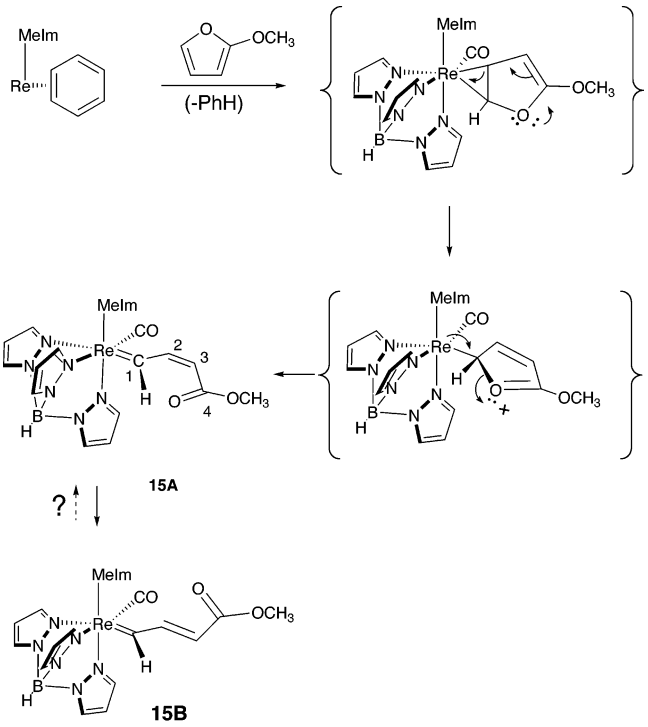
Unfortunately, the putative complex TpRe(CO)(MeIm)-(η^2-2-methoxyfuran), synthesized from TpRe(CO)(MeIm)-(η^2-benzene) and 2-methoxyfuran, is apparently unstable with respect to its carbene isomers **15A** and **15B**

(23) Hudlicky, T.; Price, J. D. *Chem. Rev.* **1989**, *89*, 1467.
(24) Danheiser, R. L.; Carini, D. J.; Basak, A. *J. Am. Chem. Soc.* **1981**, *103*, 1604.
(25) In the original communication (Scheme 2 in ref 17), the absolute stereochemistry was incorrectly shown.
(26) Schiffler, M. A.; Friedman, L. A.; Brooks, B. C.; Sabat, M.; Harman, W. D. *Organometallics* **2003**, *22*, 4966.
(27) Meiere, S. H.; Brooks, B. C.; Gunnoe, T. B.; Carrig, E. H.; Sabat, M.; Harman, W. D. *Organometallics* **2001**, *20*, 3661.

Scheme 7



Scheme 8



(9:1), the only products isolated from the reaction (Scheme 8). The structure of **15A** was assigned in part from gHSQC data, which correlated a proton signal at δ 17.30 (dd, J = 12.8, 1.2 Hz) and a peak in the ^{13}C NMR spectrum at δ 244.1, these signals corresponding to the carbene proton and carbon, respectively. Additionally, the infrared spectrum shows a C≡O stretch at 1798 cm^{-1}, remarkably similar to that of the η^2-2-methylfuran complex **1**, and an ester C=O stretch at 1696 cm^{-1}. While the latter value is low for a conjugated ester, linear conjugation with an electron-rich metal fragment is expected to decrease the stretching frequency. The ^{13}C NMR spectrum shows the ester C=O (C4) signal overlapping that of C2 (δ 166.9). In addition, gHMBC data show a correlation between a δ 9.06 signal in the ^{1}H NMR spectrum and δ 166.9 in the ^{13}C spectrum, which corroborates the existence of the ester. The ester methoxy group appears at δ 3.51 in the ^{1}H NMR spectrum and at δ 50.9 in the ^{13}C NMR spectrum. In addition to **15A**, a minor product (10%) was observed that we speculate is derived from **15A**. On the basis of coupling constants, **15B** is assigned as the all-trans carbene **15B**. The assignments of the cis/trans stereochemistries of **15A** and **15B** are corroborated by published data for similar conjugated carbenes derived from pyridine cleavage, as observed by Kleckley and coworkers.[28] Given the possibility that the isomerization shown in Scheme 8 was reversible, we combined **15** with an enone in the presence of $BF_3{\cdot}OEt_2$, hoping to see cyclopentene products. Unfortunately, all attempts to consummate such a reaction (varying Lewis acids, solvents, and temperatures) ultimately failed. When the cyclopentannulation reaction was attempted with the furan analogue of **1** and 3-penten-2-one under reaction conditions similar to those used in the preparation of **2**, an intractable paramagnetic mixture was isolated.[29]

While 2-methylfuran forms a complex with the {TpRe(CO)(MeIm)} fragment that is stable in solution at 70 °C,[30] the purported 2-methoxyfuran analogue at 25 °C apparently is unstable with respect to isomerization to form carbenes **15A** and **15B**. Assuming that such a mechanism is operative, other η^2-coordinated furan complexes may have kinetic access at ambient temperatures to this unusual type of Fischer carbene (Scheme 8). Apparently the stabilizing interaction of the methoxy group with the carbonyl (i.e., the ester) is sufficient to shift the carbene/furan equilibrium to favor the former. The low C≡O stretch for **15A/B** (1798 cm^{-1}) indicates a very electron-rich rhenium fragment, prompting us to classify these materials as Fischer carbenes, even though the carbene carbon is not bound to a heteroatom.[31] Similar carbenes have been previously reported by Gladysz and co-workers.[32,33] These electrophilic carbenes showed relatively high rotational barriers, allowing the two rotamers (stereoisomers) to be individually observed. While it is possible that **15A** and **15B** are carbene rotamers, the large difference in the vicinal coupling between H2 and H3 suggests that these stereoisomers differ in their stereochemistry of the C=C rather than the C=M bond. Although we have not exhaustively explored the reactivity of **15A/B**, nucleophiles including PMe_3 and methoxide failed to react with this complex at ambient temperatures.

We next turned our attention to carrying out the analogous cyclization with aldehydes (see Scheme 2). This reaction has been previously explored, not only for pentaammineosmium(II) furan complexes (vide supra)[15] but also for the rhenium isocyanide derivatives TpRe(CO)(^{t}BuNC)(η^2-2-methylfuran) and TpRe(CO)(^{t}BuNC)(η^2-furan).[26] In both studies, however, the liberation of the organic products was never realized. Our hope was that by changing from ^{t}BuNC to methylimidazole (i.e., **1** or **9**), the oxidized complex (i.e., Re(II)) would be less electrophilic and, therefore, would not inhibit the decomplexation of the desired dihydrofuran. Given the improved diastereomer ratios for the cyclopentannulation reaction upon switching from **1** to the 2,5-dimethylfuran complex **9** (vide supra), we limited our investigation to the reactions with the latter. When TpRe(CO)(MeIm)(η^2-2,5-dimethylfuran) (**9**) was combined with either an aromatic or aliphatic aldehyde in the presence of $BF_3{\cdot}Et_2O$, in the cosolvent CH_2Cl_2/THF at −40 °C,

(28) Kleckley, T. S.; Bennett, J. L.; Wolczanski, P. T.; Lobkovsky, E. B. *J. Am. Chem. Soc.* **1997**, *119*, 247.

(29) A similar reaction with the 2,5-dimethylfuran analogue failed to incorporate the enone, and instead, a complex tentatively assigned as TpRe(CO)(MeIm)(η^2-5-pyridin-1-yl-hex-4-en-2-one) was isolated.

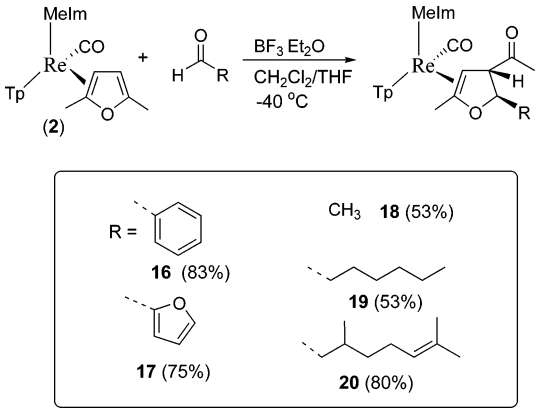
(30) Brooks, B. C.; Meiere, S. H.; Friedman, L. A.; Carrig, E. H.; Gunnoe, T. B.; Harman, W. D. *J. Am. Chem. Soc.* **2001**, *123*, 3541.

(31) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*; Wiley: New York, 2001.

(32) Patton, A. T.; Strouse, C. E.; Knobler, C. B.; Gladysz, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 5804.

(33) Kiel, W. A.; Lin, G.-Y.; Constable, A. G.; McCormick, F. B.; Strouse, C. E.; Eisenstein, O.; Gladysz, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 4865.

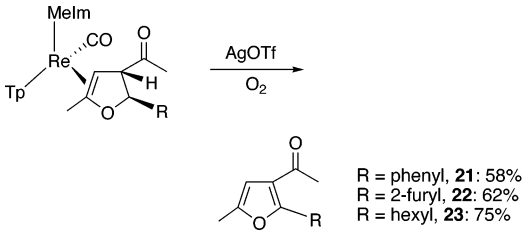
Scheme 9



the dihydrofuran complexes **16**−**19** (Scheme 9) were isolated in good yields (53−83%) as single diastereomers (dr > 20:1). While the reaction also occurs in CH_2Cl_2 alone, the mixed solvent CH_2Cl_2/THF gave a higher yield, presumably because the THF cosolvent is better able to stabilize the 3*H*-furanium intermediate (see discussion below). For the reactions with benzaldehyde and furaldehyde, the solubility of the product is low; thus, in these cases, analytically pure solids were obtained simply by filtration.

In all cases, proton NMR data indicate that the newly generated acetyl group is cis to the metal fragment, similar to cyclopentene complexes derived from **9**, while the R group is trans to the metal fragment (see Scheme 9). In the case of the benzaldehyde complex **16**, this stereochemistry was ultimately confirmed by X-ray crystallography, and an ORTEP diagram of this compound is shown in Figure 2.

Attempts to decomplex the dihydrofuran ligands of **16**, **17**, and **19** using various oxidants (e.g., silver triflate, H_2O_2) were unsuccessful. However, treatment of these complexes with AgOTf *in the presence of oxygen* gave the trisubstituted furans **21**−**23** in 58−75% yield (eq 1). Trisubstituted furans similar to **21**−**23** have



(1)

recently been prepared from β-diketones, β-keto esters, and β-keto nitriles in the presence of propargyl bromide, DBU, and a catalytic amount of CuI.[34] Other methods include selenium-promoted electrocyclization of allyl-substituted 1,3-dicarbonyl compounds[35] and the direct acylation of 2,5-disubstituted furans.[36]

To explore the ability of the metal to influence the stereochemistry of reactions after the aldol cyclization, the C2 acetyl group was reduced with several hydride sources ($LiAlH_4$, KBH_4, and Li(9-BBNH) in THF. For

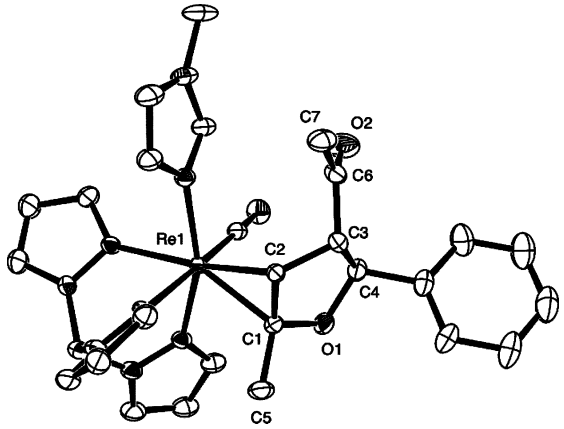


Figure 2. ORTEP drawing of compound **16** (30% ellipsoids).

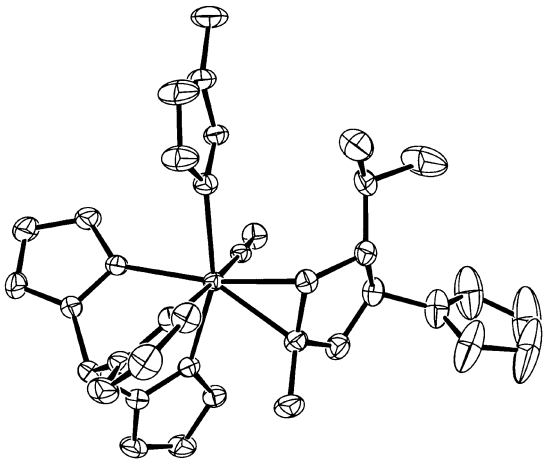
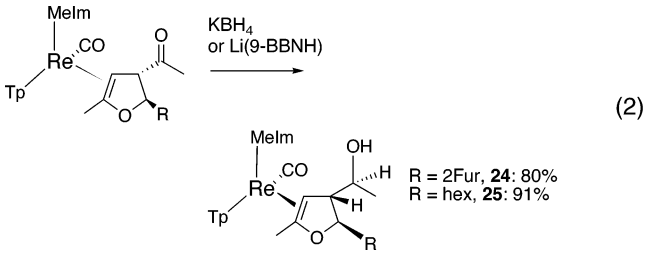


Figure 3. ORTEP diagram of the alcohol **24** (30% ellipsoids).

the 2-phenyl (**16**) and the 2-furyl compounds (**17**), reduction with LAH gave a mixture of products. However, when **17** was treated with KBH_4, alcohol **24** was produced with good stereocontrol (9.5:1; eq 2). In the



(2)

case of the heptanal-derived **23**, reduction with Li(9-BBNH) gave the best results, yielding a single diastereoisomer of the alcohol, **25**. These findings are intriguing in that the organic ligands of complexes **24** and **25** contain three contiguous stereocenters formed from prochiral organic substrates, where the rhenium stereocenter apparently influences the relative stereochemistry for all three carbons.

We were able to obtain crystals of the furaldehyde-derived alcohol **24**, and the ORTEP of this structure is shown in Figure 3. While no definitive conclusions can be made regarding the mechanism of reduction, it is worth noting that the oxygen atoms of the acetyl group and the CO ligand are arranged in a conformation that

(34) Arcadi, A.; Cerichelli, G.; Chiarini, M.; Di Giuseppe, S.; Marinelli, F. *Tetrahedron Lett.* **2000**, *41*, 9195.
(35) Tang, E.; Huang, X.; Xu, W.-M. *Tetrahedron* **2004**, *60*, 9963.
(36) Girault, J. P.; Scribe, P.; Dana, G. *Bull. Soc. Chim. Fr.* **1973**, 1760.

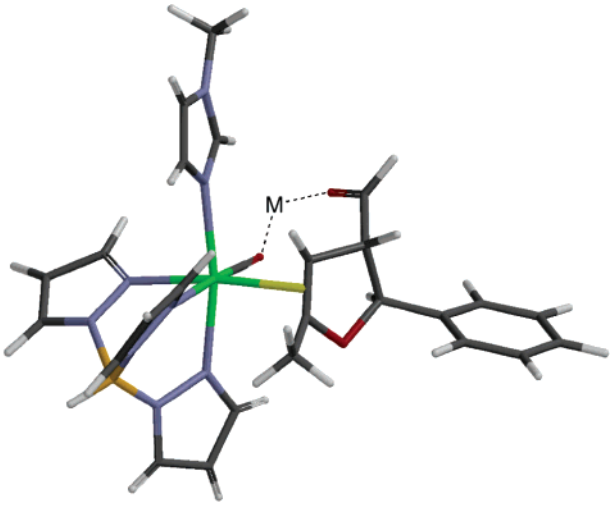


Figure 4. Possible chelation of an alkali metal by the Re−CO and acetyl oxygens.

is favorable for chelation of an alkali metal (Figure 4), and this geometry may play a role in controlling the stereochemistry of the alcohol. Unfortunately, decomplexation of the alcohol ligands from **24** or **25** could not be achieved through the oxidative procedures used earlier (e.g., AgOTf).

Conclusions

The {TpRe(CO)(MeIm)} fragment was found to promote what is formally a 1,3-dipolar cycloaddition of 2-methyl- or 2,5-dimethylfuran with aldehydes or α,β-unsaturated carbonyls. Complexation transforms the furan ring into a formal 1,3-propene dipole with a pendant acetyl group. While the coordination stereocontrol is generally poor with 2-alkylated furan, high diastereocontrol is observed when 2,5-dimethylfuran is used, owing to the high coordination diastereoselectivity present in the precursor furan complex. Cyclopentenes formed on the metal from furans and Michael acceptors were recoverable through oxidative decomplexation. A similar procedure failed to release dihydrofurans resulting from the cyclization with aldehydes, but trisubstituted furans were recovered when the decomplexation procedure was performed in air, providing a novel pathway to β-acylated furans.

Experimental Section

General Considerations. 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) using residual protonated solvent (acetonitrile-d_3 at δ 1.94) as an internal standard. Two-dimensional NMR experiments (gDQCOSY, gHSQC, gHMBC, NOE) were recorded on a Varian Inova-300 or Varian Inova-500 spectrometer. ^{1}H and ^{13}C assignments were made with the aid of gHMBC and gHSQC data. ^{13}C data were not recorded for **16**−**18** due to their low solubilities. Cyclic voltammograms were recorded 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 using cobaltocenium 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). Elemental analyses were performed by Atlantic Microlabs (Norcross, GA).

Solvents and Reagents. All solvents were purified via distillation under nitrogen or passage through an activated alumina column under an inert atmosphere and purged with nitrogen prior to use. Acetonitrile-d_3 (Cambridge Isotope Labs) was distilled over CaH_2 under an inert atmosphere prior to use. The syntheses of TpRe(CO)(MeIm)(η²-2-methylfuran) (**1**), TpRe(CO)(MeIm)(η²-2,5-dimethylfuran) (**9**),[18] TpRe(CO)(MeIm)-(η²-benzene),[37,38] and **10**−**14**[17] have been previously reported.

Compound 2. A similar procedure was used for **4**−**8**, **16**, **17**, and **19**−**22.** Complex **1** (0.100 g, 0.181 mmol) and 3-penten-2-one (0.059 g, 0.70 mmol, 4.1 equiv) were dissolved in 2.5 g of CH_2Cl_2. Separately, BF_3·OEt_2 (0.048 g, 0.34 mmol, 2.0 equiv) was dissolved in 2.5 g of CH_2Cl_2. Both solutions were cooled to −40 °C. The solution of BF_3 was added to the rhenium solution and mixed. After 1 min, pyridine (40 mg) was added. The solution was filtered through a deactivated alumina (V) plug and chromatographed on a preparatory TLC plate using EtOAc as the eluent. The desired band was cut out, extracted with acetone, and rotary evaporated to dryness to afford 0.042 g (37%) of **2**. ^{1}H NMR (CD_3CN): δ 8.07 (d, J = 1.6 Hz, 1H, Tp H), 7.95 (s, br, 1H, Im H), 7.81 (d, 2.0 Hz, 1H, Tp H), 7.72 (dd, J = 2.6, 0.6 Hz, 1H, Tp H), 7.70 (dd, J = 2.6, 0.8 Hz, 1H, Tp H), 7.58 (d, J = 2.0 Hz, 1H, Tp H), 7.48 (d, J = 1.9 Hz, 1H, Tp H), 6.92 (t, J = 1.6 Hz, 1H, Im H), 6.67 (t, J = 1.3 Hz, 1H, Im H), 6.31 (t, J = 2.3 Hz, 1H, Tp H), 6.21 (t, J = 2.3 Hz, 1H, Tp H), 6.13 (t, J = 2.3 Hz, 1H, Tp H), 4.18 (ddd, J = 8.7, 1.6, 1.6 Hz, 1H, HC3), 4.00 (ddd, J = 8.7, 1.6, 1.6 Hz, 1H, HC5), 3.69 (s, 3H, NMe), 3.18 (ddq, J = 9.0, 8.7, 6.7 Hz, 1H, HC4), 3.10 (ddd, J = 7.4, 2.2, 0.8 Hz, 1H, HC1), 2.60 (ddd, J = 7.7, 1.6, 1.6 Hz, 1H, HC2), 2.06 (s, 3H, CH_3), 1.61 (s, 3H, CH_3), 1.12 (d, J = 6.7 Hz, 3H, CH_3). ^{13}C NMR (CD_3CN): δ 213.5 (C=O, located by gHMBC), 212.3 (C=O), 200.0 (C≡O), 144.9, 143.9, 142.1, 140.4, 136.9, 136.7, 135.7 (Tp 3- and 5-positions and 1 Im), 131.2, 122.9 (Im), 107.0, 106.9 (2C, Tp 4-positions), 72.2 (C3), 71.3 (C5), 68.5 (C1), 63.9 (C2), 45.4 (C4), 34.8 (NMe), 28.2 (C(O)CH_3), 27.7 (C(O)CH_3), 17.1 (CH_3). CV: $E_{p,a}$ = 0.38, 1.42, 1.52 V (NHE). IR: 1695 ($\nu_{C=O}$), 1790 ($\nu_{C\equiv O}$), 2482 cm^{-1} (ν_{BH}).

Compound 3. Silver triflate (0.024 g, 0.093 mmol, 2.3 equiv) was dissolved in 4 mL of CH_3CN and added to complex **2** (0.027 g, 0.04 mmol). The solution was allowed to stand for 21 h and then rotary evaporated to dryness. The oil was dissolved in a minimal amount of acetone and added to 40 mL of stirred hexanes. After the mixture was stirred for 15 min, filtration followed by rotary evaporation afforded 6.6 mg (100%) of **3**. ^{1}H NMR ($CDCl_3$): δ 5.87 (s, 2H, HC1, HC2), 3.19 (d, J = 6.2 Hz, 2H, HC3, HC5), 2.79 (ddq, J = 7.0, 7.0, 6.2 Hz, 1H, HC4), 2.19 (s, 6H, 2 C(O)CH_3), 1.22 (d, J = 6.8 Hz, 3H, CH_3). ^{13}C NMR ($CDCl_3$): δ 207.5 (C=O), 130.6 (C1, C2), 66.8 (C3, C5), 36.6 (C(O)CH_3), 28.0 (C4), 20.5 (CH_3). HRMS (EI): calculated, $[M + H]^+$ = 167.1072; found, 167.1072.

Compound 4. Yield: 34%. ^{1}H NMR (CD_3CN): δ 8.05 (d, J = 1.9 Hz, 1H, Tp H), 7.84 (dd, J = 2.4, 0.6 Hz, 1H, Tp H), 7.75 (m, 2H, Tp H and Im H), 7.71 (dd, J = 2.6, 0.6 Hz, 1H, Tp H), 7.68 (d, J = 1.9 Hz, 1H, Tp H), 7.44 (d, J = 1.9 Hz, 1H, Tp H), 6.91 (t, J = 1.6 Hz, 1H, Im H), 6.66 (t, J = 1.6 Hz, 1H, Im H), 6.34 (t, J = 2.2 Hz, 1H, Tp H), 6.23 (t, J = 2.6 Hz, 1H, Tp H), 6.13 (t, J = 2.6 Hz, 1H, Tp H), 3.96 (dd, J = 9.1, 2.7 Hz, 1H, HC3 or HC5), 3.67 (s, 3H, NMe), 3.65 (dd, J = 9.6, 2.6 Hz, 1H, HC3 or HC5), 3.07 (d, J = 6.4 Hz, 1H, HC1), 2.52 (d, J = 6.4 Hz, 1H, HC2), 2.49 (ddd, J = 13.8, 9.3, 9.3 Hz, 1H, HC4), 2.38 (ddd, J = 13.5, 2.9, 2.9 Hz, 1H, HC4), 2.02 (s, 3H, (CO)-

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(38) Meiere, S. H.; Brooks, B. C.; Gunnoe, T. B.; Sabat, M.; Harman, W. D. *Organometallics* **2001**, *20*, 1038.

CH_3, 1.88 (s, 3H, $(CO)CH_3$). ^{13}C NMR (CD_3CN): 213.9 (C═O), 213.7 (C═O), 199.5 (C≡O), 144.5, 143.8, 141.9, 140.5, 136.9, 136.8, 136.7 (Tp 3- and 5-positions and Im), 131.2, 122.8 (Im), 107.0, 107.0, 106.9 (Tp 4-positions), 66.6 (C1), 63.6, 63.2 (C3 and C5), 62.0 (C2), 34.8 (NMe), 29.2 (C4), 28.0 ($(CO)CH_3$), 27.8 ($(CO)CH_3$). CV: $E_{p,a}$ = 0.27, 1.35 V (NHE). IR: 1700 ($\nu_{C=O}$), 1788 ($\nu_{C\equiv O}$), 2485 cm^{-1} (ν_{BH}).

Compounds 5A and 5B. Yield: 26% of **5A** and **5B** in a 1:1 ratio. ^1H NMR (CD_3CN): δ 8.07 (d, J = 2.0 Hz, 1H, Tp H), 7.91 (d, J = 1.8 Hz, 1H, Tp H), 7.82 (m, 2H, Tp H), 7.72 (m, 4H, Tp H), 7.66 (t, J = 1.3 Hz, 1H, Im H), 7.64 (t, J = 1.3 Hz, 1H, Im H), 7.54 (d, J = 2.0 Hz, 1H, Tp H), 7.49 (d, J = 2.0 Hz, 1H, Tp H), 7.41 (d, J = 1.8 Hz, 1H, Tp H), 7.36 (d, J = 2.0 Hz, 1H, Tp H), 6.87 (t, J = 1.5 Hz, 1H, Im H), 6.87 (t, J = 1.5 Hz, 1H, Im H), 6.63 (t, J = 1.4 Hz, 1H, Im H), 6.47 (t, J = 1.4 Hz, 1H, Im H), 6.31 (t, J = 2.2 Hz, 1H, Tp H), 6.30 (t, J = 2.2 Hz, 1H, Tp H), 6.23 (t, J = 2.2 Hz, 1H, Tp H), 6.20 (t, J = 2.2 Hz, 1H, Tp H), 6.12 (t, J = 2.2 Hz, 1H, Tp H), 6.12 (t, J = 2.2 Hz, 1H, Tp H), 4.57 (d, J = 6.6 Hz, 1H, HC4), 4.30 (d, J = 7.7 Hz, 1H, HC4), 3.86 (d, J = 7.7 Hz, 1H, HC6a), 3.66 (s, 3H, NMe), 3.63 (s, 3H, NMe), 3.49 (m, 3H, HC6a, HC3a, HC3a), 3.17 (ddd, J = 7.0, 1.3, 1.3 Hz, 1H, HC6), 3.07 (br d, J = 6.8 Hz, 1H, HC6), 2.56 (d, J = 7.0 Hz, 1H, HC5), 2.50 (br d, J = 7.03 Hz, 1H, HC5), 2.29 (m, 4H, HC2), 2.13 (s, 3H, $(CO)CH_3$), 1.99 (s, 3H, $(CO)CH_3$), 1.75 (m, 4H, HC3). ^{13}C NMR (CD_3CN): δ 223.5 (2 × C1), 213.8 (exocyclic C═O), 213.8 (exocyclic C═O), 199.8 (C≡O), 199.8 (C≡O), 144.8, 144.2, 144.0 (2C), 141.8, 141.6 (Tp 3- and 5-positions), 140.3, 140.3 (Im), 136.8, 136.8, 136.7, 136.6, 135.6 (2C) (Tp 3- and 5-positions), 131.3, 131.3, 122.7, 122.6 (Im), 107.0 (2C), 107.0, 106.9, 106.9 (2C) (Tp 4-positions), 67.1 (2C, C4), 66.1 65.7 (C6), 64.2, 64.1 (C6a), 62.5, 62.1 (C5), 47.6, 47.0 (C3a), 38.8 (2C, C2), 31.0, 30.8 (CH_3), 23.7, 23.3 (C3). CV: $E_{p,a}$ = 0.31, 1.36 V (NHE). IR: 1699 ($\nu_{C=O}$), 1725 ($\nu_{C=O}$), 1787 ($\nu_{C\equiv O}$), 2483 cm^{-1} (ν_{BH}).

Compound 6. Yield: 48%. ^1H NMR (CD_3CN): δ 9.41 (d, J = 8.0 Hz, 1H, CHO), 8.02 (d, J = 1.9 Hz, 1H, Tp H), 7.82 (d, J = 2.6 Hz, 1H, Tp H), 7.71 (m, 2H, Tp H), 7.68 (br s, 1H, Im H), 7.60 (d, J = 2.3 Hz, 1H, Tp H), 7.41 (d, J = 2.0 Hz, 1H, Tp H), 7.21 (dd, J = 15.4, 10.6 Hz, 1H, β-enal), 6.92 (t, J = 1.6 Hz, 1H, Im H), 6.65 (t, J = 1.6 Hz, 1H, Im H), 6.31 (t, J = 2.3 Hz, 1H, Tp H), 6.22 (t, J = 2.3 Hz, 1H, Tp H), 6.13 (t, J = 2.3 Hz, 1H, Tp H), 5.91 (dd, J = 15.4, 8.0 Hz, 1H, α-enal), 3.76 (d, J = 8.0 Hz, 1H, HC4), 3.70 (dd, J = 10,6 7.4 Hz, 1H, HC1), 3.68 (s, 3H, NMe), 3.44 (ddq, J = 7.7, 7.7, 7.4 Hz), 3.04 (d, J = 6.8 Hz, 1H, HC3), 2.27 (d, J = 6.8 Hz, 1H, HC2), 2.12 (s, 3H, CH_3), 0.98 (d, J = 7.7 Hz, 3H, CH_3). ^{13}C NMR (CD_3CN): δ 207.5 (C═O), 195.3, 195.2 (C═O and C≡O), 167.9 (β-enal), 146−135 (6C, Tp 3- and 5-positions), 141.9 (Im), 131.4 (α-enal), 131.3 (Im), 122.7 (Im), 107.1, 107.1, 106.8 (Tp 4-positions), 68.9 (C3), 66.1 (C4), 64.5 (C2), 57.9 (C1), 38.2 (C5), 34.7 (NMe), 29.7 ($(CO)CH_3$), 12.8 (CH_3). CV: $E_{p,a}$ = 0.35, 1.39 V (NHE). IR: 1678 ($\nu_{C=O}$), 1696 ($\nu_{C=O}$), 1789 ($\nu_{C\equiv O}$), 2477 cm^{-1} (ν_{BH}). Anal. Calcd for $C_{25}H_{30}BN_8O_3Re$: C, 43.67; H, 4.40; N, 16.30. Found: C, 43.59; H, 4.43; N, 16.14.

Compound 7. Yield: 37%. ^1H NMR (CD_3CN): δ 9.22 (s, 1H, CHO), 8.08 (d, J = 1.9 Hz, 1H, Tp H), 7.84 (d, J = 1.9 Hz, 1H, Tp H), 7.82 (s, br, Im H), 7.76 (dd, J = 2.6, 0.6 Hz, 1H, Tp H), 7.75 (d, J = 1.9 Hz, 1H, Tp H), 7.67 (dd, J = 2.2, 0.6 Hz, 1H, Tp H), 6.89 (t, J = 1.3 Hz, 1H, Im H), 6.83 (t, J = 1.6 Hz, 1H, Im H), 6.81 (d, J = 2.6 Hz, 1H, Tp H), 6.37 (t, J = 2.3 Hz, 1H, Tp H), 6.23 (t, J = 1.9 Hz, 1H, Tp H), 6.12 (t, J = 2.3 Hz, 1H, Tp H), 4.00 (d, J = 9.0 Hz, 1H, HC3), 3.62 (s, 3H, NMe), 2.96 (d, J = 6.41 Hz, 1H, HC1), 2.79 (dd, J = 13.5, 9.4 Hz, 1H, HC4 (toward Re)), 2.58 (d, J = 5.9 Hz, 1H, HC2), 2.12 (s, 3H, $(CO)CH_3$), 1.73 (d, J = 13.4 Hz, 1H, HC4 (away from Re)), 1.19 (s, 3H, CH_3). ^{13}C NMR (CD_3CN): δ 213.7 (C═O), 208.4 (CHO), 199.5 (C≡O), 144.2, 143.8, 143.8, 140.0, 137.1, 136.9, 136.0, 132.1, 122.4 (Tp 3- and 5-positions and Im), 106.9 (3C, Tp 4-positions), 72.2 (C1), 62.9 (C2), 62.5 (C3), 34.6 (NMe), 33.4 (C4), 29.7 ($(CO)CH_3$), 27.3 (CH_3) (C5 not assigned due to the presence of a minor diastereomer, which complicated the assignment). CV: $E_{p,a}$ = 0.60, 1.58 V (NHE). IR: 1704 ($\nu_{C=O}$), 1792 ($\nu_{C\equiv O}$), 2485 cm^{-1} (ν_{BH}).

Compounds 8A and 8B. Yield: 68% of complexes **8A** and **8B** in approximately a 1:1 ratio. **8A**: ^1H NMR (CD_3CN) δ 9.41 (d, J = 3.3 Hz, 1H, CHO), 8.10 (d, J = 1.8 Hz, 1H, Tp H), 7.82 (dd, J = 2.3, 0.6 Hz, 1H, Tp H), 7.73 (dd, J = 2.4, 0.7 Hz, 1H, Tp H), 7.71 (dd, J = 2.4, 0.7 Hz, 1H, Tp H), 7.66 (t, J = 1.3 Hz, 1H, Im H), 7.53 (d, J = 2.0 Hz, 1H, Tp H), 7.41 (d, J = 1.8 Hz, 1H, Tp H), 6.87 (t, J = 1.5 Hz, 1H, Im H), 6.57 (t, J = 1.5 Hz, 1H, Im H), 6.31 (t, J = 2.2 Hz, 1H, Tp H), 6.22 (dd, J = 2.4, 2.0 Hz, 1H, Tp H), 6.13 (t, J = 2.2 Hz, 1H, Tp H), 4.22 (d, J = 8.8 Hz, 1H, HC3), 3.80 (dddd, J = 9.3, 3.3, 2.4, 1.3 Hz, 1H, HC5), 3.64 (s, 3H, NMe), 3.22 (ddd, J = 7.5, 2.2, 0.9 Hz, 1H, HC1), 3.07 (ddq, J = 9.0, 8.8, 6.6 Hz, 1H, HC4), 2.59 (ddd, J = 7.7, 2.0, 1.3 Hz, 1H, HC2), 2.05 (s, 3H, $(CO)CH_3$), 1.18 (d, J = 6.8 Hz, 3H, CH_3); ^{13}C NMR (CD_3CN) δ 213.7 (C═O), 206.2 (CHO), 200.0 (C≡O), 145.1, 144.1, 141.7, 140.3, 136.8, 136.8 (Tp 3- and 5-positions), 135.7, 131.3, 122.6 (Im), 107.1, 106.9, 106.9 (Tp 4-positions), 71.6 (C3), 71.3 (C5), 64.6 (C1), 64.1 (C2), 45.2 (C4), 34.7 (NMe), 29.7 ($(CO)CH_3$), 16.7 (CH_3); CV $E_{p,a}$ = 0.40, 1.40 V (NHE); IR 1698 ($\nu_{C=O}$), 1791 ($\nu_{C\equiv O}$), 2481 cm^{-1} (ν_{BH}). **8B**: ^1H NMR (CD_3CN) δ 9.67 (d, J = 5.1 Hz, 1H, CHO), 7.89 (d, J = 1.8 Hz, 1H, Tp H), 7.83 (d, J = 2.2, Hz, 1H, Tp H), 7.72 (dd, J = 2.6, 0.5 Hz, 1H, Tp H), 7.71 (dd, J = 2.3, 0.6 Hz, 1H, Tp H), 7.69 (t, J = 1.3 Hz, 1H, Im H), 7.62 (d, J = 2.0 Hz, 1H, Tp H), 7.41 (d, J = 1.8 Hz, 1H, Tp H), 6.93 (t, J = 1.5 Hz, 1H, Im H), 6.66 (t, J = 1.4 Hz, 1H, Im H), 6.32 (t, J = 2.2 Hz, 1H, Tp H), 6.20 (d, J = 2.2 Hz, 1H, Tp H), 6.13 (t, J = 2.2 Hz, 1H, Tp H), 3.79 (d, J = 7.9 Hz, 1H, HC5), 3.68 (s, 3H, NMe), 3.44 (q, J = 7.7 Hz, 1H, HC4), 3.26 (dd, J = 8.1, 5.1 Hz, 1H, HC3), 3.10 (d, J = 6.8 Hz, 1H, HC1), 2.36 (d, J = 7.0 Hz, 1H, HC2), 2.12 (s, 3H, $(CO)CH_3$), 1.10 (d, J = 7.5 Hz, 3H, CH_3); ^{13}C NMR (CD_3CN) δ 215.5 (C═O), 210.1 (CHO), 200.0 (C≡O), 145.4, 143.7, 141.9, 140.2, 136.9, 136.6, 135.7 (Tp 3- and 5-positions and Im), 131.4, 122.8 (Im), 107.1, 107.1, 106.9 (Tp 4-positions), 69.5 (C1), 65.8 (C3), 63.9 (C5), 60.2 (C2), 37.3 (C4), 34.8 (NMe), 32.2 ($(CO)CH_3$), 12.2 (CH_3); CV $E_{p,a}$ = 0.48, 1.49 V (NHE); IR 1698 ($\nu_{C=O}$), 1789 ($\nu_{C\equiv O}$), 2487 cm^{-1} (ν_{BH}).

Compounds 15A and 15B. TpRe(CO)(MeIm)(η^2-benzene) (0.301 g, 0.513 mmol) was dissolved in 8 mL of THF. To this solution was added 2-methoxyfuran (2.50 g, 25.51 mmol, 49.7 equiv). The mixture was stirred for 17 h, at which point 400 mL of hexanes was added. After the mixture was stirred for 10 min, filtration through a fine fritted filter followed by washing with hexanes and drying in vacuo afforded 0.250 g (80%) of a gray solid (purity ∼80−85%), which consisted primarily of **15A** and **15B** in a 9:1 ratio. **15A**: ^1H NMR (CD_3CN) δ 17.30 (dd, J = 12.8, 1.2 Hz, 1H, H1), 9.03 (dd, J = 12.9, 10.9 Hz, 1H, H2), 7.93 (m 2H, Tp H), 7.83 (d, J = 2.0 Hz, 1H, Tp H), 7.67 (d, J = 2.0 Hz, 1H, Tp H), 7.45 (s, br, Im H), 7.36 (d, J = 1.8 Hz, 1H, Tp H), 7.32 (d, J = 2.0 Hz, 1H, Tp H), 6.85 (t, J = 1.3 Hz, 1H, Im H), 6.57 (t, J = 1.3 Hz, 1H, Tp H), 6.47 (t, J = 2.2 Hz, 1H, Tp H), 6.24 (t, J = 2.2 Hz, 1H, Tp H), 6.11 (t, J = 2.2 Hz, 1H, Tp H), 5.53 (dd, J = 10.8, 1.3 Hz, 1H, H3), 3.59 (s, 3H, NMe), 3.51 (s, 3H, CO_2Me); ^{13}C NMR (CD_3CN) δ 244.1 (Re═C), 203.7 (C≡O), 166.9 (C2 and C═O), 147.6 (Tp), 144.1−143.4 (3C, 2 Tp and Im), 136.5, 136.3, 136.2 (Tp), 132.9, 122.5 (Im), 107.4, 107.2 (2C) (Tp 4-positions), 97.2 (C3), 50.9 (OMe), 34.7 (NMe). **15B** (selected data): ^1H NMR (CD_3CN) δ 16.21 (dd, J = 12.8, 1.2 Hz, 1H, H1), 9.30 (dd, J = 15.0, 12.5, 1H, H2), 5.89 (dd, J = 14.7, 1.2 Hz, 1H, H3). Data for both isomers: CV $E_{p,a}$ = 0.42, 1.00 V (NHE); IR 1696 ($\nu_{C=O}$), 1798 ($\nu_{C\equiv O}$), 2485 cm^{-1} (ν_{BH}).

Compound 16. Yield: 83%. ^1H NMR (CD_3CN): 8.29 (dd, J = 2.0, 0.9 Hz, 1H, Tp H), 8.06 (t, br, 1H, Im H), 7.79 (dd, J = 2.4, 0.7 Hz, 1H, Tp H), 7.74 (d, J = 2.0 Hz, 1H, Tp H), 7.65 (dd, J = 2.4, 0.7 Hz, 1H, Tp H), 7.60 (dd, J = 1.5, 0.4 1H, Tp H), 7.58−7.56 (m, 1H, phenyl), 7.56 (d, J = 0.9 Hz, 1H, Tp H), 7.39−7.19 (m, 4H, phenyl), 7.29 (dd, J = 2.2, 0.9 1H, Tp H), 6.83 (t, J = 1.5 Hz, 1H, Im H), 6.72 (t, J = 1.5 Hz, 1H, Im H), 6.35 (t, J = 2.2 Hz, 1H, Tp H), 6.36 (t, J = 2.2 Hz, 1H, Tp H),

6.18 (t, J = 2.2 Hz, 1H, Tp H), 6.09 (d, J = 10 Hz, 1H, *H*C2), 6.04 (t, J = 2.4 Hz, 1H, Tp H), 4.49 (dd, J = 10, 5.7 Hz, 1H, *H*C3), 3.80 (s, 3H, NMe), 2.99 (d, J = 5.7 Hz, 1H, *H*C4), 1.61 (s, 3H, CH_3), 1.08 (s, 3H, CH_3). CV: $E_{p,a}$ = 0.28 V (NHE). IR: 1708 ($\nu_{C=O}$), 1789 ($\nu_{C\equiv O}$). LRMS (FAB): calcd, 712.6; found, 712.6. Anal. Calcd for $C_{27}H_{30}BN_8O_3Re$: C, 45.57; H, 4.25; N, 15.75; Found: C, 45.79; H, 4.21; N, 15.90.

Compound 17. Yield: 75% of **17**. ^{1}H NMR ($CDCl_3$): 8.22 (dd, J = 2.0, 0.7 Hz, 1H, Tp H), 7.92 (t, br, 1H, Im H), 7.72 (dd, J = 2.4, 0.7 Hz, 1H, Tp H), 7.67 (d, J = 1.8 Hz, 1H, Tp H), 7.58 (dd, J = 2.2, 0.9 Hz, 1H, Tp H), 7.50 (dd, J = 2.2, 0.7 1H, Tp H), 7.34 (dd, J = 1.8, 0.7 Hz, 1H, furyl), 7.22 (d, J = 2.2 Hz, 1H, Tp H), 6.80 (t, br, 1H, Im H), 6.66 (t, br, 1H, Im H), 6.38 (d, J = 3.2 Hz, 1H, furyl), 6.29 (t, J = 2.2 Hz, 1H, Tp H), 6.25 (dd, J = 3.2, 1.8 Hz, 1H, furyl), 6.11 (t, J = 2.0 Hz, 1H, Tp H), 5.98 (d, J = 10 Hz, 1H, *H*C2), 5.97 (t, J = 2.2 Hz, 1H, Tp H), 4.82 (dd, J = 10, 5.5 Hz, 1H, *H*C3), 3.71 (s, 3H, NMe), 2.94 (d, J = 5.5 Hz, 1H, *H*C4), 1.62 (s, 3H, CH_3), 0.94 (s, 3H, CH_3). CV: $E_{p,a}$ = 0.34 V (NHE). IR: 1702 ($\nu_{C=O}$), 1800 ($\nu_{C\equiv O}$). LRMS (FAB): calcd, 702.2; found, 702.2. Anal. Calcd for $C_{25}H_{28}BN_8O_4Re$: C, 42.80; H, 4.02; N, 15.97. Found: C, 43.05; H, 4.11; N, 15.68.

Compound 18. Compound **9** (0.105 g, 0.174 mmol) and acetaldehyde (0.066 g, 1.50 mmol) were dissolved in 1.5 g of CH_2Cl_2/1.5 g of THF. Separately, $BF_3{\cdot}OEt_2$ (0.030 g, 0.21 mmol) was dissolved in 1.0 g of CH_2Cl_2. Both solutions were cooled to −40 °C. The solution of $BF_3{\cdot}OEt_2$ was added to the rhenium complex and acetaldehyde solution at −40 °C. After 2 h, the reaction mixture was passed through the alumina plug and the solvent was reduced to 2 mL under vacuum. The concentrated solution was chromatographed using preparatory thin-layer chromatography (PTLC). The desired fraction with R_f = 0.22 (20% hexanes/80% EtOAc) was collected, and **18** was isolated as a white solid (60 mg, 0.092 mmol, 53%). ^{1}H NMR ($CDCl_3$): 8.18 (dd, J = 2.0, 0.7 Hz, 1H, Tp H), 7.91 (t, br, 1H, Im H), 7.72 (dd, J = 2.4, 0.7 Hz, 1H, Tp H), 7.674 (d, J = 1.8 Hz, 1H, Tp H), 7.59 (dd, J = 2.4, 0.9 Hz, 1H, Tp H), 7.50 (dd, J = 2.2, 0.7 1H, Tp H), 7.20 (d, J = 2.0 Hz, 1H, Tp H), 6.77 (t, br, 1H, Im H), 6.66 (t, br, 1H, Im H), 6.28 (t, J = 2.2 Hz, 1H, Tp H), 6.15 (t, J = 2.0 Hz, 1H, Tp H), 5.97 (t, J = 2.0 Hz, 1H, Tp H), 5.08 (m, J = 9.9, 5.9 Hz, 1H, *H*C2), 4.04 (dd, J = 9.9, 5.4 Hz, 1H, *H*C3), 3.72 (s, 3H, NMe), 2.83 (d, J = 5.4 Hz, 1H, *H*C4), 1.63 (s, 3H, CH_3), 1.31 (d, J = 5.9 Hz, 3H, CH_3), 0.87 (s, 3H, CH_3). CV: $E_{p,a}$ = 0.17 V (NHE). IR: 1698 ($\nu_{C=O}$), 1795 ($\nu_{C\equiv O}$). Anal. Calcd for $C_{25}H_{28}BN_8O_4Re$: C, 40.68; H, 4.35; N, 17.25. Found: C, 40.80; H, 4.21; N, 17.08.

Compound 19. Yield: 80%.^{1}H NMR (CD_3CN): 8.04 (dd, J = 2.0, 0.7 Hz, 1H, Tp H), 7.83 (d, J = 2.2 Hz, 2H, Tp H), 7.81 (t, br, 1H, Im H), 7.73 (dd, J = 2.4, 0.9 Hz, 1H, Tp H), 7.64 (dd, J = 2.2, 0.7 Hz, 1H, Tp H), 7.34 (d, J = 1.5, 1H, Tp H), 6.84 (t, J = 1.5 Hz, 1H, Im H), 6.79 (t, J = 1.5 Hz, 1H, Im H), 6.35 (t, J = 2.2 Hz, 1H, Tp H), 6.32 (dd, J = 2.0, 0.4 Hz, 1H, Tp H), 6.06 (t, J = 2.2 Hz, 1H, Tp H), 4.87 (dt, J = 10, 5.6 Hz, 1H, *H*C2), 4.10 (dd, J = 10, 5.5 Hz, 1H, *H*C3), 3.67 (s, 3H, NMe), 2.94 (d, J = 5.5 Hz, 1H, *H*C4), 1.52 (s, 3H, H_3C8), 1.45 (t, br, J = 5.6 Hz, 2H, *H*C9), 1.35−1.22 (br, 8H, 4 × CH_2), 0.89(t, J = 6.8 Hz, 3H, H_3C14), 0.76 (s, 3H, H_3C6). ^{13}C NMR (CD_3CN): 210.2 (*C*OCH_3), 200.9 (*C*O), 145.7 (Im), 145.6, 142.9, 141.8, 137.3, 136.4, 135.9 (Tp 3- and 5-positions), 132.0, 122.4 (Im), 108.3 (C5), 107.5 (Tp 4-position), 107.14, 107.08 (Tp 4-position), 77.3 (C2), 68.6 (C3), 50.3 (C4), 36.9 (C9), 35.0 (NMe), 33.1 (*C*H_2), 30.8 (C8), 29.8 (*C*H_2), 27.6 (C10), 23.81 (C6), 23.77 (*C*H_2), 14.8 (C14). CV: $E_{p,a}$ = 0.19 (NHE). IR: 1701 ($\nu_{C=O}$), 1795 ($\nu_{C\equiv O}$). LRMS (FAB): calcd, 720.4; found, 720.4. Anal. Calcd for $C_{27}H_{38}BN_8O_3Re$: C, 45.06; H, 5.32; 15.57. Found: C, 45.28; H, 5.21; 15.59.

Compound 20. Yield: 78% as a mixture of two diastereomers A + B (1:1). ^{1}H NMR (CD_3CN): 8.10 (t, $1H_A$ + $1H_B$, Im H), 7.91−7.85 (m, $3H_A$ + $3H_B$, Tp H), 7.80 (t, $1H_A$ + $1H_B$, Tp H), 7.79 (t, $1H_A$ + $1H_B$, Tp H), 7.70 (d, $1H_A$ + $1H_B$, Tp H), 7.69 (d, $1H_A$ + $1H_B$, Tp H), 7.39 (t, $1H_A$ + $1H_B$, Tp H), 6.90 (t, $1H_A$ + $1H_B$, Im H), 6.84 (t, $1H_A$ + $1H_B$, Im H), 6.40 (t, J = 2.2 Hz, $1H_A$ + $1H_B$, Tp H), 6.28 (dd, $1H_A$ + $1H_B$, Tp H), 6.12 (t, $1H_A$ + $1H_B$, Tp H), 5.20 (m, $1H_A$ + $1H_B$, *H*C13), 5.02 (m, $1H_A$ + $1H_B$, *H*C2), 4.07 (dd, $1H_A$ + $1H_B$, *H*C3), 3.74 (s, $3H_A$ + $3H_B$, NMe), 2.98 (d, J = 1.7 Hz, $1H_B$, *H*C4), 2.96 (d, J = 1.7 Hz, $1H_A$, *H*C4), 2.06 (m, overlapped), 1.74 (s, br, $3H_A$ + $3H_B$, H_3C15 or H_3C16), 1.67 (s, br, $3H_A$ + $3H_B$, H_3C15 or H_3C16), 1.58 (s, $3H_A$ + $3H_B$, H_3C8), 1.43 (t, $2H_A$ + $2H_B$), 1.24 (m, $2H_A$ + $2H_B$), 1.02 (dd, J = 12.5, 6.6 Hz, $3H_A$ + $3H_B$, H_3C17), 0.80 (d, J = 1.2 Hz, $3H_A$ + $3H_B$, H_3C6). CV: $E_{p,a}$ = 0.21 (NHE). IR: 1701 ($\nu_{C=O}$), 1797 ($\nu_{C\equiv O}$). LRMS (FAB): calcd, 760; found, 760. Anal. Calcd for $C_{27}H_{38}BN_8O_3Re$: C, 47.43; H, 5.57; 14.75. Found: C, 47.41; H, 5.50; 14.70.

Compound 21. Yield: 58%. ^{1}H NMR ($CDCl_3$): 7.88−7.82 (m, 2H, Ph *H*), 7.46−7.37 (m, 3H, Ph *H*), 6.38(q, J = 2.4, 0.88 Hz, 1H, furan *H*), 2.41 (s, 3H, *Me*CO), 2.39 (d, J = 0.88 Hz, 3H, Me). ^{13}C NMR ($CDCl_3$): 194.2 (CO), 155.2, 151.3, 130.2, 129.3, 128.3, 128.2, 123.1, 108.2, 29.8, 13.4. HRMS (EI): calcd, 200.0837; found, 200.0827.

Compound 22. Yield: 62%. ^{1}H NMR ($CDCl_3$): 7.59 (br, 1H, furan *H*), 7.52 (1H, furan *H*), 6.52 (1H, furan *H*), 6.35 (q, J = 2.4, 0.88 Hz, 1H, furan *H*), 2.43 (s, 3H, *Me*CO), 2.36 (d, J = 0.88 Hz, 3H, Me). ^{13}C NMR ($CDCl_3$): 192.8 (CO), 151.2 (furan), 146.3 (furan), 144.9 (furan), 143.4 (furan), 121.6 (furan), 112.8 (furan), 111.9 (furan), 107.9 (furan), 29.4 (CO*Me*), 13.4 (Me). HRMS (EI): calcd, 190.0630; found, 190.0627.

Compound 23. This compound was prepared in a manner similar to that for compound **21**. ^{1}H NMR ($CDCl_3$): 6.16 (br, 1H, furan *H*), 2.91 (q, J = 7.5 Hz, 2H), 2.34 (s, 3H, *Me*CO), 2.24 (d, J = 0.9 Hz, 3H, Me), 1.629 (m, 2H), 1.28 (br, 6H), 0.88 (t, J = 6.8 Hz, 3H). ^{13}C NMR ($CDCl_3$): 194.3 (CO), 161.1 (furan), 149.8 (furan), 121.5 (furan), 106.3 (furan), 31.4 (*C*H_2), 29.1 (CO*Me*), 28.9 (*C*H_2), 28.0 (*C*H_2), 27.9 (*C*H_2), 22.5 (*C*H_2), 14.0 (Me), 13.2 (Me).

Compound 24. Compound **17** (8.0 mg, 0.011 mmol) was dissolved in 1 mL of THF/0.5 mL of CH_3OH, and 2.0 mg of KBH_4 was added. The reaction mixture was stirred overnight and quenched with NH_4Cl (aq). Chromatography (PTLC; 20% hexanes/80% EtOAc) gave 6.5 mg (80%) of the reduced product **24**. ^{1}H NMR (CD_3CN): 8.25 (dd, J = 2.0, 0.7 Hz, 1H, Im H), 8.10 (t, br, 1H, Tp H), 7.73 (dd, J = 2.2, 0.7 Hz, 1H, Tp H), 7.68 (d, J = 1.8 Hz, 1H, Tp H), 7.59 (dd, J = 2.4, 0.9 Hz, 1H, Tp H), 7.52 (dd, J = 2.44, 0.9 Hz, 1H, Tp H), 7.40 (m, 1H), 7.37 (m, 1H), 7.29 (dd, J = 2.2, 0.9 Hz, 1H), 6.81 (t, J = 1.5 Hz, 1H), 6.35 (t, J = 2.2 Hz, 1H), 6.31 (t, J = 2.2 Hz, 1H), 6.29 (t, J = 2.0 Hz, 1H), 6.12 (t, J = 2.2 Hz, 1H), 6.01 (t, J = 2.2 Hz, 1H), 5.16 (d, J = 5.0 Hz, 1H), 4.02 (dd, J = 4.6 Hz, 1H, *H*C3), 3.72 (s, 3H, NMe), 2.91 (d, J = 4.6 Hz, 1H, *H*C4), 1.25 (s, 3H, H_3C6), 0.86 (d, J = 5.0 Hz, 3H, H_3C8).

Compound 25. Compound **19** (110 mg, 0.153 mmol) was dissolved in 4 mL of THF, and 0.5 mL of 1 M Li(9-BBNH) in THF was added to the solution at room temperature. The reaction was monitored by NMR. After 1 h, the reduction was quenched by 2 drops of MeOH and passed through a silica plug and the solvent was evaporated to 1 mL. Hexanes (6 mL) was added to precipitate **25** as a white solid (100 mg, 91%). ^{1}H NMR (CD_3CN): 8.14 (t, br, 1H, Im H), 8.06 (d, J = 1.5 Hz, 1H, Tp H), 7.84 (d, J = 2.0 Hz, 1H, Tp H), 7.82 (d, J = 2.2 Hz, 1H, Tp H), 7.73 (dd, J = 2.2, 0.44 Hz, 1H, Tp H), 7.65 (d, J = 2.2 Hz, 1H, Tp H), 7.59 (d, J = 2.0, 1H, Tp H), 7.22 (t, J = 1.3 Hz, 1H, Im H), 6.94 (t, J = 1.3 Hz, 1H, Im H), 6.34 (t, J = 2.2 Hz, 1H, Tp H), 6.21 (t, J = 2.2 Hz, 1H, Tp H), 6.09 (t, J = 2.2 Hz, 1H, Tp H), 4.06 (dt, J = 9.0, 2.0 Hz, 1H, *H*C2), 3.95 (m, *H*C7), 3.67 (s, 3H, NMe), 3.16 (dt, J = 9.0, 5.3 Hz, 1H, *H*C3), 2.83 (d, J = 5.3 Hz, 1H, *H*C4), 1.63 (m, 1H, *H*C9), 1.55−1.22 (m, 9H, *H*C9 + 4 × CH_2), 1.03 (d, J = 6.2 Hz, 3H, H_3C8), 0.89 (t, J = 6.6 Hz, 3H, H_3C14), 0.70 (s, 3H, H_3C6), ^{13}C NMR (CD_3CN): 201.1 (*C*O), 145.2 (Im), 144.5, 143.0, 141.0, 137.1, 136.4, 136.0 (Tp 3 and 5 positions), 132.5, 123.1 (Im), 110.9 (C5), 107.2 (Tp 4 position), 106.9 (2 Tp 4-position overlapped), 80.0

(C2), 72.4 (C7), 65.4 (C3), 51.1 (C4), 37.7 (C9), 35.0 (NMe), 33.0 (C10), 30.6 (CH_2), 27.6 (CH_2), 23.68 (*C6*), 23.65 (CH_2), 21.9 (C8), 14.7 (C14).

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Supporting Information Available: CIF files giving crystallographic details for compounds **13**, **14**, **16**, and **24**. This material is available free of charge via the Internet at http://pubs.acs.org.

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