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Diastereo- and Enantioselective Dearomatization of Rhenium-Bound Naphthalenes

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Received November 12, 2003

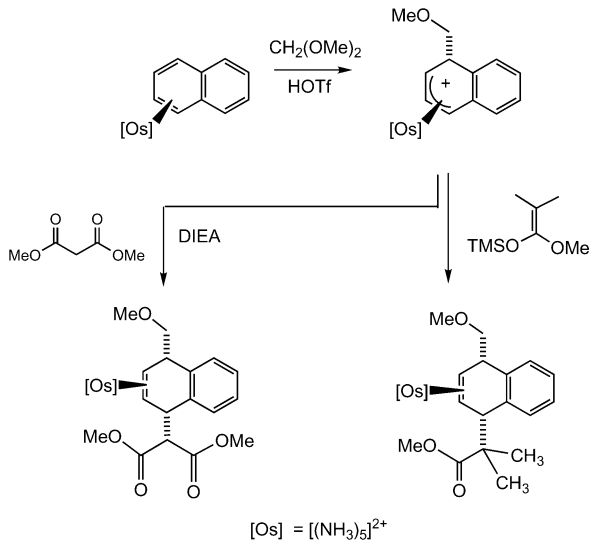
Dihapto-coordinated naphthalene complexes of the form TpRe(CO)(L)(η^2-naphthalene) (L = PMe_3, pyridine, or 1-methylimidazole) undergo electrophilic addition with dimethoxymethane and with various Michael acceptors to generate 1*H*-naphthalenium species. These naphthalenium complexes undergo intra- or intermolecular nucleophilic addition reactions with stabilized enolates, silyl ketene acetals, or enols to form the corresponding dihydronaphthalene complexes. Oxidative decomplexation generates the free dihydronaphthalene. When a resolved form of the rhenium dearomatization agent is used, these reactions can be performed enantioselectively. DFT calculations provide a useful guide in explaining the observed stereochemistry. Depending on reaction conditions, a Michael−Michael ring-closure sequence (MIMIRC) or a net [2 + 4] cycloaddition with the bound naphthalene is also observed, and the corresponding tricyclic molecules can be removed from the metal in high yield.

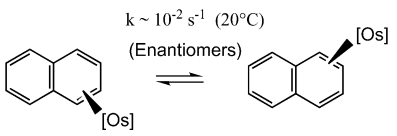
Introduction

The coordination of an arene to a transition metal profoundly affects its chemical reactivity.[1−4] In particular, our interest has been in the ability of π-basic transition-metal complexes to disrupt the aromatic stabilization of arenes through dihapto-coordination. Such a metal promotes the facile addition of electrophiles to the aromatic ring, stabilizing the resulting arenium complex so that it can be combined with a nucleophile.[5,6] An example of this methodology is shown for the pentaammineosmium-(II) complex in Scheme 1.

With the metal bound across C3 and C4, the formaldehyde acetal dimethoxymethane (DMM) adds stereoselectively to C1 in the presence of a Brønsted acid.[7] The naphthalenium ligand resists deprotonation and can be subjected to a nucleophile such as methoxymethyltrimethylsiloxypropene (MMTP) or the conjugate base of dimethyl malonate to form 1,4-dihydronaphthalene complexes in high yields (see Scheme 1). Oxidative removal of the transition metal yields the intact dihydronaphthalene.[7] Even though both the electrophile and nucleophile add to the naphthalene ring system stereoselectively, anti to the osmium, the reaction does not readily lend itself to the preparation of enantio-enriched compounds. While the osmium naphthalene complex is chiral, a resolved sample would readily racemize by either an intrafacial or interfacial linkage isomerization.[6,8]

SCHEME 1





Recently, we disclosed a second generation of rhenium-based dearomatization agents modeled on the pentaam-

(1) Pape, A. R.; Kaliappan, K. P.; Kundig, E. P. *Chem. Rev.* **2000**, *100*, 2917−2940.
(2) Semmelhack, M. F.; Schmalz, H.-G. *Tetrahedron Lett.* **1996**, *37*, 3089.
(3) Semmelhack, M. F. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon Press: Oxford, UK, 1995; Vol. 12, pp 979−1015.
(4) Hegedus, L. S. *Transition Metals in the Synthesis of Complex Organic Molecules*, 2nd ed.; University Science Books: Sausalito, 1999.
(5) Smith, P. L. C.; Mahendra D.; Harman, W. D. *Tetrahedron* **2001**, *57*, 8203−8225.
(6) Harman, W. D. *Chem. Rev.* **1997**, *97*, 1953−1978.
(7) Winemiller, M. D.; Harman, W. D. *J. Am. Chem. Soc.* **1998**, *120*, 7835.

10.1021/jo030318k CCC: $27.50
Published on Web 02/27/2004

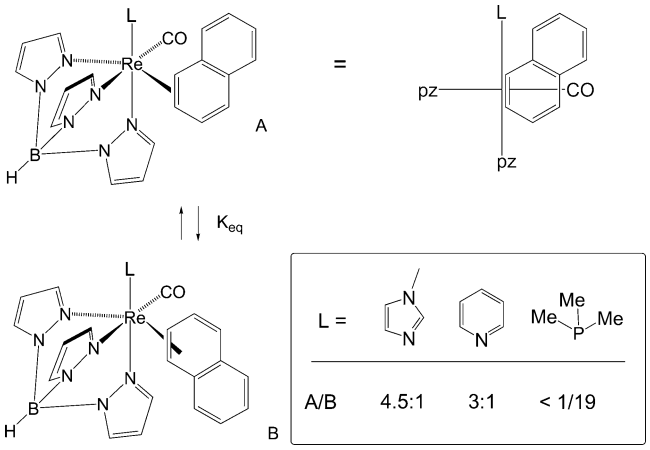
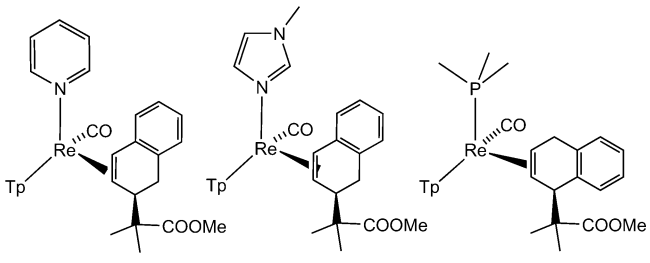


FIGURE 1. Coordination diastereomers of rhenium naphthalene complexes.

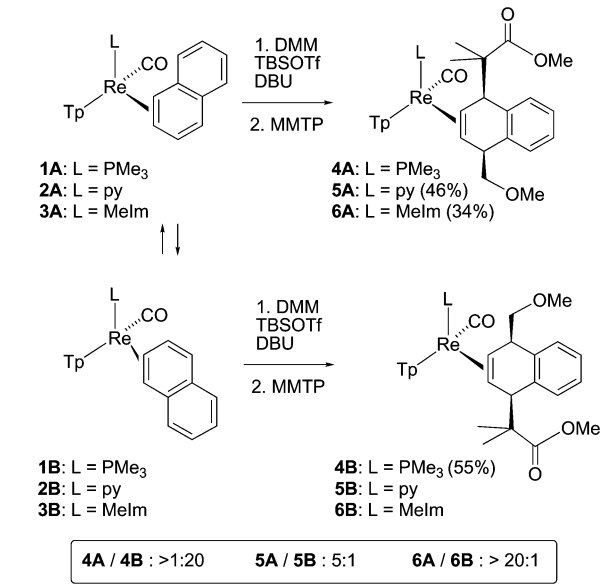
mineosmium system.[9] These complexes take the general form TpRe(CO)(L)(arene), where L can be adjusted to moderate the chemical properties of the metal. Examples for L include *t*-BuNC, PMe_3, py, 1-methylimidazole (MeIm), and ammonia, listed here in order of increased electron donation.[9] In contrast to their osmium predecessor, these rhenium systems feature stereogenic metal centers capable of differentiating between the enantiofaces of naphthalene. In Figure 1, the two coordination diastereomers are shown for three of these systems along with the equilibrium constants describing the preference of these systems for a particular enantioface of naphthalene.[8] In both the observed coordination diastereomers, the naphthalene extends over the CO ligand with the bound C═C bond perpendicular to the Re−CO bond axis. When L is pyridine or MeIm, a diastereomer is favored in which the uncoordinated ring overlaps with that heterocycle, while for L = PMe_3, steric strain between the phosphine and unbound ring of naphthalene requires that the uncoordinated ring extend away from the PMe_3 ligand.[8]

When these naphthalene complexes are protonated, the stereochemical preferences for these complexes become even more pronounced.[10] For all three systems, protonation delivers a single stereoisomer of a 1*H*-naphthalenium complex. When these 1*H*-naphthalenium complexes were treated with the nucleophile MMTP, the pyridine and imidazole systems gave single diastereomers of a 1,2-addition product, while the PMe_3 system delivered a single diastereomer of a 1,4-addition product:



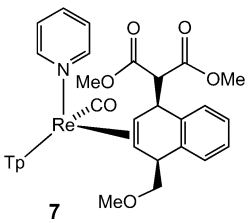
Using the methodology described above with a resolved form of the TpRe(CO)(MeIm) dearomatization agent, we recently prepared a 1,2-dihydronaphthalene in high enantiomeric excess.[11] The present study seeks to apply this new methodology to reactions of naphthalenes with carbon-based electrophiles.

SCHEME 2



Results

Naphthalene complexes **1**−**3** were prepared by established methods from their rhenium(III) precursors, TpRe(L)X_2.[9] While the osmium analogue successfully undergoes reaction with DMM in the presence of a Brønsted acid,[7] for these rhenium systems, analogous conditions result in only protonated products. However, when a mixture of DMM and TBSOTf was combined with the naphthalene complex in the presence of the proton scavenger DBU, addition of the methoxymethyl group to naphthalene resulted. Subsequent addition of the silyl ketene acetal MMPT delivered complexes **4**−**6** in moderate yield (34−55%). In contrast to what was observed for protonation,[10] the addition occurs across C1 and C4, regardless of the nature of L (**4**−**6**). However, judging from COSY and NOE data, the heterocyclic (**5A** and **6A**) and phosphine (**4B**) systems deliver complementary stereochemistries. As seen for protonation, the major isomer of the acetal addition product for the pyridine or imidazole system was derived from the coordination diastereomer A (Scheme 2), while that of the phosphine system originated from the coordination diastereomer B. No other isomer of complexes **4**−**6** was detected in crude reaction mixtures, other than those reported in Scheme 2. In a similar manner, a highly stereoselective 1,4-tandem addition occurred with DMM and dimethyl malonate to generate complexes **7** and **8**.



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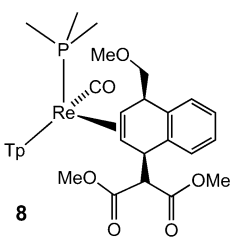
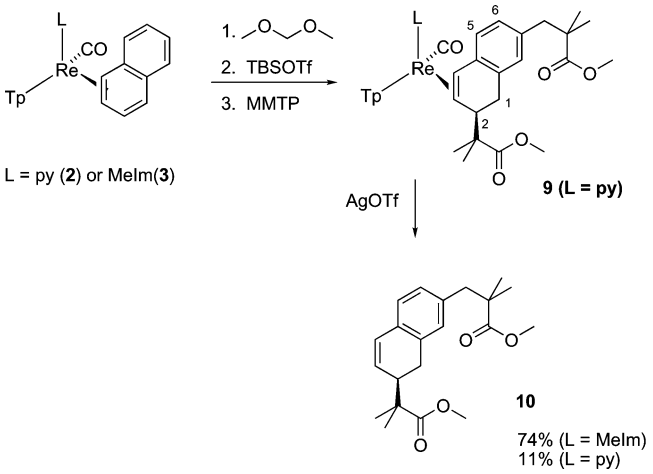


8

(8) Brooks, B. C.; Meiere, S. H.; Friedman, L. A.; Carrig, E. H.; Gunnoe, T. B.; Harman, W. D. *J. Am. Chem. Soc.* **2001**, *123*, 3541−3550.

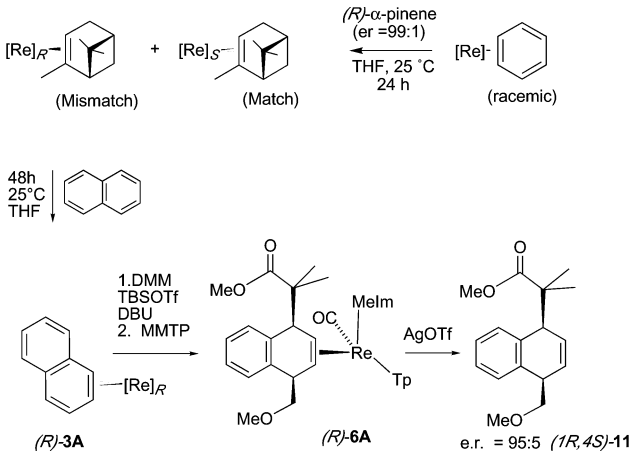
SCHEME 3



ORTEP diagrams for two of these addition products (**6A** and **7**; Supporting Information) confirm the stereochemistry assigned on the basis of earlier NMR studies.[10] In both cases, the bound ring exists in a boatlike conformation with the two carbon substituents occupying pseudoaxial positions, to minimize steric strain with the heterocyclic ligands. When complex **6A** was treated with silver triflate, the free dihydronaphthalene (**11**) was liberated. The overall yield of **11** starting from the naphthalene complex **3A** was 56% (three steps). If the synthesis of compound **11** was attempted via complexes **1**, **2**, or **3** without the addition of the base DBU, major byproducts were formed. In every case, 2-(1,4-dihydronaphthalen-1-yl)-2-methyl-propionic acid methyl ester was formed, the result of protonation at C1 rather than addition of the acetal. However, in the case of **2** or **3**, an additional product, **10**, was produced which can be formed in yields as high as 74% (from **3**).

This new material, a 1,2-dihydronaphthalene, showed two signals at δ 3.63 (3H) and δ 3.61 (3H) in the spectrum, indicating the incorporation of two methoxy groups. The ^{13}C NMR spectrum of **10** revealed the presence of two downfield resonances at δ 177.7 and 177.6 corresponding to the presence of two ester carbonyls. GCMS analysis showed that **10** had a retention time 15 min longer than that of the product resulting from 1,4 addition of dimethoxymethane/MMTP. Isolating and characterizing the corresponding rhenium complex **9** ultimately established the structure of **10**. Treatment of complex **2** and dimethoxymethane with TBSOTf followed by the addition of MMTP yields complex **9** in 14% yield. Extensive analysis by CV, IR, ^{1}H NMR, ^{13}C NMR, COSY, HMQC, 1D NOE experiments, and HMBC confirmed the structure of **9** as that shown in Scheme 3, a product of the addition of one equivalent of DMM and two of MMTP. Most notably, both naphthalene rings have been activated by the metal. In the uncoordinated ring, the new methylene group is located at the β carbon, suggesting that the metal activated the electrophilic addition from the *opposite ring* (see the Discussion).

SCHEME 4



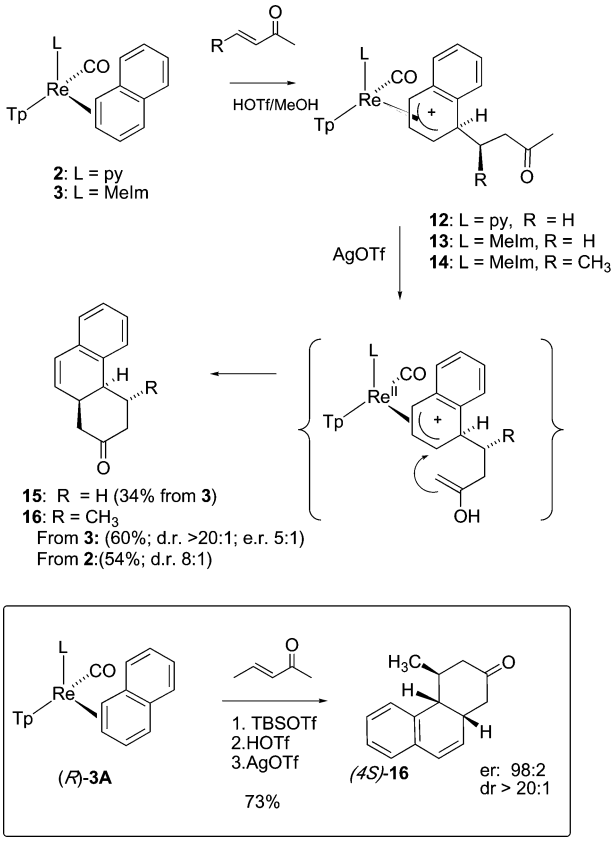
(*R*)-α-Pinene has been used previously to prepare enantioenriched rhenium-arene complexes.[11] Starting with the benzene complex (Scheme 4),[12] the pinene complex was generated in situ as a mixture of two isomers. The mixture was then treated with an excess of naphthalene at which point the mismatched isomer underwent substitution to generate (*R*)-**3A**, the resolved form of the imidazole−naphthalene complex. This mixture of the naphthalene and pinene complexes was then subjected to a mixture of DMM, TBSOTf, and DBU, followed by MMTP to afford (*R*)-**6A**. Oxidative demetalation generated the free dihydronaphthalene (*R*,*S*)-**11** (80% based on available (*R*)-**3A**). Analysis of this material by HPLC using a chiral column (OD-H) determines an er of 95:5 for (*R*,*S*)-**11**.

Reactions with Michael Acceptors

Michael acceptors have been successfully added to osmium−naphthalene complexes at C1. In some cases, the resulting naphthalenium species have undergone intramolecular nucleophilic addition via an enol intermediate to form the phenanthrene ring system.[13] When the pyridine and imidazole variants of TpRe(CO)(L)(naphthalene) (**2**, **3**) were subjected to methyl vinyl ketone and triflic acid in methanol, the 1*H*-naphthalenium species **12** and **13** formed, analogous to that observed for osmium. However, extended periods in methanol failed to bring about the desired ring closure, and eventually decomposition occurred. When the reaction was repeated, and after 1 h, silver triflate was added, the phenanthrene **15** was isolated upon heating (75 °C, 34%). Given that proton NMR data indicated high stereocontrol for the initial electrophilic addition, this reaction was attempted with the resolved rhenium complex. Unfortunately, we were unable to determine the er of the enantioenriched sample of **15**, due to our inability to separate the enantiomers using HPLC. The reaction sequence was repeated substituting 3-penten-2-one for MVK to form **14**. To our surprise, the final product, **16**, which now contains three new stereogenic centers, was isolated as a single stereoisomer (60%, dr > 20:1) where L = MeIm. Where L = py, the dr was 8:1.

(9) Meiere, S. H.; Brooks, B. C.; Gunnoe, T. B.; Carrig, E. H.; Sabat, M.; Harman, W. D. *Organometallics* **2001**, *20*, 3661−3671.
(10) Valahovic, M. T.; Gunnoe, T. B.; Sabat, M.; Harman, W. D. *J. Am. Chem. Soc.* **2002**, *124*, 3309−3315.
(11) Meiere, S. H.; Valahovic, M. T.; Harman, W. D. *J. Am. Chem. Soc.* **2002**, *124*, 15099−15103.
(12) Meiere, S. H.; Brooks, B. C.; Gunnoe, T. B.; Sabat, M.; Harman, W. D. *Organometallics* **2001**, *20*, 1038−1040.
(13) Winemiller, M. D.; Harman, W. D. *J. Org. Chem.* **2000**, *65*, 1249.

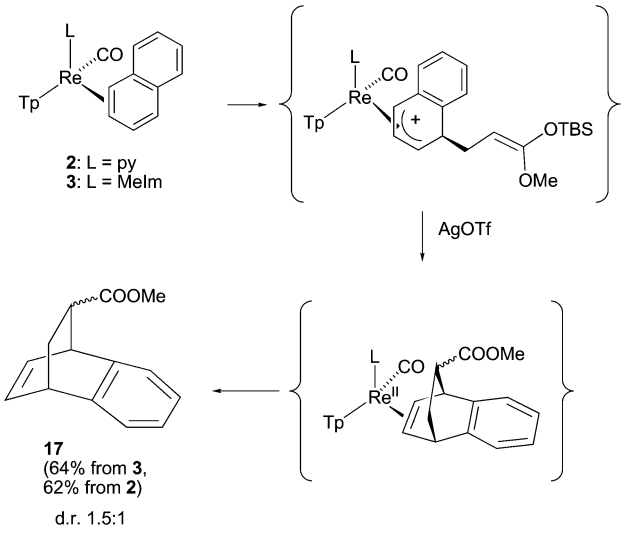
SCHEME 5



Comparing proton coupling data with that reported for a structural analogue[14] led us to assign the relative stereochemistry shown in Scheme 5. Given the high relative stereocontrol and the indication that the initial electrophilic addition was stereoselective, we again attempted to carry out this reaction sequence with resolved rhenium. To a mixture of (*R*)-α-pinene complex and resolved **2**,[10] 3-penten-2-one was added, followed by the addition of silver triflate. Analysis of the isolated organic material, (4*S*)-**16**, using HPLC revealed an er of approximately 5:1. A final modification of this procedure, in which TBSOTf was used to effect the Michael addition and then HOTf was added to form the enol, increased the er to 98:2 (yield: 73% based on available (*R*)-**3A**; see the Discussion).

The pentaammineosmium(II) naphthalene complex failed to undergo reactions with α,*β*-unsaturated esters, amides, or nitriles owing to the lower electrophilicity of these molecules. With the more electron-rich rhenium system, the bound naphthalene of **2** or **3** was expected to be more nucleophilic, and so conjugate addition reaction with these less activated Michael acceptors was explored. A solution of **3** was combined with methyl acrylate and TBSOTf, and the resulting mixture was allowed to stand for 12 h at 20 °C. At this point, silver triflate and pyridine were added and the organic material was extracted and chromatographed. The major product, 3-naphthalen-1-yl-propionic acid methyl ester, was the product of electrophilic substitution and was confirmed

SCHEME 6



by reference to the literature.[15] However, the minor product (**17**), isolated as a 1.5:1 mixture of diastereomers, showed features in the ^{1}H NMR spectrum consistent with a 1,4-dihydronaphthalene core. Further, the presence of singlets at 3.54 and 3.72 ppm along with infrared absorptions at 1731 and 1196 cm^{-1} indicated the presence of a methyl ester. Full NMR analysis utilizing ^{13}C, COSY, HMQC, and HMBC data determined that this new product **17** was a cycloadduct of naphthalene and methyl acrylate (Scheme 6). The yield of **17** was improved to 64% (isolated) by reducing the time of the Michael reaction to 2 h. When the reaction was repeated as above, but with silver triflate immediately added after the addition of methyl acrylate and TBSOTf, only naphthalene was recovered.

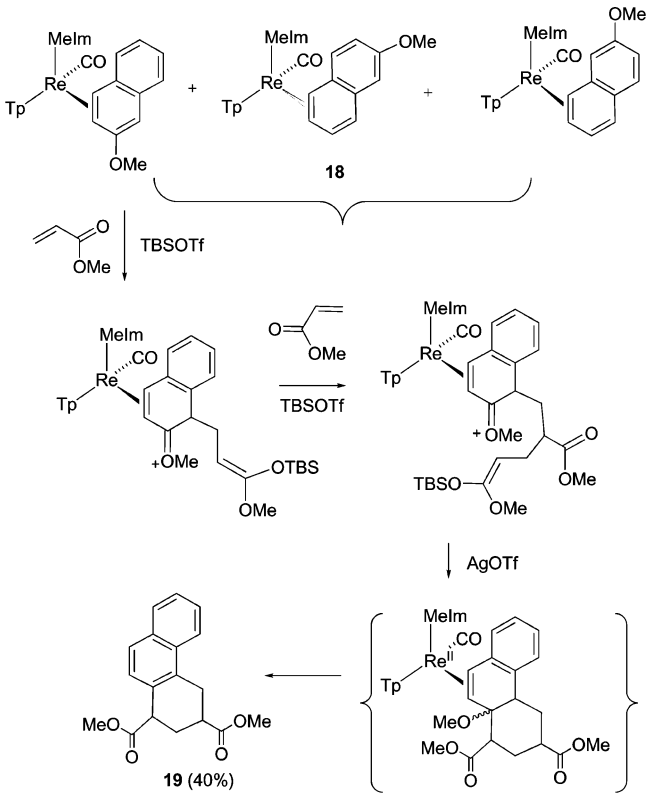
Interestingly, when the reaction was repeated under the optimized conditions, but the oxidation step was skipped, and the inorganic mixture isolated, NMR analysis failed to provide any indication of either a cycloadduct or naphthalenium species. Substituting the methylimidazole-based naphthalene complex **3** for **2**, the reaction sequence again yielded cycloadduct **17**, this time in 62% isolated yield.

We also included in our study the 2-methoxynaphthalene complex TpRe(CO)(MeIm)(η^2-2-methoxynaphthalene), **18**, to explore the *regiochemistry* of a substituted naphthalene bound to rhenium. Complexation in this case is completely unselective giving rise to the 3,4-η^2 as well as 5,6-η^2 and 7,8-η^2 linkage isomers in roughly equal amounts. In addition, the presence of several minor isomers was noted. Complex mixture **18** was treated with methyl acrylate and TMSOTf at −20 °C, and the reaction mixture was allowed to stand for 18 h. Subsequent addition of silver triflate resulted in two new products. One, comprising 11% of the mixture, was methyl 3-(2-methoxy-naphthalen-1-yl)propionate, resulting from electrophilic substitution at C1.[16] The major compound (**19**), however, was the result of a Michael−Michael ring closure reaction sequence (MIMIRC),[17] followed by elimination of methanol. This tetrahydrophenanthrene, iso-

(14) Shukla, U. S.; Barua, N. C.; Chowdhury, P. K.; Sharma, R. P.; Bordoloi, M. *Tetrahedron* **1986**, *42(4)*, 1157.

(15) Tashtoush, H. I.; Sustmann, R. *Chem. Ber.* **1993**, *126*, 1759.
(16) Koelsch, C. F.; Hood, H. E. *J. Org. Chem.* **1955**, *20*, 1282.
(17) Posner, G. H. *Chem. Rev.* **1986**, *86*, 831.

SCHEME 7



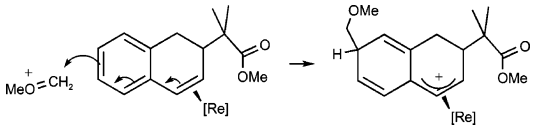
lated in 40% yield as a 2:1 ratio of diastereomers, features for each isomer two methoxy proton resonances, near 3.8 ppm, along with six aromatic protons from 7.2 to 8.0 ppm and a doublet of doublets around 4.1 ppm. The last feature is assigned to the methine next to both the α ring and the carboxylate. A ^{13}C NMR spectrum shows for each diastereomer two CO resonances around 175 ppm and four quaternary carbon resonances around 130 ppm, confirming that 2 equiv of methyl acrylate are involved in the reaction and that the original methoxy group on the naphthalene ring has been eliminated. HRMS data confirm a molecular formula consistent with the structure proposed in Scheme 7. A series of experiments were performed in which the concentrations of methyl acrylate, and that of TBSOTf were varied, as were time and temperature. A value of 40% represents an optimized yield of the MIMIRC product relative to that formed by electrophilic substitution. Unfortunately, other α,*β*-unsaturated esters (e.g., methyl crotonate), nitriles, and amides did not result in tractable products with naphthalene or 2-methoxynaphthalene complexes.

Discussion

Methods that generate functionalized dihydronaphthalenes directly from their aromatic precursors have become valuable tools for synthetic chemists. These include the Birch reduction[18] and addition of nucleophiles to electron-deficient naphthalene systems.[19−21] The use of a transition metal to activate the naphthalene toward electrophilic addition provides a complementary strategy. In comparing the reactivity of these rhenium systems to the first-generation osmium system,[7,13] we find that the naphthalene ligand bound by rhenium is considerably more reactive toward electrophiles. Weaker Brønsted acids effectively protonate the system,[22] and Michael acceptors that are unreactive with osmium (e.g., methyl acrylate) successfully combine with the corresponding rhenium system.

In comparison to the osmium analogues, the resulting rhenium−naphthalenium intermediates are less reactive with nucleophiles. In two of the cyclization reactions described above, nucleophilic addition was not observed unless the oxidant was added, an observation which raises the possibility that the nucleophile adds to a purported Re(II) naphthalenium species rather than the observed rhenium(I)−naphthalenium. For the pentaammineosmium(II) system, the acetal DMM could be added to the naphthalene ring without the addition of base. In fact, a Brønsted acid was used as the promoter. For rhenium, however, the bound naphthalene ring is more basic,[23,24] and deprotonation is not reversible under the given reaction conditions. Thus, it is not surprising that without the addition of DBU the acetal addition is preempted by protonation. The formation of compound **10** deserves further comment. Although the mechanism for this reaction is still under investigation, we are prepared to offer the following observations.

Inspection of the structure of **10** suggests that an electrophilic addition took place at C7 in the uncoordinated ring. The possibility of the metal promoting this reaction at the bound ring and then undergoing an interring isomerization is excluded given that the position of attack is the *β* carbon, rather than the α carbon. This suggests that the metal assisted the electrophilic addition through donation of electron density from the remote ring as shown below. Studies are underway exploring the generality of this apparent example of remote electrophilic substitution reaction for η^2-bound styrenes.



The most significant advantage in moving to rhenium is the presence of a stereogenic metal center and its ability to influence the stereochemistry of the organic ligand. To facilitate our interpretation of the origins of the stereochemistry in the naphthalene reactions we embarked on a series of density functional theory (DFT) calculations. According to Davidson,[25] "computational transition metal chemistry today is almost synonymous with DFT for medium size molecules". Our experience

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(19) Shimano, M.; Meyers, A. I. *J. Org. Chem.* **1995**, *60*, 7445.
(20) Meyers, A. I.; Roth, G. P.; Hoyer, D.; Barner, B. A.; Laucher, D. *J. Am. Chem. Soc.* **1988**, *110*, 4611−4624.
(21) Plunian, B.; Mortier, J.; Vaultier, M. *J. Org. Chem.* **1996**, *61*, 5206.
(22) Keane, J. M.; Chordia, M. D.; Mocella, C. J.; Sabat, M.; Trindle, C. O.; Harman, W. D. Submitted for publication.
(23) For example, the conjugate acid of naphthalene complex **3** has been estimated to have a pK_a of approximately 1 while that for pentaammineosmium(II) is −8.2.
(24) Winemiller, W. D.; Kopach, M. E.; Harman, W. D. *J. Am. Chem. Soc.* **1997**, *119*, 2096.
(25) Davidson, E. *Chem. Rev.* **2000**, *21*, 1532.

in calculating energies and structures for pentaammineosmium(II) systems[26] and TpRe(CO)(L) systems[27] has been that geometries are well represented by schemes using a local density functional with a pseudopotential representation of the heavy metal and a mixed basis including the pseudopotentials associated basis on the metal and a 6-31G* Gaussian basis on other atoms. More realistic binding energies of aromatic species with pentaammineosmium(II) and the Re agents are obtained with the gradient-corrected B3LYP functional. Since it seems plausible that either functional would describe the energy differences at issue here, we chose the less costly local functional.[28,29]

Figure 2 shows the four lowest energy isomers for naphthalene (**A**−**D**), as bound to the TpRe(CO)(MeIm) fragment. An additional set of rotationally related isomers, in which the bound C=C fragment lies parallel to the Re−CO bond axis, is estimated to be 10−20 kcal/mol higher in energy and was not considered further. Energies for each isomer are expressed relative to that of isomer **A**, which not only is calculated to be the lowest energy orientation of the naphthalene, but is shown experimentally to be so judging from solution (NOE) and solid state (X-ray) data. The next lowest isomer, **B**, is related to **A** through an intrafacial isomerization (ring-walk), and is experimentally observed by ^{1}H NMR to be the minor isomer. Judging from ^{1}H NMR data, the difference in free energy between **B** and **A** is between one and two kcal/mol. Interestingly, this minor isomer (**B**) for both the pyridine and methylimidazole systems shows severely broadened proton NMR features at 20 °C, while isomer **A** is well defined. This is readily explained by considering isomers **C** and **D**, related by rotation to **B** and **A**, respectively. Whereas the major isomer (**A**) is separated by 7 kcal/mol from it rotamer, isomer C is separated by only 1.7 kcal/mol. With an approximate rotational barrier for these systems experimentally determined to be about 12 kcal/mol, rotamers **C** and **D** are both kinetically accessible at 20 °C, but only the former is significantly populated.

The regio- and stereochemistry for the electrophilic addition to the naphthalene ligand of the methylimidazole system appears to be most influenced simply by the orientation of the naphthalene in the dominant isomer of **3** (**A**). Calculations support the notion that isomer **F** is significantly more stable than isomer **G**. Yet, with the relatively large kinetic barrier for the ring walk that interconverts isomer **A** and **B**,[8] it is surprising that the diastereomer ratio for naphthalenium **F**:**G** is greater than 4.5:1 (the equilibrium ratio of naphthalene complexes **A**:**B**).[22] Furthermore, the high er's observed for the phenanthrenone (4*S*)-**16** (98:2) and the 1,4-dihydronaphthalene (1*R*,4*S*)-**11** (95:5) are inconsistent with the ratio of **A**:**B**. The high stereoselectivity observed for the naphthalenium **F** (>20:1) has been shown in a separate study to be kinetic in origin, arising from a high preference for the **3A** isomer *in the solid state*.[30] To illustrate this phenomenon, if the naphthalene complex is warmed in acetonitrile (5 min, 60 °C) prior to protonation, then cooled, naphthalenium isomers **F** and **H** are produced in a 3.5:1 ratio. Exclusive formation of naphthalenium **F** occurs *only* if it is prepared from a *freshly dissolved* sample of **3**. The pyridine system (**2**) has a lower barrier to ring-walk isomerization by about 2 kcal/mol.[8] In addition, it is expected to be somewhat less nucleophilic than its methylimidazole analogue **3**. The pyridine system also displays solid phase selectivity for one coordination diastereomer.[25] However, in the synthesis of **5**, the naphthalene complex **2** partially equilibrates prior to the addition of the electrophile DMM. Conse-

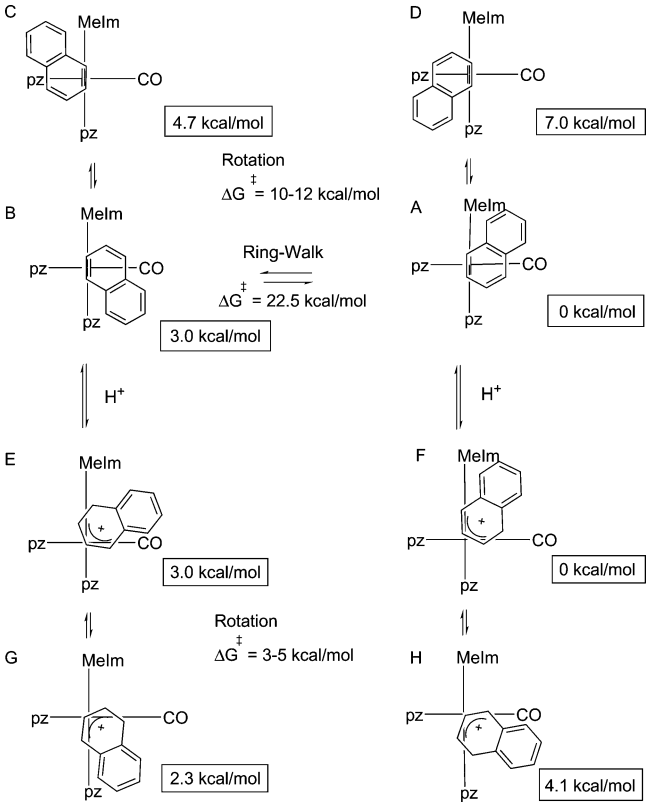

FIGURE 2. Relative energies of naphthalene and naphthalenium isomers based on DFT calculations. pz = pyrazole ring. The perspective is from the arene ligand to the rhenium along the arene−metal bond (see Figure 1).

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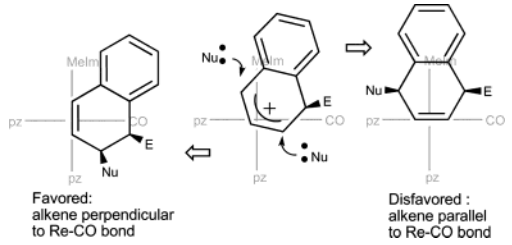
quently, the dr observed for **5** (5:1) is considerably lower than for **6** (>20:1), even though both of these ratios are higher than the corresponding ratios for their naphthalene complex precursors (**2** and **3**).

The lowest energy transition state for nucleophilic addition is expected to show a geometry that partially resembles the geometry of the product, where the coordinated double bond is oriented perpendicular to the CO π acid:

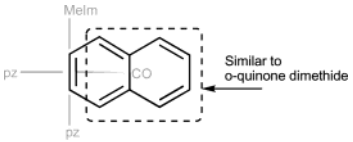


Given that experiment and calculation indicate that isomer **F** is the dominant form of naphthalenium for the imidazole system, nucleophilic addition at C2 would place the coordinated double bond of the product in the correct orientation. Indeed, a 1,2-tandem addition is heavily favored for the imidazole and pyridine systems (as opposed to a 1,4-addition), provided that the electrophile added at C1 is a proton. In the formation of **6**, as well as pyridine complexes **5** and **7**, the steric interaction between the methoxymethyl group and the incoming nucleophile is apparently sufficiently large that addition occurs at C4 instead, presumably through isomer **H**. Note that while calculations indicate that interconversion between **F** and **H** is facile, isomerization of one of these forms to **E** or **G** is shown by NMR data to be comparatively slow ($t_{1/2}$ > 1 h at 20 °C).

The PMe_3 system provides an interesting contrast to the pyridine and imidazole systems. Here, steric interactions between the PMe_3 and naphthalene make the coordination diastereomer **1B** the dominant form in solution. This leads to naphthalenium rotamers analogous to **E** and **G**. Again invoking steric interactions, the nucleophilic addition occurs at C4. However, note that in the dihydronaphthalene product, the positions of the nucleophile and electrophile are reversed compared to those in the other two systems.

The acid-catalyzed annulation that generated the tetrahydrophenanthrenones **15** and **16** has been demonstrated for the pentaammineosmium(II) complex of naphthalene, but only for the racemic mixture.[13] Using a resolved rhenium species(*R*)-**3A**,[11] the hexahydrophenanthrene **16**, which contains three new stereocenters, was generated in >20:1 dr and as high as a 5:1 ratio of enantiomers. Given that the naphthalenium intermediate **14** was prepared with dr >20:1, the loss of stereocontrol must occur after this step. In a related study, we have found that extended exposure to Brønsted acids epimerizes the rhenium stereocenter and this is likely the cause of the marginalized enantiomer ratio in **16.** The ring-closure step requires extended exposure to HOTf/MeOH (e.g., in this case 0.12 M), during which the Michael reaction apparently can reverse to reform the naphthalene complex **3**, and epimerization at rhenium can occur. By promoting the Michael addition with TBSOTf, exposure to Brønsted acid is avoided until after the first two stereocenters are set, and consequently the er of the phenanthrenone product is not degraded (er = 98:2).

Having access to an ester Michael acceptor (methyl acrylate) makes it possible to have an internal silyl ketene acetal as the potential nucleophile. In the case of naphthalene complexes **2** and **3**, this results in a ring closure at C4, providing the tricyclo[6.2.2.0]dodecatetraene ring system. While naphthalene is known to undergo photodimerization and [4 + 4] photocycloaddition with pyridones[31] and [4 + 2] cycloaddition with very electron-deficient alkynes,[32,33] the only example for a Diels−Alder reaction with alkenes was reported for maleic anhydride under refluxing with concentrated H_2SO_4.[34] The central issue in considering the mechanism for this reaction is whether it is a concerted reaction (i.e., Diels−Alder) or a Michael reaction followed by nucleophilic addition. A hypothetical 2,3-η^2-naphthalene complex was proposed as an intermediate in the intrafacial isomerization of complex **3**.[11] Due to the donation of the metal fragment, the uncoordinated part of the ligand would be similar to an *o*-quinone dimethide, a reactive intermediate for Diels−Alder reactions:[35]



However, combining complex **3** with the more reactive dienophile *N*-methyl maleimide in absence of a Lewis acid fails to show any reaction even though such a Diels−Alder reaction does occur for the benzene complex.[36] In the presence of TBSOTf, intractable materials result. Furthermore, if the reaction were concerted, isolation of the bound cycloadduct should be possible, yet we have been unable to do this. DFT calculations indicate that the 2,3-η^2 naphthalene complex intermediate shown above has an energy 16.6 kcal/mol above that of **A** (Figure 2). Taken together, these data make a concerted reaction mechanism unlikely. Rather, the stepwise mechanism shown in Scheme 6 is thought to be responsible for the formation of **17**. Given our inability to isolate the metal-bound cycloadduct, we assume that the nucleophile adds only *after* the rhenium is oxidized with silver triflate. An explanation for the inability of α,β-unsaturated ketones to undergo this cyclization reaction is found in the weaker nucleophilic character of the silyl enol ether compared to a silyl ketene acetal.

The silyl ketene acetal generated from the reaction of methyl acrylate and an η^2-naphthalene has access to another interesting reaction when a methoxy group is located at the C2 position of the naphthalene ring (**18**). Donation of π electron density from the methoxy oxygen

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apparently stabilizes the 1*H*-naphthalenium such that the internal nucleophilic addition to C4 (see Scheme 6) no longer occurs. Instead, the silyl ketene acetal attacks another methyl acrylate molecule and the new silyl ketene acetal that forms can close at C2 generating a new six-membered ring. Subsequent elimination of methanol generates the tetrahydrophenanthrene product **19**.

Conclusions

Access to a variety of novel organic transformations for naphthalene was demonstrated some time ago using the pentaammineosmium(II) dearomatization agent. The replacement of this first generation dearomatization agent by the TpRe(CO)(L) systems provides several important new features to this methodology. The control of relative stereochemistry is influenced by the choice of ligand L, and control of absolute stereochemistry can be achieved through the use of an α-pinene precursor complex. Using the more electron-rich pyridine and imidazole systems, the naphthalene ligand is more nucleophilic and reacts with methyl acrylate to give two novel cyclization reactions, a 4 + 2 cyclization and a 2 + 2 + 2 cyclization, which were not available with pentaammineosmium(II). However, by stabilizing the naphthalenium intermediate generated from an electrophilic addition, the rhenium deactivates subsequent reactions with nucleophiles. In at least two cases, the one-electron oxidation of the metal is required to consummate the nucleophilic addition.

Experimental Section

Reagents. All solvents and reagents were purified via distillation under nitrogen or passage through an activated alumina column under nitrogen. The syntheses of naphthalene complexes **1**−**3**[9] and the pinene complex[11] were previously reported. The compounds **15**[13] and **11**[7] were also previously reported. TpRe(CO)(MeIm)(η^2-2-methoxynaphthalene) (**18**) was synthesized via ligand substitution of TpRe(CO)(MeIm)(η^2-benzene) with excess 2-methoxynaphthalene in THF overnight, as earlier described.[9]

TpRe(CO)(PMe_3)(2,3-η^2-(2-(4-methoxymethyl-1,4-dihydronaphthalen-1-yl)-2-methylpropionic Acid Methyl Ester)) (4). An acetonitrile solution (∼1 mL) of TpRe(CO)(PMe_3)(η^2-naphthalene) (106 mg, 0.168 mmol), dimethoxymethane (57 mg, 0.75 mmol), and 1,8-diazabicyclco[5.4.0]undec-7-ene (DBU) (10 mg, 0.07 mmol) was treated with an acetonitrile solution (∼1 mL) of *tert*-butyldimethylsilyl trifluoromethanesulfonate (81 mg, 0.31 mmol). After 5 min of stirring, the reaction was treated with 1-methoxy-2-methyl-1-trimethylsiloxypropene (MMTP) (160 mg, 0.918 mmol). After 10 min of stirring, 2,6-lutidene (42 mg, 0.392 mmol) was added and then the reaction was subjected to column chromatography (1:1, hexanes/ether as eluent). The solvent was removed under reduced pressure and the brown residue was subjected to preparatory TLC with a 3:2 mixture of hexanes/ethyl acetate. The desired band was removed and then washed with acetone (∼25 mL). The acetone was removed under reduced pressure to yield 72 mg (55% yield) of a white solid: CV (MeCN) (TBAH) (100mV/s) $E_{1/2}$ = 560 mV (NHE); IR (HATR, glaze) ν_{BH} = 2473 cm^{-1}, ν_{CO} = 1820, 1725 cm^{-1}; ^{1}H NMR (500 MHz) (acetone-d_6) (22 °C) δ 7.84 (1H, d, ^3J = 2.2 Hz (^{CO}Tp-H5)), 7.79 (1H, d, ^3J = 1.6 Hz (^{P}Tp-H3)), 7.77 (1H, d, ^3J = 1.6 Hz (^{N}Tp-H3)), 7.76 (1H, d, ^3J = 2.6 Hz (^{P}Tp-H5)), 7.74 (1H, d, ^3J = 2.6 Hz (^{N}Tp-C5)), 7.46 (1H, d, ^3J = 1.9 Hz (^{CO}Tp-H3)), 7.23 (1H, dd, ^3J = 7.1 Hz, ^4J = 1.6 Hz (H8)), 7.18 (1H, dd, ^3J = 7.0 Hz, ^4J = 1.9 Hz (H5)), 7.09 (1H, ddd, ^3J = 7.1 Hz, 7.1, ^4J = 1.6 Hz (H6)), 7.06 (1H, ddd, ^3J = 7.1 Hz, 7.1, ^4J = 1.9 Hz (H7)), 6.31 (1H, dd, ^3J = 2.2, 2.2 Hz (^{CO}Tp-H4)), 6.23 (1H, dd, ^3J = 2.2, 2.2 Hz (^{P}Tp-H4)), 6.13 (1H, dd, ^3J = 2.2, 2.2 Hz (^{N}Tp-H4)), 4.50 (1H, br d (BH)), 4.23 (1H, br s, (H4)), 4.00 (1H, dd, ^3J = 6.7, 6.4 Hz (H1)), 3.89 (1H, dd, ^2J = 9.0 Hz, ^3J = 7.7 Hz (OCH_2)), 3.80 (1H, dd, ^2J = 9.0 Hz, ^3J = 5.8 Hz (OCH_2)), 3.44 (3H, s (OMe)), 3.35 (1H, dd, ^{PH}J = 13.8 Hz, ^3J = 9.9 Hz (H2)), 2.94 (3H, s (OMe)), 1.41 (1H, br d, ^3J = 9.8 Hz (H3)), 1.25 (9H, d, ^{PH}J = 8.5 Hz (PMe_3)), 1.19 (3H, s (*gem*-Me)), 0.94 (3H, s (gem-Me)); ^{13}C NMR(125 MHz) (acetone-d_6) (22 °C) δ 198.4 (C≡O), 178.5 (C═O), 146.1 (^{P}Tp-C5), 145.0 (^{N}Tp-C3), 140.3 (C9 or C10), 139.7 (^{CO}Tp-C3), 136.7 (^{CO}Tp-C5), 136.0 (^{N}Tp-C5), 135.4 (^{P}Tp-C3), 131.5 (C5), 131.4 (C8), 126.9 (C6), 125.7 (C7), 106.6 (^{CO}Tp-C4), 106.5 (^{N}Tp-C4), 106.2 (^{P}Tp-C4), 84.7 (OCH_2), 58.9 (OMe), 52.0 (C3), 50.9 (OMe), 50.1 (C4), 48.6 (C1), 48.0 (^{PC}J = 10 Hz (C2)), 25.9 (*gem*-Me), 22.8 (*gem*-Me), 15.7 (^{PC}J = 31 Hz (PMe_3)).

TpRe(CO)(pyridine)(2,3-η^2-(2-(4-methoxymethyl-1,4-dihydro-naphthalen-1-yl)-2-methylpropionic Acid Methyl Ester)) (5). An acetonitrile solution (∼1 mL) of TpRe(CO)(pyridine)(η^2-naphthalene) (72 mg, 0.11 mmol), dimethoxymethane (41 mg, 0.54), and 1,8-bis(dimethylamino)naphthalene (38 mg, 0.18 mmol) was cooled to −40 °C and treated with a chilled (−40 °C) acetonitrile solution (∼1 mL) of *tert*-butyldimethylsilyl trifluoromethanesulfonate (56 mg, 0.21 mmol). After 60 min, the reaction was treated with a chilled (−40 °C) acetonitrile solution of 1-methoxy-2-methyl-1-trimethylsiloxypropene (MMTP) (297 mg, 1.70 mmol) and then warmed to room temperature. After 60 min of stirring, 2,6-lutidene (227 mg, 2.11 mmol) was added, and the reaction was subjected to column chromatography (1:1, hexanes/ether as eluent). The solvent was removed under reduced pressure, and the yellow residue was subjected to preparatory TLC with a 3:1 mixture of hexanes/ethyl acetate. The desired band was removed and washed with acetone (∼25 mL). The acetone was removed under reduced pressure to yield the product with a 5:1 dr (79 mg, 46%) as a yellow solid: CV (MeCN) (TBAH) (100mV/s) $E_{1/2}$ = 230 mV (NHE); IR (HATR, glaze) ν_{BH} = 2476 cm^{-1}, ν_{CO} = 1810, 1721 cm^{-1}. Major diastereomer: ^{1}H NMR (500 MHz) (acetone-d_6) (−10 °C) δ 8.87 (1H, d, ^3J = 5.5 Hz (*o*-pyr)), 8.01 (1H, d, ^3J = 1.9 Hz (^{CO}Tp-H5)), 7.94 (1H, d, ^3J = 1.6 Hz (Tp-H3)), 7.90 (1H, t, ^3J = 7.7 Hz (*p*-pyr)), 7.82 (1H, d, ^3J = 2.2 Hz (Tp-H5)), 7.76 (1H, d, ^3J = 2.6 Hz (Tp-H5)), 7.71 (1H, d, ^3J = 4.2 Hz (*o*-pyr)), 7.57 (1H, d, ^3J = 1.6 Hz (^{CO}Tp-H3)), 7.53 (1H, dd, ^3J = 6.4, 6.4 Hz (*m*-pyr)), 7.35 (1H, d, ^3J = 7.4 Hz (H8)), 7.14 (3H, m, (unbound ring)), 7.10 (1H, m, (*m*-pyr)), 6.95 (1H, d, ^3J = 1.6 Hz (Tp-H3)), 6.47 (1H, dd, ^3J = 1.9, 1.9 Hz (^{CO}Tp-H4)), 6.24 (1H, dd, ^3J = 2.2, 2.2 Hz (Tp-H4)), 6.01 (1H, dd, ^3J = 1.9, 1.9 Hz (Tp-H4)), 4.57 (1H, br d (BH)), 4.17 (1H, dd, ^3J = 6.7, 6.7 Hz (H1)), 3.79 (1H, dd, ^2J = 8.7 Hz, ^3J = 5.4 Hz (OCH_2)), 3.61 (1H, dd, ^2J = 8.7 Hz, ^3J = 5.4 Hz (OCH_2)), 3.59 (1H, s (H4)), 3.29 (3H, s, (OMe)), 3.19 (3H, s, (OMe)), 2.82 (1H, d, ^3J = 9.6 Hz (H2)), 2.60 (1H, d, ^3J = 9.9 Hz (H3)), 1.13 (3H, s, (*gem*-Me)), 0.97 (3H, s, (*gem*-Me)); ^{13}C NMR (125 MHz) (acetone-d_6) (−10 °C) δ 198.0 (C≡O), 178.8 (C═O), 159.4 (*o*-pyr), 152.8 (*o*-pyr), 145.0 (Tp-C3), 142.9 (Tp-C3), 140.1, 139.2 (^{CO}Tp-C3), 137.0 (^{CO}Tp-H5), 136.7 (Tp-C5), 136.6 (*p*-pyr), 135.5 (Tp-C5), 131.8 (unbound ring), 131.4 (C8), 126.8 (unbound ring), 126.7 (*m*-pyr), 125.7 (unbound ring), 125.6 (*m*-pyr), 107.2 (^{CO}Tp-C4), 106.8 (Tp-C4), 106.6 (Tp-C4), 83.8 (OCH_2), 58.9 (C3), 58.3 (OMe), 54.9 (C2), 52.0 (OMe), 50.9 (quaternary C), 50.5 (C4), 46.1 (C1), 25.8 (*gem*-Me), 22.8 (*gem*-Me). Anal. Calcd for $C_{32}H_{37}N_7O_4BRe$: C, 49.24; H, 4.77; N, 12.56. Found: C, 49.24; H, 4.81; N, 12.56.

TpRe(CO)(MeIm)(2,3-η^2-(2-(4-methoxymethyl-1,4-dihydro-naphthalen-1-yl)-2-methyl Propionic Acid Methyl Ester) (6). An acetonitrile solution (1 mL) of TpRe(CO)(MeIm)(η^2-naphthalene) (102 mg, 0.160 mmol), dimethoxymethane (51 mg, 0.67 mmol), and 1,8-diazabicyclco[5.4.0]undec-7-ene (DBU) (20 mg, 0.13 mmol) was treated with an acetonitrile solution (1 mL) of *tert*-butyldimethylsilyl trifluoromethanesulfonate (81 mg, 0.31 mmol). After 5 min, the reaction was treated with an acetonitrile solution of 1-methoxy-2-methyl-1-trimethylsiloxypropene (MMTP) (177 mg, 1.01 mmol). After 15 min of

stirring, 2,6-lutidene (47 mg, 0.44 mmol) was added, and then the reaction was subjected to column chromatography with 3:1 hexanes/ether as eluent. The solvent was removed under reduced pressure, and the leftover brown residue was subjected to preparatory TLC with a 3:1 mixture of hexanes/ethyl acetate. The desired band was removed and washed with acetone (∼25 mL). The acetone was removed under reduced pressure to yield 79 mg (34% yield) of a yellow solid. X-ray quality crystals were obtained by layering hexanes on top of a saturated THF solution: CV (MeCN) (TBAH) (100mV/s) $E_{p,a}$ = 180 mV (NHE); IR (HATR, glaze) ν_{BH} = 2487 cm^{-1}, ν_{CO} = 1796, 1719 cm^{-1}; ^{1}H NMR (500 MHz) (acetone-d_6) (22 °C) δ 7.90 (1H, d, ^3J = 1.9 Hz (^{CO}Tp-H5)), 7.83 (1H, d, ^3J = 1.8 Hz (^{Im}Tp-H3)), 7.76 (1H, d, ^3J = 2.2 Hz (^{Im}Tp-H5)), 7.64 (1H, d, ^3J = 2.2 Hz (^{N}Tp-H5)), 7.61 (1H, m (MeIm)), 7.60 (1H, d (^{CO}Tp-H3)), 7.28 (1H, dd, ^3J = 1.9 Hz, ^4J = 1.6 Hz (H8)), 7.13 (1H, d, ^3J = 1.6 Hz (^{N}Tp-H3)), 7.08 (3H, m (H5, H7, and MeIm)), 7.03 (1H, ddd, ^3J = 7.7, 6.4 Hz, ^4J = 1.6 Hz (H6)), 6.59 (1H, br s, (MeIm)), 6.39 (1H, dd, ^3J = 2.2, 1.9 Hz (^{CO}Tp-H4)), 6.19 (1H, dd, ^3J = 2.2, 2.2 Hz (^{Im}Tp-H4)), 5.97 (1H, dd, ^3J = 2.2, 1.9 Hz (^{N}Tp-H4)), 4.56 (1H, br d (BH)), 4.00 (1H, dd, ^3J = 6.7, 5.8 Hz (H1)), 3.88 (3H, s (Me)), 3.75 (1H, dd, ^2J = 9.0 Hz, ^3J = 5.8 Hz (OCH_2)), 3.69 (1H, s (H4)), 3.57 (1H, dd, ^2J = 9.0 Hz, ^3J = 8.0 Hz (OCH_2), 3.49 (3H, s (OMe)), 3.17 (3H, s (OMe)), 2.50 (1H, d, ^3J = 9.6 Hz (H3)), 2.44 (1H, d, ^3J = 9.6 Hz (H2)), 1.15 Hz (3H, s (*gem*-Me)), 1.01 (3H, s (*gem*-Me)); ^{13}C NMR(125 MHz) (acetone-d_6) (22 °C) δ 179.2 (C═O), 145.1, 142.8, 142.0, 140.4, 139.5 (MeIm), 139.5, 136.9, 136.6, 136.4, 134.8, 132.2, 131.3 (C8), 126.5, 125.4 (C6), 122.4, 106.6 (^{CO}Tp-C4), 106.4 (^{Im}Tp-C4), 106.2 (^{N}Tp-C4), 84.4 (OCH_2), 58.3 (OMe), 55.8 (C3), 53.5 (C2), 52.5 (C4), 51.8 (OMe), 45.9 (C1), 25.6 (*gem*-Me), 23.6 (*gem*-Me).

TpRe(CO)(pyridine)(2,3-η^2-(2-(4-methoxymethyl-1,4-dihydronaphthalen-1-yl)malonic Acid Dimethyl Ester)) (7). An acetonitrile solution (∼1 mL) of TpRe(CO)(pyridine)-(η^2-naphthalene) (102 mg, 0.161 mmol), dimethoxymethane (51 mg, 0.67), and 1,8-diazabicyclco[5.4.0]undec-7-ene (DBU) (18 mg, 0.12 mmol) was treated with *tert*-butyldimethylsilyl trifluoromethanesulfonate (72 mg, 0.28 mmol). After 5 min of stirring, the reaction was treated with a premixed acetonitrile solution of dimethyl malonate (128 mg, 0.968 mmol) and DBU (88 mg, 0.578 mmol). After 15 min of stirring, the reaction was added to 50 mL of stirring ether and filtered through a 1 in. plug of silica in a 30 mL medium porosity frit. The solvent was removed under reduced pressure, and the yellow residue was subjected to preparatory TLC with a 3:1 mixture of hexanes/ethyl acetate. The desired band was removed and washed with acetone (∼25 mL). The acetone was removed under reduced pressure to yield 41 mg (32% yield) of a yellow solid: CV (MeCN) (TBAH) (100mV/s) $E_{1/2}$ = 290 mV (NHE); IR (HATR, glaze) ν_{BH} = 2485 cm^{-1}, ν_{CO} = 1811, 1749, 1731 cm^{-1}; ^{1}H NMR (500 MHz) (acetone-d_6) (−10 °C) δ 8.00 (1H, d, ^3J = 2.2 Hz (^{CO}Tp-H5)), 7.93 (1H, dd, ^3J = 7.7, 7.4 Hz), 7.83 (1H, d, ^3J = 1.6 Hz (^{Py}Tp-H3)), 7.82 (1H, d, ^3J = 2.2 Hz (^{Py}Tp-H5)), 7.77 (1H, d, ^3J = 2.2 Hz (^{N}Tp-H5)), 7.59 (1H, d, ^3J = 1.6 Hz (^{CO}Tp-H3)), 7.30 (1H, d, ^3J = 7.4 Hz (H8)), 7.15 (1H, ddd, ^3J = 7.4, 7.4 Hz, ^4J = 1.3 Hz (H7)), 7.10 (1H, ddd, ^3J = 7.4, 7.4 Hz, ^4J = 1.3 Hz (H6)), 7.01 (1H, d, ^3J = 7.4 Hz (H5)), 6.97 (1H, d, ^3J = 1.9 Hz (^{N}Tp-H3)), 6.43 (1H, dd, ^3J = 2.2, 1.9 Hz (^{CO}Tp-H4)), 6.25 (1H, dd, ^3J = 2.2, 2.2 Hz (^{Py}Tp-H4)), 6.02 (1H, dd, ^3J = 2.2, 2.2 Hz (^{N}Tp-H4)), 4.59 (1H, br d (BH)), 3.89 (1H, dd, ^3J = 6.7, 6.7 Hz (H1)), 3.76 (1H, d, ^3J = 10.9 Hz (H_X)), 3.73 (1H, d, ^3J = 11.2 Hz (H4)), 3.65 (1H, dd, ^2J = 8.7 Hz, ^3J = 5.8 Hz (OCH_2)), 3.53 (1H, s (OCH_2)), 3.52 (3H, s, (OMe)), 3.34 (3H, s, (OMe)), 3.19 (3H, s, (OMe)), 2.88 (1H, d, ^3J = 9.6 Hz (H3)), 2.67 (1H, d, ^3J = 9.3 Hz (H2)); ^{13}C NMR (125 MHz) (acetone-d_6) (−10 °C) δ 197.7 (C≡O), 169.5 and 169.2 (C═O), 145.5 (^{Py}Tp-C3), 142.8 (^{N}Tp-C3), 139.9 (C9 or C10), 139.4 (^{CO}Tp-C3), 136.9 (^{CO}Tp-C5), 136.8 (C9 or C10), 136.5 (^{Py}Tp-C5), 135.6 (^{N}Tp-C5), 131.2 (C8), 129.9 (C5), 127.4 (C7), 126.6 (C6), 107.2 (^{CO}Tp-C4), 106.9 (^{Py}Tp-C4), 106.8 (^{N}Tp-C4), 83.8 (OCH_2), 65.8 (C_X), 60.6 (C3), 58.5 (OMe), 54.2 (C2), 52.4 (OMe), 52.0 (OMe), 46.8 (C1), 45.4 (C4).

TpRe(CO)(PMe_3)(2,3-η^2-(2-(4-methoxymethyl-1,4-dihydronaphthalen-1-yl)malonic Acid Dimethyl Ester)) (8). An acetonitrile solution (∼1 mL) of TpRe(CO)(PMe_3)(η^2-naphthalene) (72 mg, 0.11 mmol), dimethoxymethane (41 mg, 0.54 mmol), and 1,8-diazabicyclco[5.4.0]undec-7-ene (DBU) (14 mg, 0.09 mmol) was treated with *tert*-butyldimethylsilyl trifluoromethanesulfonate (56 mg, 0.21 mmol). After 5 min of stirring, the reaction was treated with a premixed acetonitrile solution of dimethyl malonate (100 mg, 0.756 mmol) and DBU (82 mg, 0.54 mmol). After 15 min of stirring, 2,6-lutidene (42 mg, 0.39 mmol) was added, and the reaction was subjected to column chromatography (1:1 hexanes/ether as eluent). The solvent was removed under reduced pressure, and the brown residue was subjected to preparatory TLC with a 5:1 mixture of hexanes/ethyl acetate. The desired band was removed and washed with acetone (∼25 mL). The acetone was removed under reduced pressure to yield 28 mg (30% yield) of a white solid: CV (MeCN) (TBAH) (100 mV/s) $E_{1/2}$ = 410 mV (NHE); IR (HATR, glaze) ν_{BH} = 2471 cm^{-1}, ν_{CO} = 1826, 1756, 1732 cm^{-1}; ^{1}H NMR (500 MHz) (acetone-d_6) (22 °C) δ 7.89 (1H, d, ^3J = 1.6 Hz (^{P}Tp-H3)), 7.84 (1H, d, ^3J = 2.6 Hz (^{CO}Tp-H5)), 7.79 (1H, d, ^3J = 1.9 Hz (^{N}Tp-H3)), 7.76 (1H, d, ^3J = 2.2 Hz (^{N}Tp-H5)), 7.72 (1H, d, ^3J = 2.6 Hz (^{P}Tp-H5)), 7.48 (1H, d, ^3J = 1.9 Hz (^{CO}Tp-H3)), 7.18 (1H, d, ^3J = 7.7 Hz (unbound ring proton)), 7.07 (3H, m (unbound ring protons)), 6.30 (1H, dd, ^3J = 2.2, 2.2 Hz (^{CO}Tp-H4)), 6.24 (1H, dd, ^3J = 2.2, 2.2 Hz (^{P}Tp-H4)), 6.16 (1H, dd, ^3J = 2.2, 2.2 Hz (^{N}Tp-H4)), 4.47 (1H, br d (BH)), 4.38 (1H, br d, ^3J = 10.3 Hz (H4)), 3.85 (1H, dd, ^3J = 8.3, 5.8 Hz (H1)), 3.76 (2H, m (OCH_2)), 3.68 (1H, d, ^3J = 10.3 Hz (H_X), 3.43 (3H, s (OMe)), 3.36 (3H, s (OMe)), 3.34 (OMe)), 3.28 (1H, dd, ^{PH}J = 13.5 Hz, ^3J = 9.9 Hz (H2)), 1.73 (1H, ddd, ^3J = 9.6, 1.6 Hz, ^{PH}J = 1.6 Hz (H3)), 1.23 (9H, d, ^{PH}J = 9.0 Hz (PMe_3)); ^{13}C NMR(125 MHz) (acetone-d_6) (22 °C) δ 197.8 (C≡O), 169.4 and 169.1 (C═O), 146.3, 145.2, 139.6 (^{CO}Tp-C3), 139.4, 137.2, 136.7, 136.4, 136.4, (131.3, 129.7, 127.6, 126.7 − unbound ring carbons), 106.7 (^{N}Tp-C4), 106.5 (^{CO}Tp-C4), 106.2 (^{P}Tp-C4), 84.0 (OCH_2), 65.7 (C5), 59.3 (OMe), 52.6 (C3), 51.8 (OMe), 51.8 (OMe), 49.2 (C1), 46.6 (^{PC}J = 12 Hz (C2)), 45.8 (C4), 15.6 (^{PC}J = 32 Hz (PMe_3)).

3-[7-(1-Methoxycarbonyl-1-methylethyl)-7,8-dihydronaphthalen-2-yl]-2,2-dimethylpropionic Acid Methyl Ester (10). An acetonitrile solution (∼1 mL) of TpRe(CO)(MeIm)-(η^2-naphthalene) (115 mg, 0.180 mmol) and dimethoxymethane (52 mg, 0.68 mmol) was treated with an acetonitrile solution (∼1 mL) of *tert*-butyldimethylsilyl trifluoromethanesulfonate (108 mg, 0.41 mmol). After 5 min, the reaction was treated with an acetonitrile solution (∼1 mL) of 1-methoxy-2-methyl-1-trimethylsiloxypropene (MMTP) (166 mg, 0.95 mmol). After 15 min of stirring, 2,6-lutidene (85 mg, 0.79 mmol) was added followed by silver trifluoromethanesulfonate (81 mg, 0.314 mmol). The mixture was allowed to stir for 16 h, at which point it was added to 50 mL of diethyl ether and filtered through a 1 cm silica plug in a 30 mL medium porosity frit. The solvent was removed under reduced pressure, and the leftover brown residue was subjected to preparatory TLC with a 5:1 mixture of hexanes/ethyl acetate. The desired band was removed and washed with acetone (∼25 mL). The acetone was removed under reduced pressure to yield 46 mg (71% yield) of a colorless oil: ^{1}H NMR (500 MHz) (acetone-d_6) (22 °C) δ 6.90 (3H, m), 6.51 (1H, dd, ^3J = 15.0, 2.5 Hz (olefin)), 5.80 (1H, dd, ^3J = 16.5, 5.5 Hz (olefin)), 3.63 (3H, s (OMe)), 3.61 (3H, s (OMe)), 2.72 (5H, m), 1.18, 1.17, 1.16, 1.14 (each 3H, s (*gem*-Me's)); ^{13}C NMR(125 MHz) (acetone-d_6) (22 °C) δ 177.7 and 177.6 (C═O) 138.4, 135.4, 132.7, 130.2, 129.4, 129.1, 128.9, 125.2, 52.0, 51.7, 46.8, 46.1, 44.3, 42.4, 30.5; 25.4, 25.2, 22.8, and 22.2 (*gem*-Me's).

Complex 9. An acetonitrile solution (∼1 mL) of TpRe(CO)-(pyridine)(η^2-naphthalene) (100 mg, 0.158 mmol) and dimethoxymethane (30 mg, 0.39) was cooled to −40 °C and treated with a chilled (−40 °C) acetonitrile solution (∼1 mL) of *tert*-

butyldimethylsilyl trifluoromethanesulfonate (68 mg, 0.26 mmol). After 20 min, the reaction was treated with a chilled (−40 °C) acetonitrile solution of 1-methoxy-2-methyl-1-trimethylsiloxypropene (MMTP) (93 mg, 0.53 mmol) and then warmed to room temperature. After 60 min of stirring, 2,6-lutidene (69 mg, 0.64 mmol) was added, and then the reaction was subjected to column chromatography with1:1 hexanes/ether as eluent. The solvent was removed under reduced pressure, and the yellow residue was subjected to preparatory TLC with a 4:1 mixture of hexanes/ethyl acetate. The desired band was removed and then washed with acetone (∼25 mL). The acetone was removed under reduced pressure to yield 17 mg (14% yield) of a yellow solid: CV (MeCN) (TBAH) (100mV/s) $E_{p,a}$ = 590 mV (NHE); IR (HATR, glaze) ν_{BH} = 2485 cm^{-1}, ν_{CO} = 1800, 1724 cm^{-1}; ^{1}H NMR (500 MHz) (acetone-d_6) (−10 °C) δ 8.02 (1H, d, ^3J = 2.2 Hz (^{CO}Tp-H5)), 8.01 (1H, d, ^3J = 1.6 Hz (^{Py}Tp-H3)), 7.91 (1H, d, ^3J = 1.9 Hz (^{CO}Tp-H3)), 7.88 (1H, d, ^3J = 2.6 Hz (^{Py}Tp-H5)), 7.82 (1H, d, ^3J = 2.2 Hz (^{N}Tp-H5)), 7.80 (2H, m, (*o*-/*p*-pyr)), 7.58 (1H, d, ^3J = 5.6 Hz (*o*-pyr)), 7.11 (1H, dd, ^3J = 5.1, 4.8 Hz (*m*-pyr)), 7.10 (1H, dd, ^3J = 5.4, 4.8 Hz (*m*-pyr)), 7.00 (1H, d, ^3J = 1.6 Hz (^{N}Tp-H3)), 6.77 (1H, s, (H8)), 6.48 (1H, d, ^3J = 7.7 Hz (H6)), 6.45 (1H, dd, ^3J = 2.2, 2.2 Hz (^{CO}Tp-H4)), 6.33 (1H, dd, ^3J = 2.2, 2.2 Hz (^{Py}Tp-H4)), 6.08 (1H, dd, ^3J = 2.2, 2.2 Hz (^{N}Tp-H4)), 5.67 (1H, d, ^3J = 7.7 Hz (H5)), 4.62 (1H, br s (BH)), 3.68 (1H, d, ^3J = 9.0 Hz (H4)), 3.63 (3H, s (OMe)), 3.56 (1H, dd, ^2J = 17.3 Hz, ^3J = 8.7 Hz (H1-syn to Re)), 3.26 (3H, s (OMe)), 3.19 (1H, d, ^3J = 8.7 Hz (H2)), 2.80 (1H, d, ^2J = 12.8 Hz (CH_2)), 2.71 (1H, d, ^2J = 13.1 Hz (CH_2)), 2.47 (1H, d, ^2J = 16.7 Hz (H1-anti to Re)), 2.45 (1H, d, ^3J = 9.0 (H3)), 1.19 (3H, s (*gem*-Me), 1.14 (3H, s (*gem*-Me)), 1.08 (3H, s (*gem*-Me)), 0.87 (3H, s (*gem*-Me)); ^{13}C NMR (125 MHz) (acetone-d_6) (−10 °C) δ 199.4 (C≡O), 178.7 and 177.7 (C═O), 159.6 (*o*-pyr), 152.5 (*o*-pyr), 145.1 (^{Py}Tp-C3), 143.3 (^{N}Tp-C3), 143.2, 139.8 (^{CO}Tp-C3), 136.9 (^{CO}Tp-C5), 136.6 (^{Py}Tp-C5), 136.4 (*p*-pyr), 135.6 (^{N}Tp-C5), 133.8, 133.6, 129.8 (C8), 127.5 (C5) 126.1 (*m*-pyr), 125.5 (C6), 125.2 (*m*-pyr), 107.2 (^{CO}Tp-C4), 107.0 (^{N}Tp-C4), 106.7 (^{Py}Tp-C4), 60.3 (C4), 56.1 (C3), 51.7 (OMe), 51.2 (quaternary C), 51.2 (OMe), 46.9 (CH_2), 45.5 (C2), 44.7 (quaternary C), 29.1 (ring CH_2), 25.4, (*gem*-Me), 25.1 (*gem*-Me), 23.1 (*gem*-Me), 22.9 (*gem*-Me).

2-(4-Methoxymethyl-1,4-dihydronaphthalen-1-yl)-2-methylpropionic Acid Methyl Ester (11). To determine the er of the dihydronaphthalene, the above procedure was followed. Complex **3** was resolved with (*R*)-(+)-α-pinene (ee = 97%) according to the procedure in ref 11. The 1:1 mixture of the naphthalene complex (*R*)-**2** and the matched α-pinene complex was used for further reactions. A sample of this mixture (172 mg, 0.134 mmol (*R*)-**2**) was used in the place of complex **2** and the amount of other reagents was proportionated accordingly. After the completion of the reaction, the reaction mixture was added to 50 mL of hexanes, and the oily residue was subjected to chromatography. Elution with 10% hexanes in ethyl acetate yielded complex **4** (R_f = 0.82, 21.5 mg, 41%). The complex was redissolved in 0.5 g of CD_3CN, and AgOTf (8 mg, 0.03 mmol) was added before sitting in a 75 °C for 1.0 h. After cooling to 20 °C, the reaction mixture was passed through a silica plug and then subjected to HPLC. NMR spectra showed ∼80% conversion using an internal integration standard. The ee of the product was determined to be 90%. (chiral OD-H column, 2% 2-propanol in hexanes as eluents, 0.1 mL/min; major, t_R = 45.1 min; minor, t_R = 54.7 min): ^{1}H NMR (CD_3CN) 7.29 (1H, dd, J = 7.2, 1.6 Hz), 7.25−7.12 (2H, m), 7.02 (1H, d, J = 7.8 Hz), 6.12 (1H, dd, J = 10.0, 4.6 Hz), 5.88 (1H, dd, J = 10.0, 4.6 Hz), 3.90 (1H, m), 3.72 (3H, s), 3.61 (3H, m), 3.35 (3H, s), 1.10 (3H, s), 0.98 (3H, s).

[TpRe(CO)(MeIm)(2,3,4-η^3-[1-(methyl-3-oxobutyl)]-1*H*-naphthalenium](OTf) (14). To complex **3** (40 mg, 0.063 mmol) was added a solution of 3-penten-2-one (10 mg, 0.077 mmol) in 0.5 g CD_3CN at −20 °C and then triflic acid (16 mg, 0.11 mmol). The reaction mixture was allowed to stand for 15 min before analysis by HNMR. The naphthalenium **14** was observed as a single diastereomer along with protonated naphthalene complex: ^{1}H NMR (CD_3CN) 8.38 (1H, t, J = 2.0 Hz), 8.05 (1H, t, J = 2.0 Hz), 7.68 (1H, t, J = 2.1 Hz) (Tp 4) 8.05 (1H, d, J = 2.0 Hz), 7.82 (1H, d, J = 1.8 Hz, 7.51 (1H, d, J = 2.0 Hz), 6.64 (1H, J = 2.0 Hz), 6.33 (1H, d, J = 2.0 Hz), 6.14 (1H, d, J = 2.0 Hz) (Tp 3,5), 7.44 (1H, t, J = 2.0 Hz), 7.08 (1H, t, J = 2.0 Hz), 6.16 (1H, t, J = 2.0 Hz), 3.54 (3H, s) (MeIm) 7.27 (1H, d, J = 7.2 Hz, H8), 7.06 (1H, dd, J = 7.2, 1.2 Hz, H7), 7.01 (1H, dd, J = 7.2, 1.2 Hz, H6), 6.15 (1H, m, H5), 5.26 (1H, dt, J = 6.9, 2.4 Hz, H2), 5.06 (1H, td, J = 6.9, 2.4 Hz, H3), 4.85 (1H, d, J = 2.4 Hz, H4), 3.02 (1H, m, C*H*(CH_3)), 2.87 (1H, dd, J = 9.9, 6.0 Hz, CHC*H*$_2$CO), 2.59 (1H, m, CHC*H*$_2$-CO), 2.50 (1H, m, C*H*CH(CH_3)), 2.21 (3H, s, $COCH_3$), 0.75 (3H, d, CH(C*H*$_3$)).

4-Methyl-3,4,4a,10a-tetrahydro-1*H*-phenanthren-2-one (16). To a mixture of α-pinene complex and resolved complex **3** (50 mg, 0.0390 mmol complex (*R*)-**3**) was added a solution of 3-penten-2-one (30 mg, 0.23 mmol) and TBSOTf (21 mg, 0.080 mmol) in 0.5 g of CH_3CN at −40 °C. The resulting mixture was allowed to sit for 12 min. A separate solution of HOTf (18 mg, 0.12 mmol) in 0.5 g of MeOH was cooled to −40 °C, added to the above solution, and allowed to sit for 0.5 h. The solution was then warmed to 20 °C and allowed to stand another 0.5 h before AgOTf (20 mg, 0.080 mmol) was added. After 15 min, the reaction mixture was placed in a 75 °C oil bath for 1.0 h. After the solution was returned to 20 °C, the solvents were evaporated and 1 mL of water was added to the oil-like residue. The water layer was extracted with 50 mL of ether, which was then washed with 2 mL of brine and dried over Na_2SO_4. After the evaporation of ether, the elution of 10% ethyl acetate in hexanes from a preparatory TLC silica plate yielded the product (6 mg, 73%) as slightly yellow oil (R_f = 0.32). The ee was determined as 95% by HPLC (chiral OD-H column, 2% 2-propanol in hexanes as eluents, 0.1 mL/min; minor, t_R = 72.8 min; major, t_R = 78.7 min): ^{1}H NMR ($CDCl_3$) δ 7.08−7.28 (4H, m, β ring), 6.64 (1H, dd, J = 9.5, 3.0 Hz, H4), 5.71 (1H, ddd, J = 9.5, 3.0, 1.3 Hz, H3), 3.28 (1H, m, H2), 2.69 (1H, dd, J = 13.5, 6.0 Hz, COC*H*$_2$-CH), 2.62 (1H, dd, J = 9.5, 6.4 Hz, H1), 2.46 (1H, m, COC*H*$_2$-CH), 2.40 (1H, m, COC*H*$_2$CH(CH_3)CH), 2.33 (1H, m, CH), 2.19 (1H, dd, J = 13.0, 5.5 Hz, COC*H*$_2$CH(CH_3)CH), 0.88 (3H, d, J = 6.0 Hz, CH_3); ^{13}C NMR ($CDCl_3$, 0−200 ppm) δ 137.11, 133.05, 129.10, 127.39, 127.03, 126.84 (β ring), 131.05 (C3), 128.53 (C4), 49.35 (CO*C*H$_2$CH(CH_3)CH), 46.34 (C1), 45.35 (CO*C*H$_2$-CH), 37.91 (C2), 32.35 (CH), 20.99 (CH_3); HRMS calcd for $C_{15}H_{17}O^+$ 213.1279, found 213.1279. Purity (^{1}H NMR): >95%.

Tricyclo[6.2.2.0^{2,7}]dodeca-2(7),3,5,11-tetraene-9-carboxylic Acid Methyl Ester (17). To a suspension of complex **3** (100 mg, 0.152 mmol) in 3.0 g of CH_3CN were added methyl acrylate (40 mg, 0.47 mmol) and TBSOTf (40 mg, 0.15 mmol) consecutively. The reaction mixture was allowed to stir for 2.0 h before AgOTf (39 mg, 0.15 mmol) was added. After the mixture was stirred for 0.5 h, pyridine (18 mg, 0.23 mmol) was added, and the reaction mixture was heated at 75 °C for 1.0 h. The workup procedure was the same as for **16**. Elution with 10% ethyl acetate in hexanes yielded the product (21 mg, 64%) as a clear oil (R_f = 0.39) with a dr of 1.5:1. Major diastereomer: ^{1}H NMR ($CDCl_3$) δ 7.04−7.24 (4H, m, β ring), 6.30 (1H, m, olefin), 6.28 (1H, m, olefin), 4.28 (1H, m, bridgehead), 3.98 (1H, m, bridgehead), 3.54 (3H, s, CH_3), 2.78 (1H, td, J = 6.3, 2.4 Hz, CH), 1.86 (2H, m, CH_2); ^{13}C NMR ($CDCl_3$) δ 174.38 (CO), 144.47, 140.60, 125.85, 125.38, 124.41, 122.79 (β ring), 137.10, 134.93 (olefin), 51.90, 43.31 (bridgehead), 51.90 (CH_3), 43.31 (CH), 30.19 (CH_2). Minor diastereomer: ^{1}H NMR ($CDCl_3$) δ 7.04−7.24 (4H, m, β ring), 6.32 (1H, m, olefin), 6.22 (1H, m, olefin), 4.34 (1H, m, bridgehead), 3.98 (1H, m, bridgehead), 3.72 (3H, s, CH_3), 2.62 (1H, m, CH), 2.00 (1H, m, CH_2), 1.84 (1H, m, CH_2); ^{13}C NMR ($CDCl_3$) δ 175.17 (CO), 143.18, 140.60, 125.79, 125.42, 123.26, 123.06 (β ring), 136.88, 132.90 (olefin), 52.10, 40.47 (bridgehead), 52.02 (CH_3), 43.91 (CH), 30.85 (CH_2); HRMS calcd for $C_{14}H_{15}O_2^+$, 215.1072, found 215.1072. Purity (^{1}H NMR): >95%.

1,2,3,4-Tetrahydrophenanthrene-1,3-dicarboxylic Acid

Methyl Ester (19). To a solution of complex **18** (100 mg, 0.150 mmol) in 1.2 g of CH_2Cl_2 was added methyl acrylate (39 mg, 0.45 mmol), and the mixture was cooled to −20 °C. TMSOTf (19 mg, 0.12 mmol) was added, and the reaction mixture was allowed to stand for 18 h before AgOTf (44 mg, 0.17 mmol) was added. The mixture was allowed to stand in a 75 °C oil bath for 1.0 h. The workup procedure is similar to that for **16**. Chromatography yielded the product (18 mg, 40%) as a clear oil ($R_f = 0.25$) with a dr of 2:1. Major diastereomer: ^{1}H NMR ($CDCl_3$) δ 8.03 (1H, d, J = 8.5 Hz, H8), 7.83 (1H, d, J = 5.5 Hz, H5), 7.68 (1H, d, J = 8.5 Hz, H4), 7.54 (1H, t, J = 5.5 Hz, H7), 7.49 (1H, t, J = 5.5 Hz, H6), 7.21 (1H, d, J = 8.5 Hz, H3), 4.05 (1H, dd, J = 6.0, 2.0 Hz, $CH_2CH(CO_2CH_3)C$), 3.80 (3H, s, CH_3), 3.73 (3H, s, CH_3), 3.60 (1H, m, $CH(CO_2CH_3)CH_2C$), 3.27 (1H, m, $CH_2CH(CO_2CH_3)CH_2$), 3.18 (1H, dd, J = 16.5, 11.0 Hz, $CH(CO_2CH_3)CH_2C$), 2.63 (1H, d, J = 13.5 Hz, $CH_2CH(CO_2CH_3)C$), 2.08 (1H, td, J = 13.5, 6.0 Hz, $CH_2CH(CO_2CH_3)C$); ^{13}C NMR ($CDCl_3$) δ 175.92, 175.05 (CO), 132.89, 132.29 (C9 or C10), 130.95 (C1), 129.52 (C2), 128.71 (C5), 126.72 (C4), 126.55 (C7), 125.98 (C6), 125.88 (C3), 123.26 (C8), 52.49, 51.43 (CH_3), 44.43 ($CH_2CH(CO_2CH_3)C$), 36.72 ($CH_2CH(CO_2CH_3)CH_2$), 28.17 ($CH(CO_2CH_3)CH_2C$), 27.99 ($CH_2CH(CO_2CH_3)C$). Minor diastereomer: ^{1}H NMR ($CDCl_3$) δ H4, H5, H6, H7 overlapped, 8.02 (1H, d, J = 8.5 Hz, H8), 7.36 (1H, d, J = 8.5 Hz, H3), 4.15 (1H, m, $CH_2CH(CO_2CH_3)C$), 3.77 (3H, s, CH_3), 3.73 (3H, s, CH_3), 3.60 (1H, m, $CH(CO_2CH_3)CH_2C$), 3.21 (1H, dd, J = 16.5, 11.0 Hz, $CH(CO_2CH_3)CH_2C$), 2.84 (1H, m, $CH_2CH(CO_2CH_3)CH_2$), 2.58 (1H, d, J = 13.5 Hz, $CH_2CH(CO_2CH_3)C$), 2.20 (1H, td, J = 13.5, 6.0 Hz, $CH_2CH(CO_2CH_3)C$); ^{13}C NMR ($CDCl_3$) δ 175.28, 174.49 (CO), 132.70, 132.29 (C9 or C10), 130.70 (C1), 129.81 (C2), 128.66 (C5), 127.09 (C4), 126.64 (C7), 125.98 (C6), 127.97 (C3), 123.26 (C8), 52.49, 52.28 (CH_3), 46.96 ($CH_2CH(CO_2CH_3)C$), 36.26 ($CH_2CH(CO_2CH_3)CH_2$), 29.45 ($CH_2CH(CO_2CH_3)C$), 28.52 ($CH(CO_2CH_3)CH_2C$); HRMS calcd for $C_{18}H_{19}O_4^+$ 299.1283, found 299.1282. Purity (^{1}H NMR): >95%.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the ACS, for partial support of this research (ACS-PRF No. 36638-AC1). This work was also supported by the NSF (CHE0111558 and 9974875) and the NIH (NIGMS: R01-GM49236).

Supporting Information Available: General experimental details; ^{13}C spectra for compounds not previously reported; X-ray data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

JO030318K