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Ligand-Modulated Stereo- and Regioselective Tandem Addition Reactions of Rhenium-Bound Naphthalene

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Abstract: A series of complexes of the form TpRe(CO)(L)(η^2-naphthalene) (Tp = hydridotris(pyrazolyl)-borate) undergoes tandem electrophile/nucleophile addition reactions with a high degree of regiocontrol depending on the auxiliary ligand, L. When L = PMe_3, the reaction of the η^2-naphthalene complex with triflic acid followed by a silyl ketene acetal favors the 1,4-addition product, whereas when L = pyridine, *N,N*-dimethylaminopyridine, *N*-methylimidazole, or NH_3 the 1,2-addition product is favored. These reactions proceed with excellent stereocontrol: both electrophile (H^+, D^+) and nucleophile (silyl ketene acetal) add anti to the face of metal coordination, and a single coordination diastereomer can be isolated for each reaction. One-electron oxidation of the Re complex affords the corresponding free dihydronaphthalene in good yield.

Introduction

The ability to regio-, stereo-, and enantioselectively manipulate aromatic substrates for the construction of complex carbocyclic ring systems is of considerable interest to synthetic chemists. Transition-metal-based methodologies that allow for this type of manipulation through chiral auxiliary control include electrophilic addition to η^2-arene complexes of pentaammineosmium(II)[1,2] and the complementary approach of nucleophilic addition to η^6-arene complexes of chromium[3−7] and manganese.[8−10] Two additional methodologies utilize either planar chiral η^6-arene complexes[11−15] or external chiral ligands[16] to induce asymmetry. The most common of the non-transition-metal-based dearomatization methodologies is the Birch reduction[17] and the related "misoriented Birch reduction."[18] Less common but noteworthy are methodologies that induce asymmetry, which include reductive alkylation,[19] enzymatic dihydroxylation,[20] and electrophilic addition governed by intramolecular hydrogen bonding.[21]

A prominent methodology for the dearomatization of naphthalenes is the use of chiral oxazolines in promoting the regio-, stereo-, and enantioselective tandem addition of a nucleophile proceeded by an electrophile to generate nonracemic *trans*-1,2-dihydronaphthalenes.[22] In contrast, the pentaammineosmium(II) fragment has been used to coordinate naphthalene and to promote the tandem addition of an electrophile followed by a nucleophile to regio- and stereoselectively generate *cis*-1,4-dihydronaphthalenes.[23]

Many of the aforementioned approaches to dearomatization proceed with high regio- and stereocontrol, and the synthesis of either enantiomer of a desired product can be achieved by using the appropriate antipode of the chiral auxiliary. However, these methods do not provide a simple means of adjusting the regiochemistry for the addition sequence. Herein we report the development of a new methodology for the dearomatization of naphthalene using the chiral and π-basic metal fragment {TpRe(CO)(L)} (L = PMe_3, pyridine, *N,N*-dimethylaminopyridine (DMAP), *N*-methylimidazole (MeIm), or NH_3). Similar to the tandem addition sequences performed with the $\{Os(NH_3)_5\}^{2+}$, both the electrophile and the nucleophile add anti to the face of metal coordination to yield *cis*-dihydronaphthalenes. However, for these {TpRe(CO)(L)} systems, the regiochemistry of the

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(1) Chordia, M. D.; Harman, W. D. *J. Am. Chem. Soc.* **2000**, *122*, 2725.
(2) Chordia, M. D.; Harman, W. D. *J. Am. Chem. Soc.* **1998**, *120*, 5637.
(3) Pearson, A. J.; Gontcharov, A. V. *J. Org. Chem.* **1998**, *63*, 152.
(4) Kündig, E. P.; Amurrio, D.; Anderson, G.; Beruben, D.; Khan, K.; Ripa, A.; Liu, R. *Pure Appl. Chem.* **1997**, *69*, 543.
(5) Pearson, A. J.; Gontcharov, A. V.; Woodgate, P. D. *Tetrahedron Lett.* **1996**, *37*, 3087.
(6) Semmelhack, M. F.; Schmalz, H.-G. *Tetrahedron Lett.* **1996**, *37*, 3089.
(7) Kündig, E. P.; Ripa, A.; Bernardinelli, G. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1071.
(8) Pearson, A. J.; Milletti, M. C.; Zhu, P. Y. *J. Chem. Soc., Chem. Commun.* **1995**, 1309.
(9) Pearson, A. J.; Milleti, M. C.; Zhu, P. Y. *J. Chem. Soc., Chem. Commun.* **1995**, 853.
(10) Pearson, A. J.; Zhu, P. Y. *J. Am. Chem. Soc.* **1993**, *115*, 10376.
(11) Schellhaas, K.; Schmalz, H.-G.; Bats, J. W. *Chem. Eur. J.* **1998**, *4*, 57.
(12) Quattropani, A.; Anderson, G.; Bernardinelli, G.; Kündig, E. P. *J. Am. Chem. Soc.* **1997**, *119*, 4773.
(13) Schmalz, H.-G.; Schellhaas, K. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2146.
(14) Schmalz, H.-G.; Schellhaas, K. *Tetrahedron Lett.* **1995**, *36*, 5511.
(15) Price, D. A.; Simpkins, N. S.; MacLeod, A. M.; Watt, A. P. *J. Org. Chem.* **1994**, *59*, 1961.
(16) Amurrio, D.; Kahn, K.; Kündig, E. P. *J. Org. Chem.* **1996**, *61*, 2258.
(17) Rabideau, P. W.; Marcinow, Z. *Organic Reactions*; John Wiley & Sons Inc.: New York, 1992; Vol. 42.
(18) Rabideau, P. W.; Karrick, G. L. *Tetrahedron Lett.* **1987**, *28*, 2481.
(19) Schultz, A. G.; Pettus, L. *Tetrahedron Lett.* **1997**, *38*, 5433.
(20) Hudlicky, T.; Tian, X.; Konigsberger, K.; Maurya, R.; Roudan, J.; Fan, B. *J. Am. Chem. Soc.* **1996**, *118*, 10752.
(21) Fujita, M.; Matsushima, H.; Sugimura, T.; Tai, A.; Okuyama, T. *J. Am. Chem. Soc.* **2001**, *123*, 2946.
(22) Meyers, A. I. *J. Heterocycl. Chem.* **1998**, *35*, 991.
(23) Winemiller, M. D.; Harman, W. D. *J. Am. Chem. Soc.* **1998**, *120*, 7835.

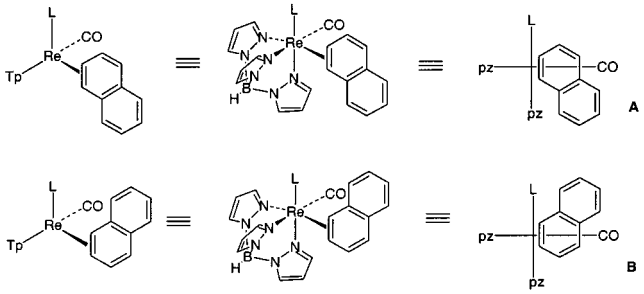
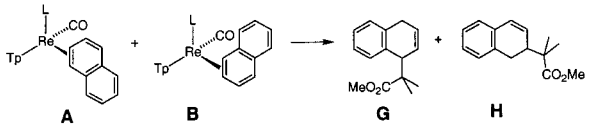


Figure 1. Representations of rhenium-bound naphthalene complexes

Table 1. Regioisomeric Ratios and Yields of Dihydronaphthalenes



				method A[a]		method B[b]	
complex	L	*T* (°C)	A:B	G:H	yield (%)	G:H	yield (%)
1	PMe_3	0				13:1	29
		20	10:1	12:1	52	12:1	24
2	pyridine	−40		1:15	63		
		0				1:7	80
		20	1:3	1:8	89	1:7	66
3	DMAP	−40		1:25	19		
		20	1:1.5	1:10	50		
4	MeIm	0				1:25	55
		20	1:5	1:23	83	1:16	63
5	NH_3	−40		1:7	25		
		20	1:4				

[a] Reaction sequence performed in inert atmosphere. [b] Reaction sequence performed on benchtop, with ∼500 mg of metal complex, and blanketed under dinitrogen.

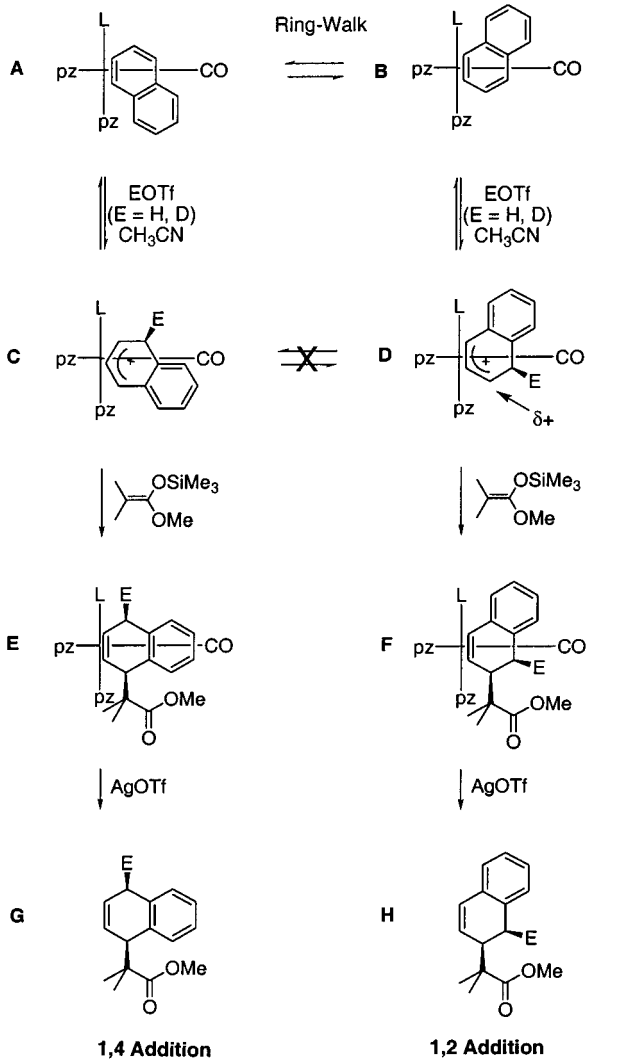
reaction can be modulated by the choice of L such that either a 1,2- or 1,4-dihydronaphthalene may be produced as the dominant product.

Results and Discussion

The complexes TpRe(CO)(L)(η^2-naphthalene) (**1**−**5**) were prepared by established methods from their Re^{III} precursors, TpRe(L)Br_2, and were characterized by ^1H and ^{13}C NMR data.[24,25] To maximize π-back-bonding interactions, the coordinated double bond orients orthogonally to the Re−CO π bonds [26] providing two possible coordination diastereomers (Figure 1). In all cases, spin saturation experiments confirmed the presence of two coordination diastereomers (**A**, **B**) in equilibrium, and the diastereomeric ratio (dr) for each system is listed in Table 1. For each diastereomer, two rotamers are predicted; however, to minimize steric interactions with the scorpionate, the unbound ring of naphthalene adopts an orientation over the CO ligand. Thus, only one rotamer is observed for each coordination diastereomer.[26]

Previous reports from our laboratories have shown that the naphthalene ligand in the complex $[Os(NH_3)_5(\eta^2\text{-naphthalene})]^{2+}$ is basic and undergoes protonation at C1 with triflic acid (HOTf) to give a 1*H*-naphthalenium cation.[23,27] Subsequent treatment of the 1*H*-naphthalenium species with a variety of nucleophiles

Scheme 1. Regio- and Stereoselective Pathways for the Tandem Addition to η^2-Naphthalene



(e.g., silyl enolates, malonate esters, alkyl- and aryllithiums) followed by oxidative decomplexation yields 1,4-dihydronaphthalenes.[23] Initial investigations with rhenium involved the PMe_3 (**1**, dr = 10:1) and the MeIm (**4**, dr = 1:5) derivatives since these two complexes exhibit the highest ratios of coordination diastereomers, but with opposite preferences (Table 1). Similar to that observed for osmium, when these rhenium−naphthalene complexes were treated with 2.5 equiv of HOTf, followed by 4 equiv of 1-methoxy-2-methyl-1-trimethylsiloxypropene (MMTP) and 2 equiv of AgOTf (25 °C), the formation of dihydronaphthalenes was observed (method A, Table 1). When L = PMe_3, the nucleophile prefers to add at C4, yielding the 1,4-dihydronaphthalene **G** (52%; Scheme 1), analogous to the behavior of the osmium system. However, when L = *N*-MeIm, nucleophilic addition occurs predominantly at C2 to give the 1,2-dihydronaphthalene **H** in 83% yield. Akin to its imidazole analogue, the pyridine complex **2** favors coordination diastereomer **B**, and when this species was subjected to the same sequence of reagents, an 8:1 ratio of 1,2- to 1,4-dihydronaphthalenes was obtained in 89% yield. Repeating this reaction sequence at −40 °C improved the ratio to 15:1, but with a slight

(24) Meiere, S. H.; Brooks, B. C.; Gunnoe, T. B.; Carrig, E. H.; Sabat, M.; Harman, W. D. *Organometallics* **2001**, *20*, 3661.
(25) 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.
(26) Gunnoe, T. B.; Sabat, M.; Harman, W. D. *Organometallics* **2000**, *19*, 728.
(27) Winemiller, W. D.; Kopach, M. E.; Harman, W. D. *J. Am. Chem. Soc.* **1997**, *119*, 2096.

Table 2. Crystal Data and Structure Refinement for $C_{30}H_{32}BN_7O_3Re$ (**2F**)

empirical formula	$C_{30}H_{32}BN_7O_3Re$
formula weight	736.64
temperature	153(2) K
wavelength	0.71073 Å
crystal system	monoclinic
space group	*P*2(1)/*c*
unit cell dimensions	$a = 14.1407(6)$ Å
	$b = 11.5859(5)$ Å; $\beta = 99.4720(10)°$
	$c = 18.3748(7)$ Å
volume	2969.3(2) Å^3
Z	4
density (calculated)	1.648 Mg/m^3
absorption coefficient	4.137 mm^{-1}
F(000)	1464
crystal size	0.32 × 0.28 × 0.16 mm
instrument	Bruker SMART APEX CCD diffractometer
θ range for data collection	1.46−28.29°
index ranges	$-18 \le h \le 18$
	$-15 \le k \le 14$
	$-17 \le l \le 24$
reflections collected	21 877
independent reflections	7363 [R(int) = 0.0254]
completeness to $\theta = 28.29°$	99.6%
absorption correction	empirical (transmission factors: 0.4921−0.8015)
refinement method	full-matrix least-squares on F^2
data/restraints/parameters	7363/0/511
goodness-of-fit on F^2	0.985
final R indices [$I > 2\sigma(I)$]	$R1 = 0.0229$, w$R2 = 0.0508$
R indices (all data)	$R1 = 0.0282$, w$R2 = 0.0523$
largest diff. peak and hole	1.651 and −0.615 e·Å^{-3}

loss of yield. The DMAP complex **3** also favored 1,2-addition with a **G**:**H** ratio of 1:10. Of note, these reactions can be performed outside of the glovebox on a scale of 500 mg (naphthalene complex) with little compromise in selectivity (method B, Table 1), but the yields are somewhat diminished, presumably due to slow oxidation of the rhenium center.

To elucidate the origin of the regioselectivity of these tandem addition reactions, the complexes **1**−**4** were subjected to the same reaction conditions as before, but the products were isolated prior to oxidation with silver triflate and analyzed by ^{1}H and ^{13}C NMR. Not only were the reactions regioselective, but the diastereomeric ratio for each of the tandem addition intermediates (Scheme 1; **E**, **F**) was much higher (dr > 20:1) than the dr's of their respective starting materials (Table 1). Naphthalene complexes with L = pyridine, DMAP, or MeIm (**2A/B**, **3A/B**, and **4A/B**) formed **2F**, **3F**, and **4F** respectively, whereas the PMe_3 analogue (**1A/B**) formed the 1,4-dihydronaphthalene complex **1E**. The COSY, HSQC, and NOE data for these complexes indicate that the silyl ketene acetal adds anti to the metal. Substituting DOTf for HOTf in the reaction sequence generated dihydronaphthalene complexes **1E-*d***, **2F-*d***, and **4F-*d*** with ^{1}H NMR spectra similar to those of their fully protonated analogues, save the chemical shift and coupling data that correspond to the exchanged proton. This observation confirms that the addition of the electrophile (H^+/D^+) occurs anti to the metal and suggests that the high diastereoselectivity for the overall reaction is based on the selective protonation of *one* of the equilibrating naphthalene linkage isomers (**A** or **B**), not the interfacial isomerization (i.e., a face flip) of an allyl intermediate (**C**/**D**; Scheme 1).

The above discussion assumes that a single diastereomer for each of the 1*H*-naphthalenium intermediates (**C**, **D**) dominates,

Table 3. Selected Bond Distances and Angles for the 1,2-Dihydronaphthalene Complex **2F**

Re−C(16)	1.839(3)	C(2)−C(3)	1.482(4)
Re−N(1)	2.140(2)	C(3)−C(4)	1.390(4)
Re−N(5)	2.159(2)	C(3)−C(8)	1.402(4)
Re−N(7)	2.174(2)	C(4)−C(5)	1.389(4)
Re−C(2)	2.188(3)	C(5)−C(6)	1.372(5)
Re−C(1)	2.211(2)	C(6)−C(7)	1.383(4)
Re−N(3)	2.241(2)	C(7)−C(8)	1.390(4)
C(1)−C(2)	1.437(4)	C(8)−C(9)	1.505(4)
C(1)−C(10)	1.523(3)	C(9)−C(10)	1.523(4)
C(16)−Re−N(1)	90.97(10)	C(2)−Re−C(1)	38.11(9)
C(16)−Re−N(5)	92.03(10)	C(16)−Re−N(3)	173.70(10)
N(1)−Re−N(5)	81.27(8)	C(30)−N(7)−Re	122.55(19)
C(16)−Re−N(7)	91.83(10)	C(1)−C(2)−Re	71.80(14)
N(1)−Re−N(7)	160.87(8)	O(3)−C(16)−Re	175.6(2)

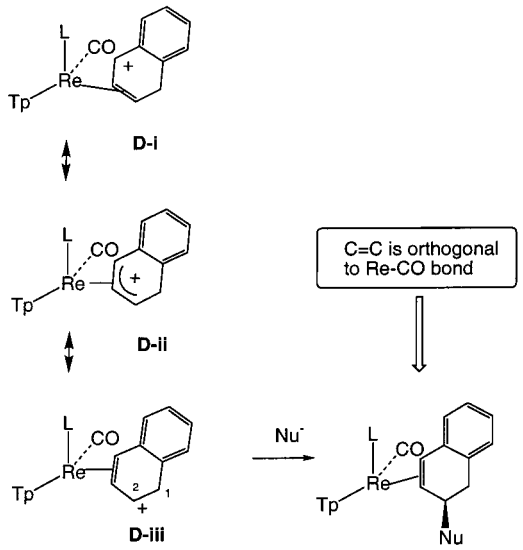


Figure 2. Resonance contributors for the naphthalenium species **D**.

and this notion was confirmed by observing the products at the allyl stage where possible. Complexes **1A/B**, **2A/B**, and **3A/B** were each treated with ∼1 equiv of HOTf in CD_3CN, generating **1C**, **2D**, and **3D**, respectively, in situ. The ^{1}H NMR spectra of these cationic intermediates revealed that a single diastereomer had formed in each reaction with chemical shifts and splitting patterns consistent with an η^3-bound 1*H*-naphthalenium species.[27] The ^{13}C data for **1C** (L = PMe_3) were typical for an η^3-allyl complex with bound carbon resonances at 78.2 (C4), 73.1 (C2), and 72.5 (C3) ppm. However, the ^{13}C NMR spectra for **2D** (L = pyridine) and **3D** (L = DMAP) displayed bound allyl signals at 71.1/71.6 (C4), 80.5/80.4 (C3), and 105.4/105.4 (C2) ppm, respectively. The latter values are a significant departure from typical η^3-allyl complexes of rhenium or osmium ($\delta \sim 75$)[27] and suggest that C2 may be unusually electrophilic due to a resonance contributor of the η^3-allyl complex that places a double bond orthogonal to the Re−CO π bonds and a positive charge on C2 (**D-iii**, Figure 2). Similar behavior was observed for the protonated *m*-xylene complex of pentaammineosmium-(II), where ^{13}C NMR data indicated an allylic structure that approximated dihapto coordination geometry.[27] This comparison would explain the observed preference for complexes **2D**, **3D**, and **4D** to undergo nucleophilic attack at C2 rather than at C4, as was observed for the {TpRe(CO)(PMe_3)} and $\{Os(NH_3)_5\}^{2+}$ derivatives. Attempts to observe this feature in the putative imi-

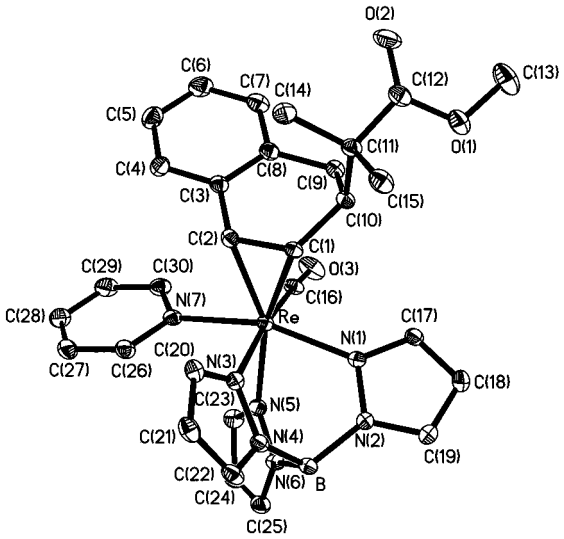


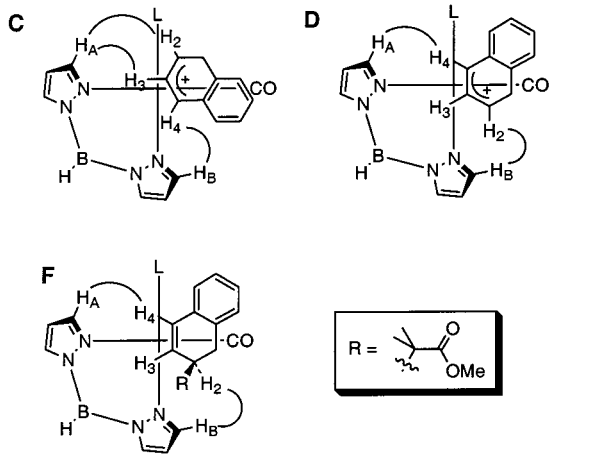
Figure 3. ORTEP diagram (30% ellipsoids) for the complex of 1,2-dihydronaphthalen-2-yl)-2-methylpropionic acid methyl ester (**2F**).

dazole naphthalenium complex **4D** were unsuccessful due to significant decomposition of this species during data collection.

An additional experiment which confirmed that the naphthalenium was not undergoing an interfacial isomerization was one in which the pyridine naphthalenium complex, **2D**, was treated with several drops of methanol-d_4 and observed over time by ^{1}H NMR spectroscopy. Within the first hour (20 °C), all naphthalenium protons remained unscrambled, even in the presence of the weak base, methanol. Over the next several hours, the proton at C1, oriented anti to the rhenium, slowly exchanged with deuterium while the other proton signals remained unscathed. The above observations indicate that even in the presence of methanol, a stronger base than acetonitrile, deprotonation of the naphthalenium occurs on a time scale of hours. Thus, the selective protonation of only one naphthalene isomer *is kinetically controlled* under the conditions used in the tandem addition sequence.

It is proposed that the origin of the stereoselectivity for the overall reaction is a direct result of the exclusive protonation of one of the two naphthalene diastereomers (**A** or **B**), while the regioselectivity is a direct result of the orientation of the 1*H*-naphthalenium intermediates (**C** and **D**, Scheme 1). Possible factors determining these stereochemical and conformational preferences likely include the energies of the rhenium dπ orbitals, steric interactions of the naphthalenium ligand with the ligand set, and π/π interactions between L and the uncoordinated ring of the naphthalene. With regard to the last of these factors, X-ray diffraction data for a single crystal of the 1,2-addition complex, **2F** (ORTEP diagram shown in Figure 3), suggest a geometry conducive to π stacking between the unbound ring of the coordinated naphthalene and the pyridine ring. Although the two rings are not completely parallel (the angle between plane normals is 25°), the distance between C(4) of the dihydronaphthalene ligand and C(30) of the pyridine is ~3.1 Å, and the C(3)−N(7) interligand distance is ~3.3 Å, allowing for considerable π interactions. By analogy, it is likely that similar interactions are present in the naphthalenium species (**2D**, **3D**, and **4D)** in which the unbound ring is directed over that of the bound imidazole or pyridine ring.

Table 4. Selected NOE Enhancements, IR, and Electrochemical Data



	atoms				
complex	% enhancements			ν_{CO} (cm^{-1})	$E_{p,a}$ (mV)
	H_2-H_A	H_3-H_A	H_4-H_B		
1C	6	12	10		
	H_4-H_A	H_3-H_A	H_2-H_B		
2D	19	6	18		
3D	23		19		
	H_4-H_A	H_3-H_A	H_2-H_B		
2F	12		7	1803	380
3F	17		17	1794	250
4F	20		21	1791	220

Although π interactions can be invoked in explaining the stereochemistry and regioselectivity observed for the pyridine, DMAP, and MeIm intermediates (**2D**, **3D**, and **4D**), the corresponding metal fragments are more electron-rich than the PMe_3 system (cf. for naphthalene complexes **1A/B**, ν_{CO} = 1825 cm^{-1}; **2A/B**, ν_{CO} = 1812 cm^{-1}; **3A/B**, ν_{CO} = 1808 cm^{-1}; **4A/B**, ν_{CO} = 1803 cm^{-1}) and sterically better for the bound naphthalene. In an attempt to differentiate these factors, we examined the case of L = ammonia where the metal is most electron-rich (ν_{CO} = 1796 cm^{-1}), the ligand is least sterically destabilizing, and no π stacking interactions are possible (L = NH_3, **5A/B**). Unfortunately, the ammonia naphthalene complex could not be isolated free of impurities, and the tandem addition sequence was performed on material that was ~50% pure (the remainder was the precursor complex TpRe(CO)(NH_3)(η^2-cyclopentene)). Nevertheless, performing the reaction sequence delivered a product mixture in which the 1,2-addition product was favored over the 1,4-product (**G**:**H** 1:7). For comparison, the **G**:**H** ratio for L = MeIm is 1:23; thus, electronic and steric factors alone cannot account for the high preference for the 1,2-addition pathway found for L = pyridine, DMAP, and MeIm.

Additional data that link the orientation of the naphthalenium to the regioselectivity are percent enhancements from 1D NOE experiments listed in Table 4. Importantly, NOE percent enhancements for naphthalenium complexes **2D** and **3D** (H_A-H_4; H_B-H_2) are similar to those for **2F** and **3F**, suggesting that the orientation of the naphthalenium, in these cases, resembles that of the bound 1,2-dihydronaphthalene product (e.g., **2F** shown in Figure 3). In contrast, NOE data for the trimethylphosphine analogue differ significantly and fit a model in which the unbound ring of the naphthalenium extends in the direction of the CO ligand (**1C** in Table 4). Thus, the orientation

of the naphthalenium ligand appears to directly determine the regiochemistry of the nucleophilic addition reaction.

Steric factors are likely to play a significant role in the reversal of regiocontrol experienced with L = PMe_3. An earlier study[28] that explored the ability of the {TpRe(CO)(MeIm)} fragment to bind substituted olefins and carbonyls determined that the metal preferentially places bulky substituents in the MeIm/CO quadrant followed by the CO/pz quadrant, as is reflected in the **A**:**B** ratio for complex **3**. It is assumed that the pyridine and DMAP fragments would behave similarly, but when L = PMe_3, the corresponding diastereomer (**D**, Table 4) would be unstable as a result of the comparatively bulky phosphine overlapping with the unbound ring of naphthalene. Thus, for L = PMe_3, a different naphthalenium intermediate, **1C**, is formed such that the unbound ring of the naphthalene can avoid the PMe_3 ligand and the pyrazolyl ring trans to the phosphine (H_B in Table 4). In this orientation, attack at C4 generates a double bond orthogonal to the Re−CO π bonds, and the resulting 1,4-dihydronaphthalene ligand has the unbound ring away from both the PMe_3 and H_B.

Conclusions

A series of complexes of the form TpRe(CO)(L)(η^2-naphthalene) reacts with triflic acid and a silyl ketene acetal to give either 1,2- or 1,4-dihydronaphthalenes in yields as high as 89%. The regiocontrol for this reaction is highly dependent on the nature of L, and a key to this selectivity appears to be the formation of single 1*H*-naphthalenium intermediates and the orientation of the ligand with respect to the rhenium−CO bond. When the unbound ring of the naphthalenium extends toward L (e.g., pyridine, DMAP, MeIm, and NH_3), nucleophilic attack at C2 allows the C═C bond of the resulting 1,2-dihydronaphthalene to be orthogonal to the Re−CO π bonds, thus maximizing the back-bonding interaction with the dihydronaphthalene. Alternatively, if the 1*H*-naphthalenium orients the unbound ring toward the carbonyl, a 1,4-addition produces the most stable geometry for the product. Still undetermined is whether this ligand-modulated regiochemistry and high stereocontrol can be extended to other types of electrophiles.

Given the high diastereoselectivity expressed in these systems, the preparation of enantio-enriched tetralins should be accessible by this method, provided that these asymmetric rhenium cores can be resolved and do not undergo racemization under the acidic reaction conditions required.

Experimental Section

General Methods. NMR spectra were obtained on a 500 MHz Varian INOVA spectrometer unless otherwise noted. All chemical shifts are reported in ppm and are referenced to tetramethylsilane (TMS), utilizing residual ^{1}H or ^{13}C signals of the deuterated solvents as an internal standard. Coupling constants (*J*) are reported in hertz (Hz). The following abbreviations will be used to discriminate among the pyrazolyl rings: ^{CO}Tp, pyrazolyl ring trans to CO; ^{N}Tp, pyrazolyl ring trans to naphthalene; ^{P}Tp, pyrazolyl ring trans to PMe_3; ^{Py}Tp, pyrazolyl ring trans to pyridine; ^{D}Tp, pyrazolyl ring trans to DMAP; ^{Im}Tp, pyrazolyl ring trans to *N*-methylimidazole. Infrared spectra (IR) were recorded on a MIDAC Prospect Series (model PRS) spectrometer as a glaze (evaporated diethyl ether) on a horizontal attenuated total reflectance (HATR) accessory (Pike Industries). Values were reproducible within ±1 cm^{-1}. Electrochemical experiments were performed under a dinitrogen atmosphere using a PAR model 362 potentiostat driven by a PAR model 175 universal programmer. Cyclic voltammograms (CV) were recorded (Kipp and Zonen BD90 XY recorder) at 100 mV/s (25 °C) in a standard three-electrode cell from +1.7 to −1.7 V with a glassy carbon working electrode, acetonitrile (CH_3CN) solvent, and tetrabutylammonium hexafluorophosphate (TBAH) electrolyte. All potentials are reported versus NHE (normal hydrogen electrode) using cobaltocenium hexafluorophosphate ($E_{1/2}$ = −780 mV) or ferrocene ($E_{1/2}$ = 550 mV) as an internal standard. Elemental analysis (EA) was performed with a Perkin-Elmer 2400 Series II CHNS/O analyzer. All synthetic reactions were performed under a dinitrogen atmosphere in a drybox, except where specified. Acetonitrile and hexanes were purged with nitrogen and purified by passage through a column packed with activated alumina.[29] Other solvents were used as received from Fisher Chemicals. Deuterated solvents were used as received from Cambridge Isotopes. Other reagents were used as received.

2-(1,2-Dihydronaphthalen-2-yl)-2-methylpropionic Acid Methyl Ester (G). Method A. An acetonitrile solution (541 mg) of triflic acid (71 mg, 0.47 mmol) and an acetonitrile solution (522 mg) of 1-methoxy-2-methyl-1-trimethylsiloxypropene (MMTP) (106 mg, 0.61 mmol) were cooled to −40 °C. The triflic acid solution was added to a vial containing TpRe(CO)(pyridine)(η^2-naphthalene) (**2A/B**) (78 mg, 0.12 mmol) at room temperature, followed by addition of the MMTP solution. The reaction mixture was stirred for 10 min and then treated with 2,6-lutidine (91 mg, 0.85 mmol). It was allowed to react for 10 min, and then AgOTf (61 mg, 0.24 mmol) was introduced. After 16 h of stirring, the reaction mixture was added to 50 mL of stirring ether and filtered through a 2.5 cm silica plug in a 30 mL medium porosity frit. The ether was removed under reduced pressure. The resulting residue was removed from the inert atmosphere and subjected to preparatory TLC using 3:1 hexanes/ethyl acetate. The desired band was removed and washed with 25 mL of acetone. The acetone was removed by rotary evaporation to afford 25 mg (89%) of a colorless oil with a 13:1 ratio of regioisomers (**H**:**G**) by ^{1}H NMR. (*Note*: The same conditions can be applied using TpRe(CO)(MeIm)(η^2-naphthalene) (**4A/B**) (82 mg, 0.13 mmol) with the appropriate equivalents of reagents to yield 24 mg (83%) of a clear oil with a 23:1 ratio of regioisomers (**H**:**G**) by ^{1}H NMR. The complex TpRe(CO)(DMAP)(η^2-naphthalene) (**3A/B**) (142 mg, 0.21 mmol) yields 24 mg (50%) of a clear oil with a 10:1 ratio of regioisomers (**H**:**G**) by ^{1}H NMR.)

Method B. An acetonitrile solution (10 mL) of TpRe(CO)(pyridine)-(η^2-naphthalene) (**2A/B**) (507 mg, 0.800 mmol) was cooled to 0 °C and blanketed with dinitrogen. An acetonitrile solution (3 mL) of triflic acid (205 mg, 1.36 mmol) (cooled to 0 °C) was added to the Re complex followed by an acetonitrile solution (3 mL) of MMTP (421 mg, 2.42 mmol) (cooled to 0 °C). After 15 min of stirring, the solution was allowed to warm to room temperature, and pyridine (198 mg, 2.50 mmol) dissolved in CH_3CN (3 mL) was added to the reaction mixture. After 15 min of stirring, the reaction mixture was treated with AgOTf (339 mg, 1.32 mmol) and stirred for 72 h. The solution was then added to 150 mL of stirring ether and filtered through a 2.5 cm silica plug in a 60 mL medium porosity frit. The ether was removed under reduced pressure. The resulting residue was subjected to preparatory TLC using 5:1 hexanes/ethyl acetate. The desired band was removed and washed with 25 mL of acetone. The acetone was removed by rotary evaporation to afford 147 mg (80%) of a colorless oil with a 15:1 ratio of regioisomers (**H**:**G**) by ^{1}H NMR. (*Note*: The same conditions can be applied using TpRe(CO)(MeIm)(η^2-naphthalene) (**4A/B**) (503 mg, 0.79 mmol) with equivalent amounts of reagents to yield 101 mg (55%) of a clear oil with a 25:1 ratio of regioisomers (**H**:**G**) by ^{1}H NMR.)

2-(1,4-Dihydronaphthalen-1-yl)-2-methylpropionic Acid Methyl Ester (H). Method A. The same procedure used to generate 2-(1,2-dihydronaphthalen-2-yl)-2-methylpropionic acid methyl ester, with

(28) Meiere, S. H.; Harman, W. D. *Organometallics* **2001**, *18*, 3876.

(29) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.

equivalent amounts of reagents, was applied using TpRe(CO)(PMe_3)-(η^2-naphthalene) (**1A/B**) (66 mg, 0.10 mmol) to yield 13 mg (54%) of a colorless oil with a 12:1 ratio of regioisomers (**G**:**H**) by ^{1}H NMR.

Method B. The same procedure used to generate 2-(1,2-dihydronaphthalen-2-yl)-2-methylpropionic acid methyl ester (benchtop procedure), with equivalent amounts of reagents, was applied using TpRe(CO)(PMe_3)(η^2-naphthalene) (**1A/B**) (408 mg, 0.65 mmol) to yield 44 mg (29%) of a colorless oil with a 13:1 ratio of regioisomers (**G**:**H**) by ^{1}H NMR.

[TpRe(CO)(PMe_3)(2,3,4-η^3-(1*H*-naphthalenium))](OTf) (1C). The complex TpRe(CO)(PMe_3)(1,2-η^2-(naphthalene) (**1A/B**) (40.1 mg, 0.064 mmol) was dissolved in an acetonitrile-d_3 solution (624 mg) of triflic acid (12.0 mg, 0.08 mmol). ^{1}H NMR (500 MHz, CD_3CN, −10 °C): δ 8.13 (1H, d, ^3J = 2.0 (^{N}Tp-H3)), 8.08 (1H, d, ^3J = 2.2 (^{CO}Tp-H3)), 8.05 (1H, d, ^3J = 2.6 (^{CO}Tp-H5)), 7.94 (1H, d, ^3J = 2.6 (^{N}Tp-H5), 7.85 (1H, d, ^3J = 2.6 (^{P}Tp-H5)), 7.19 (1H, d, ^3J = 7.1 (H8)), 7.10 (2H, m (H6 and H7)), 6.77 (1H, dd, ^3J = 7.4, ^4J = 1.3 (H5)), 6.59 (1H, dd, ^3J = 2.6, 2.6 (^{CO}Tp-H4)), 6.42 (1H, dd, ^3J = 2.2, 2.2 (^{N}Tp-H4)), 6.36 (1H, d, 2.0 (^{P}Tp-H3)), 6.12 (1H, dd, ^3J = 2.2, 2.2 (^{P}Tp-H3)), 5.47 (1H, m (H2)), 4.81 (1H, ddd, ^3J = 6.4, 6.4, $^3J_{PH}$ = 3.5 (H3)), 4.62 (1H, dd, ^3J = 6.4, ^4J = 2.2 (H4)), 3.66 (1H, dd, ^2J = 22.5, ^3J = 3.5 (H1-anti to Re)), 3.34 (1H, d, ^2J = 22.5 (H1-syn to Re)), 1.07 (9H, d, $^3J_{PH}$ = 9.9 (PMe_3)). ^{13}C NMR (125 MHz, CD_3CN, −10 °C): δ 199.0 (C≡O), 146.9 (^{N}Tp-C3), 145.7 (^{P}Tp-C3), 143.0 (^{CO}Tp-C3), 139.4 (^{CO}Tp-C5), 139.2 (^{N}Tp-C5), 138.7 (^{P}Tp-C5), 138.1 (C9 or C10), 131.2 (C5), 130.0 (C9 or C10), 129.0 (C6 or C7), 128.3 (C8), 126.5 (C6 or C7), 109.1 (^{N}Tp-C4), 108.9 (^{CO}Tp-C4), 107.4 (^{P}Tp-C4), 78.2 (C4), 73.1 (C2), 72.5 (d, $^2J_{PC}$ = 3.1 (C3)), 33.0 (CH_2), 12.6 (d, $^1J_{PC}$ = 36 (PMe_3)).

TpRe(CO)(PMe_3)(2,3-η^2-(2-(1,4-dihydronaphthalen-1-yl)-2-methylpropionic acid methyl ester)) (1E). An acetonitrile solution (1 mL) of triflic acid (59 mg, 0.39 mmol) and an acetonitrile solution (1 mL) of 1-methoxy-2-methyl-1-trimethylsiloxypropene (MMTP) (102 mg, 0.585 mmol) were cooled to −40 °C. The triflic acid solution was then added to a vial containing TpRe(CO)(PMe_3)(η^2-naphthalene) (**1A/B**) (67 mg, 0.11 mmol) and stirred for 20 min, followed by addition of the MMTP solution. After 30 min of stirring, the reaction was quenched with 2,6-lutidine (74 mg, 0.69 mmol) and subjected to flash chromatography first with 50 mL of hexanes and then with 3:2 hexanes/ether as eluents. The clear solution was removed from the inert atmosphere. The solvent was then removed under reduced pressure, and the resulting white residue was subjected to preparatory TLC with 3:1 hexanes/ethyl acetate as eluents. The desired band was removed and washed with 25 mL of acetone. The acetone was rotary evaporated to afford 47 mg (61%) of a white solid as a single diastereomer by ^{1}H NMR. CV (CH_3CN, TBAH, 100 mV/s): $E_{1/2}$ = 290 mV (NHE). IR (HATR, glaze): ν_{BH} = 2477 cm^{-1}, ν_{CO} = 1827, 1726 cm^{-1}. ^{1}H NMR (500 MHz, acetone-d_6, 22 °C): δ 7.88, 7.82, 7.78, 7.73, 7.72, 7.55 (each 1H, d, ^3J = 2.0 (Tp 3/5-positions)), 7.14 (1H, m (unbound ring)), 7.05 (3H, m (unbound ring)), 6.29, 6.22, 6.14 (each 1H, dd, ^3J = 2.2, 2.2 (Tp 4-positions)), 4.47 (1H, br d (BH)), 4.70 (1H, dd, ^2J = 17.4, ^3J = 4.8 (H4-anti to Re)), 4.01 (1H, br s (H1)), 3.52 (1H, d, ^2J = 17.4 (H4-syn to Re)), 3.29 (1H, ddd, $^3J_{PH}$ = 14.7, ^3J = 9.9, 4.8 (H3)), 3.08 (3H, s (OCH_3)), 1.64 (1H, d, ^3J = 9.9 (H2)), 1.26 (9H, d, $^3J_{PH}$ = 8.35 (PMe_3)), 1.17, 1.01 (each 3H, s (gem CH_3's)). ^{13}C NMR (125 MHz, acetone-d_6, 22 °C): δ 198.1 (C≡O), 178.4 (C═O), 146.2, 144.8, 139.8 (Tp 3/5-postions), 139.3, 136.7 (C9 and C10), 136.6, 135.2, 136.1 (Tp 3/5-positions), 131.5, 129.6, 127.0, 125.6 (unbound ring), 106.5, 106.5, 106.0 (Tp 4-positions), 53.1 (C1), 51.5 ($^2J_{PC}$ = 52.5 (C2)), 50.9 (OCH_3), 46.8 ($^2J_{PC}$ = 18.1 (C3)), 38.2 (CH_2), 25.0, 21.1 (gem CH_3's), 16.1 ($^1J_{PC}$ = 52.6 (PMe_3)). Anal. Calcd for $C_{28}H_{37}N_6O_3BPRe$: C, 45.84; H, 5.08; N, 11.46. Found: C, 45.99; H, 5.04; N, 11.08.

[TpRe(CO)(pyridine)(2,3,4-η^3-(1*H*-naphthalenium))](OTf) (2D). The complex TpRe(CO)(pyridine)(η^2-(naphthalene) (**2A/B**) (36.5 mg, 0.058 mmol) was dissolved in an acetonitrile-d_3 solution (624 mg) of triflic acid (11.3 mg, 0.075 mmol). ^{1}H NMR (500 MHz, CD_3CN, −10 °C): δ 8.37 (1H, d, ^3J = 2.4 (^{CO}Tp-H3)), 8.16 (1H, d, ^3J = 2.4 (^{Py}Tp-H3)), 8.11 (1H, d, ^3J = 2.4 (^{CO}Tp-H5)), 7.83 (1H, d, ^3J = 2.4 (^{Py}Tp-H5)), 7.83 (1H, m (pyr)), 7.75 (1H, d, ^3J = 2.4 (^{N}Tp-H5)), 7.36 (1H, m (pyr)), 7.35 (1H, d, ^3J = 7.7 (H8)), 7.26 (1H, d, ^3J = 2.2 (^{N}Tp-H3)), 7.12 (2H, m (pyr)), 7.06 (1H, ddd, ^3J = 7.4, 7.4, ^4J = 1.0 (H7)), 6.99 (1H, dd, ^3J = 7.4, 7.4 (H6)), 6.69 (1H, dd, ^3J = 2.4, 2.4 (^{CO}Tp-H4)), 6.35 (1H, dd, ^3J = 2.4, 2.4 (^{Py}Tp-H4)), 6.12 (1H, dd, ^3J = 2.4, 2.4 (^{N}Tp-H4)), 6.09 (1H, dd, ^3J = 7.3, ^4J = 1.2 (H5)), 5.90 (1H, dddd, ^3J = 7.0, 2.8, 2.8, ^4J = 2.8 (H2)), 5.09 (1H, dd, ^3J = 7.0, 6.4 (H3)), 4.97 (1H, dd, ^3J = 6.1, ^3J = 2.4 (H4)), 4.54 (1H, br s (BH)), 4.16 (1H, dd, ^2J = 24.0, ^3J = 2.4 (1/2-CH_2)), 3.94 (1H, dd, ^2J = 23.8, ^3J = 3.0 (1/2-CH_2)). ^{13}C NMR (125 MHz, CD_3CN, −10 °C): δ 196.1 (C≡O), 150.7 (^{Py}Tp-C3), 145.7 (^{N}Tp-C3), 141.6 (^{CO}Tp-C3), 139.8 (^{N}Tp-C5), 139.2 (^{Py}Tp-C5), 138.9 (^{CO}Tp-C5), 138.2 (pyr), 138.0 (C9 or C10), 137.1 (pyr), 131.4 (pyr), 130.6 (C5), 129.7 (C9 or C10), 129.1 (C7), 128.1 (pyr), 128.0 (C8), 126.8 (pyr), 126.0 (C6), 108.8 (^{CO}Tp-C4), 108.6 (^{Py}Tp-C4), 108.6 (^{N}Tp-C4), 105.4 (C2), 80.5 (C3), 71.1 (C4), 32.4 (CH_2).

TpRe(CO)(pyridine)(3,4-η^2-(2-(1,2-dihydronaphthalen-2-yl)-2-methylpropionic acid methyl ester)) (2F). An acetonitrile solution (1 mL) of triflic acid (48 mg, 0.32 mmol) and an acetonitrile solution (1 mL) of 1-methoxy-2-methyl-1-trimethylsiloxypropene (MMTP) (89 mg, 0.51 mmol) were cooled to −40 °C. The triflic acid solution was then added to TpRe(CO)(pyridine)(η^2-naphthalene) (**2A/B**) (68 mg, 0.11 mmol) and stirred for 10 min, followed by addition of the MMTP solution. After 10 min of stirring, the reaction was quenched with 2,6-lutidine (76 mg, 0.71 mmol) and subjected to flash chromatography first with 50 mL of hexanes and then with 3:1 hexanes/ether. The clear solution was removed from the inert atmosphere. The solvent was then removed under reduced pressure, and the resulting yellow residue was subjected to preparatory TLC with 3:1 hexanes/ethyl acetate. The desired band was removed and washed with 25 mL of acetone. The acetone was rotary evaporated to afford 62 mg (78%) of a yellow solid as a single diastereomer by ^{1}H NMR. CV (CH_3CN, TBAH, 100 mV/s): $E_{p,a}$ = 380 mV (NHE). IR (HATR, glaze): ν_{BH} = 2481 cm^{-1}, ν_{CO} = 1803, 1725 cm^{-1}. ^{1}H NMR (500 MHz, acetone-d_6, −10 °C): δ 8.03 (1H, d, ^3J = 2.4 (^{CO}Tp-H5)), 7.99 (1H, d, ^3J = 5.7 (*o*-pyr)), 7.97 (1H, d, ^3J = 1.7 (^{Py}Tp-H3)), 7.89 (1H, d, ^3J = 2.0 (^{CO}Tp-H3)), 7.88 (1H, d, ^3J = 2.5 (^{Py}Tp-H5)), 7.83 (2H, m (*p*-pyr and ^{N}Tp-H3 or H5)), 7.64 (1H, d, ^3J = 5.7 (*o*-pyr)), 7.14 (1H, dd, ^3J = 7.0, 6.4 (*m*-pyr)), 7.11 (1H, dd, ^3J = 7.0, 6.4 (*m*-pyr)), 7.02 (1H, d, ^3J = 7.4 (H8)), 7.00 (1H, d, ^3J = 2.0 (^{N}Tp-H3 or H5)), 6.81 (1H, ddd, ^3J = 7.4, 7.4, ^4J = 1.3 (H7)), 6.75 (1H, dd, ^3J = 7.4, 7.0 (H6)), 6.46 (1H, dd, ^3J = 2.4, 2.0 (^{CO}Tp-H4)), 6.33 (1H, dd, ^3J = 2.4, 2.0 (^{Py}Tp-H4)), 6.08 (1H, dd, ^3J = 2.4, 2.0 (^{N}Tp-H4)), 5.77 (1H, dd, ^3J = 7.0, ^4J = 1.4 (H5)), 4.6 (1H, br d (BH)), 3.69 (1H, d, ^3J = 9.1 (H4)), 3.54 (1H, dd, ^2J = 17.1, ^3J = 8.4 (H1-syn to Re)), 3.20 (3H, s (OCH_3)), 3.15 (1H, d, ^3J = 8.4 (H2)), 2.53 (1H, d, ^2J = 17.1 (H1-anti to Re)), 2.41 (1H, d, ^3J = 8.7 (H3)), 1.08, 0.85 (each 3H, s (gem CH_3's)). ^{13}C NMR (125 MHz, acetone-d_6, −10 °C): δ 199.3 (C≡O), 178.7 (C═O), 159.5 (*o*-pyr), 152.6 (*o*-pyr), 145.1 (^{Py}Tp-C3), 145.0 (C9 or C10), 143.1 (^{N}Tp-C3 or C5), 139.6 (^{CO}Tp-C3), 136.7 (^{CO}Tp-C5), 136.6 (^{Py}Tp-C5 and *p*-pyr), 135.7 (^{N}Tp-C3 or C5), 134.4 (C9 or C10), 128.0 (C8), 127.9 (C5), 126.1 (*m*-pyr), 125.4 (*m*-pyr), 124.3 (C7), 124.2 (C6), 107.2 (^{CO}Tp-C4), 107.0 (^{N}Tp-C4), 106.7 (^{Py}Tp-C4), 59.9 (C4), 56.6 (C3), 51.3 (4°-C), 51.1 (OCH_3), 45.2 (C2), 29.0 (C1), 23.2, 22.8 (gem CH_3's). Anal. Calcd for $C_{30}H_{33}N_7O_3BRe$: C, 48.91; H, 4.51; N, 13.30. Found: C, 48.84; H, 4.71; N, 13.47.

TpRe(CO)(DMAP)(η^2-naphthalene) (3A/B). 3A/B was synthesized by the same procedure as the pyridine analogue. Assignments were made with naphthalene bound at the 3,4-position. K_{eq} = 1.5 (22 °C). CV (CH_3CN, TBAH, 100 mV/s): $E_{p,a}$ = 90 mV (NHE). IR (HATR, glaze): ν_{BH} = 2479 cm^{-1} (w), ν_{CO} = 1808 cm^{-1} (vs). ^{1}H NMR (300 MHz, acetone-d_6, 20 °C), major diastereomer (β ring toward DMAP): δ 8.20, 8.00, 7.83, 7.83, 7.78, 7.72 (6H, 1:1:1:1:1:1, each a d (Tp 3,5)), 6.43, 6.27, 6.01 (3H, 1:1:1, each a dd (Tp 4)), 7.47, 7.40

(2H, 1:1, br s (DMAP 2,6)), 6.38, 6.36 (2H, 1:1, each a d, $J = 2$ (DMAP 3,5)), 3.04 (6H, s (NMe_2)), 7.32 (1H, dd, $J = 8.0$, 2.0 (naphthalene H8)), 7.24 (1H, dd, $J = 9.0$, 5.0 (naphthalene H2)), 6.97 (1H, ddd, $J = 8.0$, 8.0, 2.0 (naphthalene H7)), 6.88 (1H, ddd, $J = 8.0$, 8.0, 2.0 (naphthalene H6)), 6.45 (1H, d, $J = 9.0$ (naphthalene H1)), 6.27 (1H, d, $J = 8.0$ (naphthalene H5)), 4.24 (1H, d, $J = 8.0$ (naphthalene H4)), 3.26 (1H, dd, 8.0, 5.0 (naphthalene H3)). Selected minor diastereomer resonances (β ring toward pz): δ 3.86 (1H, br s (naphthalene H3)), 3.50 (1H, br s (naphthalene H4)), 3.06 (6H, s (NMe_2)). ^{13}C NMR (300 MHz, acetone-d_6, 20 °C): δ carbonyl not observed, 154.6, 154.3, 151.3, 145.7, 145.3, 143.6, 139.6 (2), 138.8, 137.9, 136.8, 136.6, 136.4, 136.1, 135.4, 132.3, 129.4, 128.2, 126.7, 126.4, 124.0, 123.9, 119.9 (Tp 3,5, DMAP, naphthalene unbound), 108.5, 107.1, 106.6 (2), 106.5, 105.6 (Tp 4), 65.4 (major naphthalene C4), 59.6 (major naphthalene C3), 62.6 (minor naphthalene C3), 61.2 (minor naphthalene C4), 39.1 (NMe_2 major and minor).

[TpRe(CO)(DMAP)(2,3,4-η^3-(1*H*-naphthalenium))](OTf) (3D). The complex TpRe(CO)(DMAP)(η^2-(naphthalene) (**3A/B**) (32.6 mg, 0.048 mmol) was dissolved in an acetonitrile-d_3 solution (697 mg) of triflic acid (11.3 mg, 0.075 mmol). ^{1}H NMR (500 MHz, CD_3CN, −10 °C): δ 8.32 (1H, d, $^3J = 2.4$ (^{CO}Tp-H3)), 8.18 (1H, d, $^3J = 2.1$ (^{D}Tp-H3)), 8.13 (1H, d, $^3J = 2.1$ (^{CO}Tp-H5)), 7.84 (1H, d, $^3J = 2.4$ (^{D}Tp-H5)), 7.79 (1H, d, $^3J = 2.4$ (^{N}Tp-H3 or H5)), 7.67 (1H, br s (DMAP)), 7.40 (1H, d, $^3J = 7.3$ (H8)), 7.34 (2H, br m (DMAP)), 7.27 (1H, d, $^3J = 2.1$ (^{N}Tp-H3 or H5)), 7.12 (1H, ddd, $^3J = 7.3$, 7.3, $^4J = 1.5$ (H7)), 7.07 (1H, ddd, $^3J = 7.3$, 7.3, $^4J = 1.2$ (H6)), 6.98 (1H, br s (DMAP)), 6.70 (1H, dd, $^3J = 2.4$, 2.1 (^{CO}Tp-H4)), 6.35 (1H, dd, $^3J = 2.4$, 2.4 (^{D}Tp-H4)), 6.15 (1H, dd, $^3J = 2.4$, 2.1 (^{N}Tp-H4)), 6.14 (1H, dd, $^3J = 7.3$, $^4J = 1.5$ (H5)), 5.94 (1H, dddd, $^3J = 6.7$, 2.8, 2.1, $^4J = 2.4$ (H2)), 5.09 (1H, dd, $^3J = 6.7$, 6.7 (H3)), 4.92 (1H, dd, $^3J = 6.4$, $^4J = 2.4$ (H4)), 4.64 (1H, br s (BH)), 4.16 (1H, dd, $^2J = 23.8$, $^3J = 2.1$ (1/2 CH_2)), 3.96 (1H, dd, $^2J = 23.8$, $^3J = 2.8$ (1/2 CH_2)), 3.21 (6H, s (N-Me)). ^{13}C NMR (125 MHz, CD_3CN, −10 °C): δ 196.1 (C≡O), 150.8 (^{D}Tp-C3), 146.0 (^{N}Tp-C3 or C5), 141.7 (^{CO}Tp-C3), 139.9 (^{D}Tp-C5), 139.0 (^{CO}Tp-C5), 137.2 (^{N}Tp-C3 or C5), 130.9 (C5), 129.2 (C7), 129.1 (DMAP), 128.1 (C8), 126.3 (C6), 108.9 (^{CO}Tp-C4), 108.8 (^{N}Tp-C4), 108.6 (^{D}Tp-C4), 105.4 (C2), 80.4 (C3), 71.6 (C4), 47.0 (N-Me), 32.5 (CH_2).

TpRe(CO)(DMAP)(3,4-η^2-(2-(1,2,-dihydronaphthalen-2-yl)-2-methylpropionic acid methyl ester)) (3F). An acetonitrile solution (1 mL) of triflic acid (43 mg, 0.29 mmol) was added to TpRe(CO)-(DMAP)(η^2-naphthalene) (**3A/B**) (76 mg, 0.11 mmol) dissolved in acetonitrile (1 mL). An acetonitrile solution (1 mL) of 1-methoxy-2-methyl-1-trimethylsiloxypropene (MMTP) (84 mg, 0.48 mmol) was then added to the red solution, and after 10 min of stirring, the reaction was quenched with 2,6-lutidine (89 mg, 0.83 mmol) and subjected to flash chromatography first with 50 mL of hexanes, then with 3:1 hexanes/ether, and finally with 1:1 hexanes/ether. The yellow solution was removed from the inert atmosphere. The solvent was then removed under reduced pressure, and the resulting yellow residue was subjected to preparatory TLC with 3:1 hexanes/ethyl acetate. The desired band was removed and washed with 25 mL of acetone. The acetone was rotary evaporated to afford 56 mg (64%) of a white solid as a single diastereomer by ^{1}H NMR. CV (CH_3CN, TBAH, 100 mV/s): $E_{p,a}$ = 250 mV (NHE). IR (HATR, glaze): $\nu_{BH} = 2480$ cm^{-1}, $\nu_{CO} = 1794$, 1723 cm^{-1}. ^{1}H NMR (500 MHz, acetone-d_6, −10 °C): δ 8.00 (1H, d, $^3J = 2.4$ (^{CO}Tp-H5)), 7.90 (1H, d, $^3J = 1.5$ (^{D}Tp-H3)), 7.87 (1H, d, $^3J = 2.4$ (^{D}Tp-H5)), 7.82 (1H, d, $^3J = 1.8$ (^{CO}Tp-H3)), 7.80 (1H, d, $^3J = 1.8$ (^{N}Tp-H5)), 7.66 (1H, d, $^3J = 6.4$ (*o*-DMAP)), 7.07 (1H, d, $^3J = 1.5$ (^{N}Tp-H3)), 7.05 (1H, d, $^3J = 6.7$ (*o*-DMAP)), 6.99 (1H, dd, $^3J = 5.2$ $^4J = 2.8$ (H8)), 6.78 (2H, m (H6 and H7)), 6.45 (1H, dd, $^3J = 2.1$, 2.1 (^{CO}Tp-H4)), 6.33 (2H, m (*m*-DMAP)), 6.31 (1H, dd, $^3J = 2.1$, 2.1 (^{D}Tp-H4)), 6.09 (1H, dd, $^3J = 2.4$, 2.1 (^{N}Tp-H4)), 6.02 (1H, m (H5)), 4.55 (1H, br d (BH)), 3.67 (1H, d, $^3J = 8.9$ (H4)), 3.51 (1H, dd, $^2J = 16.8$, $^3J = 8.2$ (H1-syn to Re)), 3.21 (3H, s (OCH_3)), 3.06 (1H, d, $^3J = 8.5$ (H2)), 3.01 (6H, s (N-Me)), 2.50 (1H, d, $^2J = 17.1$ (H1-anti to Re)), 2.26 (1H, d, $^3J = 8.8$ (H3)), 1.08, 0.86 (each 3H, s (gem CH_3's)). ^{13}C NMR (125 MHz, acetone-d_6, −10 °C): δ 199.5 (C≡O), 178.8 (C═O), 158.2 (*o*-DMAP), 154.0 (ipso-DMAP), 151.0 (*o*-DMAP), 146.1 (C9 or C10), 144.9 (^{D}Tp-C3), 143.1 (^{N}Tp-C3), 139.2 (^{CO}Tp-C3), 136.6 (^{CO}Tp-C5), 136.4 (^{D}Tp-C5), 135.3 (^{N}Tp-C5), 134.3 (C9 or C10), 128.2 (C5), 127.8 (C8), 124.1 and 123.7 (C6 and C7), 108.2 and 108.0 (*m*-DMAP), 107.0 (^{CO}Tp-C4), 106.7 (^{N}Tp-C4), 106.5 (^{D}Tp-C4), 58.0 (C4), 55.7 (C3), 51.1 (4°-C), 51.0 (OCH_3), 45.0 (C2), 38.9 (N-Me), 29.2 (C1), 23.7, 22.9 (gem CH_3's).

TpRe(CO)(MeIm)(3,4-η^2-(2-(1,2-dihydronaphthalen-2-yl)-2-methylpropionic acid methyl ester)) (4F). An acetonitrile solution (1 mL) of triflic acid (38 mg, 0.25 mmol) and an acetonitrile solution (1 mL) of 1-methoxy-2-methyl-1-trimethylsiloxypropene (MMTP) (73 mg, 0.41 mmol) were cooled to −40 °C. The triflic acid solution was then added to TpRe(CO)(N-MeIm)(η^2-naphthalene) (**4A/B**) (61 mg, 0.10 mmol) and stirred for 10 min, followed by addition of the MMTP solution. After 10 min of stirring, the reaction was quenched with 2,6-lutidine (73 mg, 0.68 mmol) and subjected to flash chromatography first with 50 mL of hexanes and then with 3:2 hexanes/ether. The colorless solution was removed from the inert atmosphere. The solvent was then removed under reduced pressure, and the resulting white residue was subjected to preparatory TLC using 3:1 hexanes/ethyl acetate. The relevant band was removed and washed with 25 mL of acetone. The acetone was removed by evaporation to afford 50 mg (70%) of a white solid as a single diastereomer by ^{1}H NMR. CV (CH_3CN, TBAH, 100 mV/s): $E_{p,a}$ = 220 mV (NHE). IR (HATR, glaze): $\nu_{BH} = 2479$ cm^{-1}, $\nu_{CO} = 1791$, 1723 cm^{-1}. ^{1}H NMR (500 MHz, acetone-d_6, 22 °C): δ 7.94 (1H, d, $^3J = 2.0$ (^{Im}Tp-H3)), 7.92 (1H, d, $^3J = 2.4$ (^{CO}Tp-H5)), 7.83 (1H, d, $^3J = 2.0$ (^{CO}Tp-H3), 7.81 (1H, d, $^3J = 2.4$ (^{Im}Tp-H5), 7.71 (1H, d, $^3J = 2.4$ (^{N}Tp-H3 or H5)), 7.24 (1H, d, $^3J = 2.0$ (^{N}Tp-H3 or H5)), 7.01 (1H, br s (N-MeIm)), 6.99 (1H, dd, $^3J = 1.7$, $^4J = 1.7$ (N-MeIm)), 6.96 (1H, d, $^3J = 7.4$ (H8)), 6.81 (1H, dd, $^3J = 7.4$, 7.4 (H6)), 6.73 (1H, ddd, $^3J = 7.4$, 7.4, $^4J = 1.3$ (H7)), 6.39 (1H, dd, $^3J = 2.0$, 2.0 (^{CO}Tp-H4)), 6.30 (1H, br s (N-MeIm)), 6.28 (1H, dd, $^3J = 2.0$, 2.0 (^{Im}Tp-H4)), 6.04 (1H, dd, $^3J = 2.0$, 2.0 (^{N}Tp-H4)), 5.77 (1H, d, $^3J = 7.4$ (H5)), 4.6 (1H, br d (BH)), 3.71 (3H, s (N-Me)), 3.51 (1H, dd, $^2J = 17.1$, $^3J = 8.7$ (H1-syn to Re)), 3.42 (1H, d, $^3J = 9.1$ (H4)), 3.23 (1H, s (OCH_3)), 3.08 (1H, d, $^3J = 8.7$ (H2)), 2.49 (1H, d, $^2J = 17.1$ (H1-anti to Re)), 2.20 (1H, d, $^3J = 8.7$ (H3)), 1.10, 0.89 (each 3H, s (gem CH_3's)). ^{13}C NMR (125 MHz, acetone-d_6, 22 °C): δ 199.0 (C≡O), 179.0 (C═O), 147.1 (C9 or C10), 144.9 (^{Im}Tp-C3), 143.1 (^{N}Tp-C3 or C5 and N-MeIm), 139.8 (^{CO}Tp-C3), 136.4 (^{CO}Tp-C5), 136.3 (^{Im}Tp-C5), 135.0 (^{N}Tp-C3 or C5), 134.4 (C9 or C10), 130.4 (N-MeIm), 128.0 (C8), 126.6 (C5), 123.9 (C6), 123.6 (C7), 121.9 (N-MeIm), 106.6 (^{CO}Tp-C4), 106.4 (^{Im}Tp and ^{N}Tp-C4's), 57.8 (C4), 54.8 (C3), 51.4 (4°-C), 51.0 (OCH_3), 45.5 (C2), 34.1 (N-Me), 29.4 (C1), 23.5, 23.1 (gem CH_3's). Anal. Calcd for $C_{29}H_{34}N_8O_3BRe$: C, 47.09; H, 4.63; N, 15.15. Found: C, 47.42; H, 4.70; N, 15.34.

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Supporting Information Available: X-ray diffraction data for **2F** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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