Binding Selectivity of Dihapto-Coordinated Olefins, Ketones, and Aldehydes Utilizing the Asymmetric π-Basic Metal Fragment {TpRe(CO)(1-methylimidazole)} (Tp = Hydridotris(pyrazolyl)borate)

Scott H. Meiere and W. Dean Harman*

Department of Chemistry, University of Virginia, Charlottesville, Virginia 22901

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The metal fragment {TpRe(CO)(1-methylimidazole)} (Tp = hydridotris(pyrazolyl)borate) forms stable complexes with a variety of arenes and aromatic heterocycles via dihapto coordination. In this study, a series of olefins, ketones, and aldehydes are bound to ascertain the relative steric environment near the stereogenic metal center. Utilizing this information, predictions of the diastereomeric selectivity of η^2-aromatic systems can be made.

Introduction

Recently, we reported the development of a new class of chiral rhenium dearomatization agents of general formula {TpRe(CO)(L)} (Tp = hydridotris(pyrazolyl)-borate, L = ^{t}BuNC, PMe_3, pyridine (py), 1-methylimidazole (MeIm), NH_3).[1−5] Among these, {TpRe(CO)-(MeIm)} was found to be the most versatile, binding a wide range of aromatic ligands in a dihapto manner similar to the established pentaammineosmium(II) system.[6]

Complexes of olefins[7] and carbonyls[8,9] are well represented in the literature.[10,11] Although our primary interest has been in the coordination and manipulation of aromatic molecules, assessing the stereochemistry and stability of complexes with other unsaturated ligands is also valuable in that it provides information concerning the steric and electronic features of the rhenium binding site. Assessing the stereochemical features of the corresponding {TpRe(CO)(MeIm)} olefin, aldehyde, and ketone complexes could facilitate the identification and quantification of the steric and electronic factors leading to diastereoselectivity in similar complexes of aromatic compounds.

Results and Discussion

All compounds were synthesized from TpRe(CO)-(MeIm)(η^2-benzene) (**11**) and the desired alkene, ketone, or aldehyde by taking advantage of the labile benzene ligand in **11**.[3,4] With few exceptions, isolated yields were 75−85%. Comparisons among these systems can be made utilizing ν_{CO} as well as II/I reduction potentials (Table 1).

For the set of olefin complexes (**1**−**9**), the more sterically hindered the olefin, the weaker its back-bonding interaction with the metal. This situation causes complexes of sterically congested alkenes to be more electron-rich at the metal, and thus their ν_{CO} values are generally 5−10 cm^{-1} lower than those observed for complexes of less bulky olefins. Although this trend could be explained by invoking that alkyl groups are electron-donating, steric factors clearly play a role. This point is demonstrated by comparing the cyclohexene (**9**) and the cyclopentene complexes (**8**) (equivalent alkyl donation but smaller steric profile). In this case the more sterically demanding cyclohexene results in a 4 cm^{-1} bathochromic ν_{CO} shift. A conjugated alkene is more π-acidic than a nonconjugated one, and this depletes electron density from the rhenium. Correspondingly, the diene complex **10** has a ν_{CO} (1788 cm^{-1}) that is higher energy than the cyclohexene analogue **9** (1775 cm^{-1}), and the benzene system (**11**) has a still higher stretching frequency (1794 cm^{-1}). Electrochemical measurements show Re(II/I) couples over a range of −260 to 170 mV for simple olefins, but the correlation between degree of substitution and reduction potential is poor.

Compounds in the set of η^2-ketone complexes (**12**−**16**) show similar carbon monoxide stretching frequencies despite differences in substitution. Additional groups attached to the α-carbons have little steric effect due to their ability to be oriented away from the metal complex (pinacolone is an exception, vide infra). However, in comparing formaldehyde with either acetaldehyde or acetone as ligands, the former appears to be the best π-acid, leading to a CO stretch for **17** greater than 1800 cm^{-1}. Carbonyls are stronger π-acids and weaker σ-donors than their olefinic counterparts, a point demonstrated when comparing the IR data for the isosteric complexes of formaldehyde (**17**) and ethene (**1**), acetal-

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Table 1. Infrared and Cyclic Voltammetric Data for TpRe(CO)(MeIm)(L)

Complex	Ligand	ν_{CO} (cm^{-1})	II/I vs NHE(mV)[a]
1		1786	-30[b]
2		1781	0[b,d]
3		1781	170[b], -260[b]
4		1780	-60[b]
5		1781	-60[b, d]
6		1778	70[b], -40[c]
7		1777	40[c]
8		1779	0[b]
9		1775	-50[b]
10		1788	20[b, d]
11		1794	-160[c]
12		1796	185[c]
13		1797	110[c]
14		1796	180[c]
15		1798	20[c]
16		1799	120[c]
17		1804	230[c]
18		1790	120[c]

[a] Two values represent different isomers. [b] $E_{1/2}$. [c] $E_{p,a}$. [d] Two isomers overlapping.

dehyde (**18**) and propene (**2**), or acetone (**12**) and 2-methylpropene (**4**).

For the present study, olefins were chosen with a varying degree of substitution to determine the steric environment around the metal coordination site. The rate of ethene rotation has been studied for **1**,[12] and although this study does not reveal details about the steric properties of the various quadrants, it establishes a benchmark for infrared, electrochemical, and NMR data.

To establish a reference frame for discussing olefin and carbonyl complexes bound to a stereogenic metal center, a quadrant designation was utilized.[1,2,11,13] In particular, Gladysz et al. have performed similar olefin binding studies with the Lewis acidic metal fragment $\{CpRe(NO)(PPh_3)\}^+$,[14,15] and herein analogous quadrant assignments are made (Figure 1). The bound double bond for these systems orients orthogonally to the

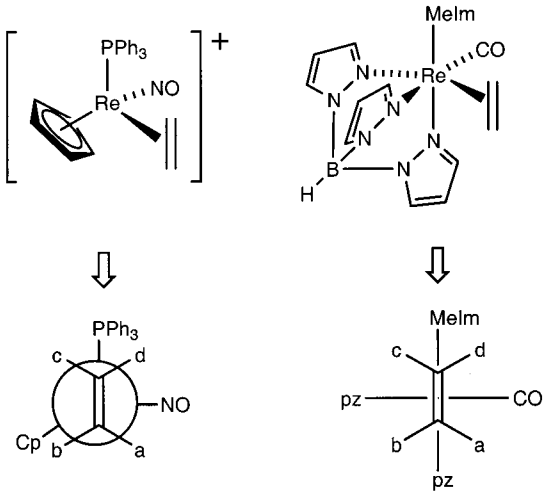

Figure 1. Comparing quadrant assignments for $[CpRe(NO)(PPh_3)(\eta^2\text{-olefin})]^+$ and $TpRe(CO)(MeIm)(\eta^2\text{-olefin})$.

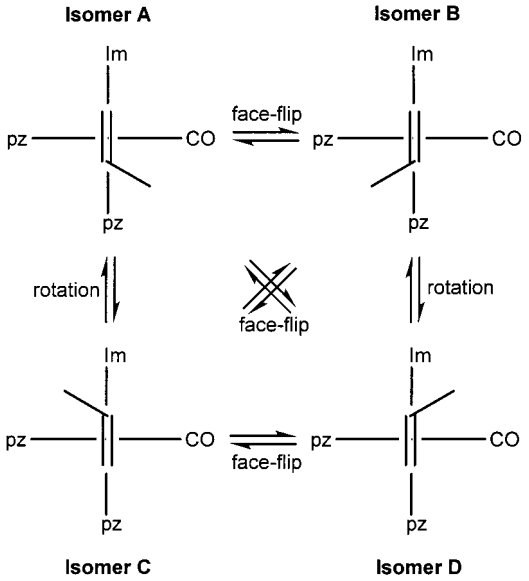

Figure 2. Interconversion of stereoisomers for TpRe(CO)(MeIm)(η^2-propene) (**2**).

metal−carbonyl bond to optimize back-bonding interactions.[2] As a result of this restriction, two diastereomers, each with a rotamer, are possible for prochiral unsaturated ligands. The routes of interconversion of these four possible species are demonstrated for the propene complex (**2**) in Figure 2 (note that no mechanisms for these linkage isomerizations are implied). Previous studies on olefin complexes have shown that the barrier for rotation is lower than interfacial isomerization (face-flip) by ~20 kcal/mol[12,16] such that at 20 °C rotations occur readily, while face-flips do not. The same can be said for aldehyde and ketone species even though these ligands can undergo an $\eta^2 \rightarrow \eta^1$ isomerization (vide infra).

Herein, diastereomers and rotamers are referenced by the quadrant where substituents off the core olefin or carbonyl unit orient themselves (see Figure 1). For example, the isomer of the propene complex (**2**) where the methyl group is oriented toward the pyrazole(pz)/

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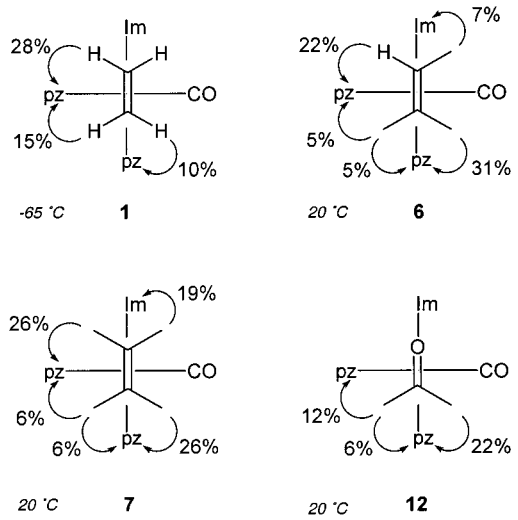
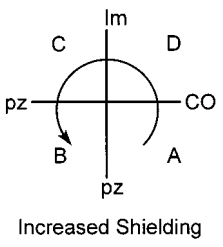


Figure 3. Observed NOE interactions for compounds **1**, **6**, **7**, and **12**.

CO quadrant, quadrant A, will be referred to as the A isomer. Rotation of isomer A 180° yields C. A face-flip of C can yield B or D, which in turn are related to each other by a rotation. It is important to note that A and C cannot be converted to B and D unless a face-flip occurs (see Figure 2).

NOE interactions with substituents in the various quadrants allow for the convenient assignment of the stereochemistry for a given complex (Figure 3). Substituents in quadrant A have a strong NOE with H3 of the pyrazole ring *trans* to MeIm. Note that for ethyl groups (e.g., in 3-pentanone) only one of the diastereotopic methylene protons shows an NOE with this pyrazole proton. In quadrant B, olefinic protons show an NOE with the pyrazole ring *trans* to CO, while methyl groups in this quadrant show a weak NOE with the pyrazole rings *trans* to CO and MeIm. Concerning quadrant C, olefinic protons and methyl groups show an NOE interaction with the pyrazole ring *trans* to CO; however no NOE with the MeIm ligand was observed. Last, an NOE for olefinic protons and methyl groups in quadrant D is observed with the methylimidazole ligand.

A comparison of complexes **1**−**9** reveals a trend for the chemical shifts for the hydrogen or methyl groups attached to the bound alkene carbons. The chemical shift is directly related to the quadrant that the substituent projects into. Specifically, a trend of B < C < D < A was observed in order of increasing δ value for substituents. The $\Delta\delta$ from B to A was found to be ∼1.5 ppm for both hydrogen or methyl signals.



The propene complex (**2**), when isolated at 22 °C, is present in a 1:1 ratio of facial isomers (i.e., (A+C):(B+D)). ^{1}H NMR shows two sets of resonances, one broad and one sharp. After lowering the temperature to −20 °C, the sharp resonances remain so, and NOE experiments confirm these stem from isomer A (favored over its rotamer by >20:1). The broad resonances develop into two sets of sharp signals with a 9:1 ratio favoring rotamer D over B.

When **2** is heated (145 °C, diglyme-d_{14}), the ratio of B/D to A/C increases. However, new signals also appear, and it is difficult to determine whether the increased ratio is a result of an interfacial isomerization or selective decomposition. Heating at a lower temperature (115 °C) in acetone-d_6 slowly produces the acetone complex ($t_{1/2}$ > 2 days), but the B/D to A/C ratio also increases. These experiments do not confirm but suggest that B/D is thermodynamically favored over A/C. Furthermore, they suggest the initial 1:1 ratio is a result of similar kinetic barriers for complexation rather than differences in stability of the products.

Some conclusions can be made about the steric environment about the metal with data from the propene complex (**2**) alone. Quadrants A and D are the favored quadrants in which to place a methyl group. Reliable comparisons, however, cannot be made between A/C and B/D due to the inability to observe an interfacial isomerization. In any case, a comparison of the quadrants in question can be accomplished through the study of additional olefins.

The complex of the 1,1-disubstituted olefin 2-methylpropene (**4**) has only two possible orientations, the rotamers AB and CD, since the alkene is not prochiral. NMR data show only one static compound, the AB rotamer, revealing an energetic preference for methyl groups in quadrants A and B relative to quadrants C and D. The complex of the *cis*-1,2-disubstituted olefin cyclohexene (**9**), like the 1,1-disubstituted analogue, can exist as only two rotamers. NMR reveals only one set of well-defined resonances, the AD rotamer, demonstrating a steric preference for the combination of quadrants A and D over the combination of quadrants B and C.

Aromatic systems that we have previously studied[4,16] are analogous to *cis*-1,2-disubstituted olefins with inequivalent substituents. These systems are better suited for comparing quadrants A and D due to a much lower barrier to interfacial isomerization. However, these systems can only provide information about steric interactions with the β-position of the coordinated double bond, not the α-position, as would be the case with propene. An example of this selectivity is found in the naphthalene analogue, which favors the unbound β-ring toward quadrant D over A by 5:1 at 20 °C and >20:1 at −20 °C.[3]

The complex of the 1,1,2-trisubstituted olefin 2-methyl-2-butene (**6**) initially resembles the distribution of coordinated products observed for the propene complex (**2**). Here again, ^{1}H NMR data show two sets of resonances, one broad and one sharp, in a 1:1 ratio. The sharp signals correspond to the ABD isomer, which is favored over its rotamer, BCD. Signals for the other species, ABC and ACD, are broadened together due to interconversion of the rotamers.

When an NMR tube of 2-methyl-2-butene complex (**6**) is heated at 60 °C for 5 h (acetone-d_6), complete (> 95%) conversion to the ABD isomer occurs. The face-flip

barrier, too large to be overcome in the case of propene or ethene,[16] now is low enough to yield a thermodynamic ratio of products upon heating. With this observation, it is clear that quadrant C is the most sterically congested. The *trans*-2-butene complex (**3**), present initially as a 1:1 ratio of AC and BD facial isomers, also has an isomer (AC) that cannot avoid placing a methyl group in quadrant C. Thus, an interfacial isomerization can be achieved by prolonged heating. Since *trans*-2-butene possesses a smaller steric profile than 2-methyl-2-butene, **3** must be heated at a higher temperature and for a longer time compared to **6** for complete (>95%) isomerization (AC to BD) to occur (100 °C, 30 h, acetone-d_6). No distinguishable difference for these isomers was observed in their infrared spectra, and the observed ν_{CO} shows no significant broadeneing (<10% larger fwhm, cf. compounds **1**, **9**) when both AC and BD isomers are present. Electrochemical experiments on the *trans*-2-butene complex (**3**), however, provided an unexpected contrast. As seen in Table 1, the cyclic voltammogram for this compound features two reversible II/I couples *greater than 400 mV apart* (170 mV; BD isomer, and −260 mV; AC isomer). A cyclic voltammogram in acetone yielded a result similar to that obtained in *N*,*N*-dimethylacetamide, suggesting that solvent is not displacing an arm of the Tp ligand. By steric arguments, the BD isomer is expected to have a stronger bonding interaction with rhenium and therefore have a more positive II/I couple, provided that the back-bonding interaction dominates (vide supra). This hypothesis was confirmed by taking a cyclic voltammogram of the AC/BD mixture after heating that showed a couple with $E_{1/2}$ = 170 mV as the dominant feature.

A separation of 400 mV in reduction potentials between isomers is much larger than expected, and this observation suggests that the steric environment in quadrant C (vide infra) is significantly more destabilizing than the other quadrants. By utilizing the reduction potentials of the *trans*-2-butene complex (**3**), free energies of isomerization can be related by establishing a thermodynamic cycle (Figure 4). Here we make the assumption that for Re(II) ΔG for facial isomerization of the *trans*-2-butene complex **3** from its BD to AC form is greater than zero. In other words, we assume that the steric environment for rhenium(II) resembles that of Re(I) in that the BD isomer should be thermodynamically favored. By combining half-reactions for the two isomers and taking isomerization free-energy for Re(II) as $\Delta G > 0$, a lower limit of $\Delta G > 9.9$ kcal/mol is determined favoring the BD isomer over the AC isomer.

At this point, it is known that quadrant C is the most sterically congested and quadrant D is the least congested. To compare steric environments of quadrants A and B, complexes of prochiral 1,1-disubstituted olefins would be revealing; however these olefins are unlikely to undergo a face-flip (as in the case of 2-methyl-1-butene (**5**), present in a 1:1 ratio of A and B isomers), rendering the determination of the equilibrium constant difficult. Olefins of the *trans*-1,2-disubstituted variety, such as *trans*-2-butene (**3**), will face-flip upon extended heating. However, quadrant C biases any comparison between quadrants A and B. Aldehydes and ketones offer a possible solution to this dilemma, as their barriers to interfacial isomerization are considerably lower than for olefins, owing to a purported oxygen-bound η^1 intermediate.[17−19]

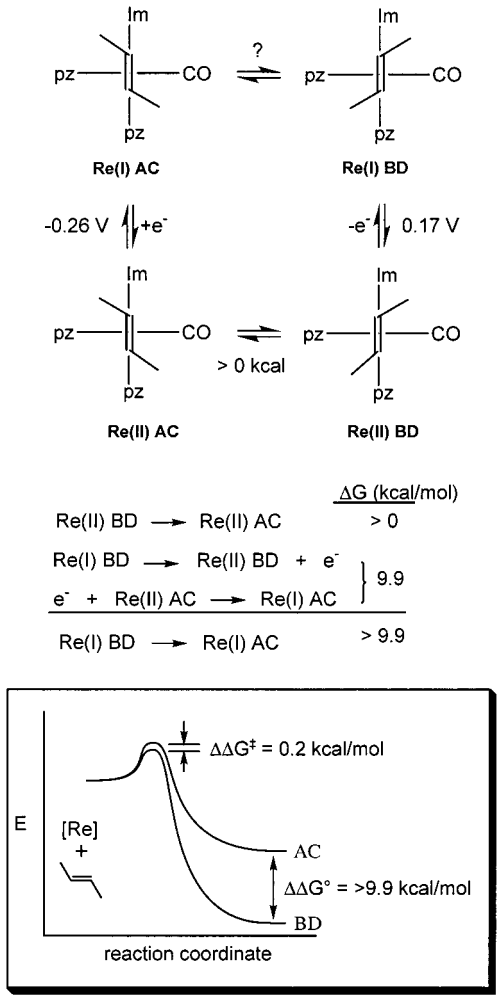


Figure 4. Thermodynamic cycle for the *trans*-2-butene complex (**3**).

Similarly to the 2-methylpropene complex (**4**), the acetone complex (**12**) exists as a single isomer. More surprisingly, the formaldehyde complex (**17**) only shows one set of proton NMR resonances, slightly broadened at 20 °C, but sharp at −20 °C. This observation could indicate that the aldehydic hydrogen atom is sterically significant when placed in quadrant C; however, the highly dipolar nature of the carbonyl may also prove significant. For all carbonyl compounds examined in this study (**12**−**18**), the only isomers observed (by NMR) are η^2-coordinated with the carbonyl oxygen oriented toward the imidazole ligand.

The NMR resonances corresponding to the acetaldehyde complex (**18**) are slightly broadened at 20 °C, but at −20 °C a 4:1 thermodynamic preference for isomer A over isomer B is observed. Prochiral ketone complexes, however, show little selectivity concerning quadrants A and B. Presumably, this observation is due to the ability of any substituents off the α-carbon being able to rotate away from the metal. For example, the methylene protons of the methyl ethyl ketone (MEK)

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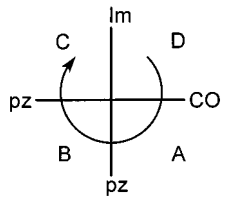
complex (**13**) are diastereotopic (^{1}H NMR), and the observed thermodynamic ratio is 1:1 for the ethyl group in quadrants A or B. For the methyl isopropyl ketone complex (**15**) selectivity is slightly improved over the MEK complex (**13**) with a thermodynamic ratio of 2:1 favoring the isopropyl group in quadrant A over B. A bound pinacolone (*tert*-butyl methyl ketone) ligand, however, would be unable to avoid a steric interaction of at least one methyl group with the metal, and in fact this ketone complex could not be isolated or observed in situ by ^{1}H NMR. Note that pentaammineosmium(II) is also unable to bind pinacolone in a dihapto fashion.[20] The rate of equilibration (20 °C) of the rhenium-bound carbonyl isomers for MEK (**13**) and isopropyl methyl ketone (**15**) was considerably slower than that for their osmium analogues.[20] This difference is likely due to the increased electron richness of the rhenium fragment. Starting with a single isomer of the MEK complex (**15**) (separated by chromatography), equilibrium was established after 16 h at 20 °C ($k = 8.9 \times 10^{-6}$ s^{-1}).[21] For $[Os(NH_3)_5(\eta^2\text{-acetone})]^{2+}$ the rate constant was found to be 1.3 s^{-1}. The sterically larger isopropyl methyl ketone complex (**15**) equilibrates after 2 h at 20 °C. The increased steric interaction decreases the energy difference between η^2 and η^1 bound states.[10]

Finally, cyclohexanone was coordinated (**16**) to ascertain if extending substituents out over the pyrazole ring *trans* to imidazole would have any effect on AB versus CD selectivity. As expected, only the AB isomer was observed due to the sterically congested quadrant C, the preference for oxygen to orient toward imidazole, and the ability of the ring to pucker away from the metal.

Taking stock, the order of steric congestion, from most hindered to least hindered, for the four quadrants has been established: $E_C > E_B > E_A > E_D$ (where E_A represents strain energy for a methyl group in quadrant A, etc.).



Increased Steric Crowding

Utilizing data from the propene complex (**2**) to compare steric strain in quadrants B and D ($E_B > E_D$; $K > 9$; $\Delta G = 1.1$ kcal/mol at −20 °C), the acetaldehyde complex (**18**) to compare quadrants A and B ($E_B > E_A$; $K = 4$, $\Delta G = 0.8$ kcal/mol at 20 °C), isomerization information from the *trans*-2-butene complex (**3**) ($E_A + E_c \gg E_B + E_D$; see Figure 4), and kinetic information from face-flip and rotation dynamics (~32 and ~12 kcal, respectively based on earlier studies)[12,16] a graphical representation can be constructed (Figure 5) of the relative steric strain energies of the four quadrants with a methyl group (e.g., propene complex **2**). On the basis of these numbers, the relationship among the quadrant strain energies is more accurately expressed as $E_c \gg E_B > E_A > E_D$.

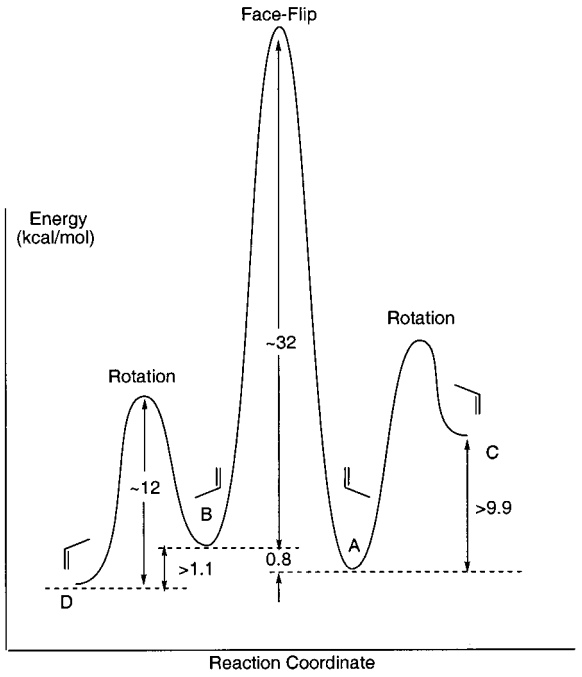


Figure 5. Relative energies for various rotamers or stereoisomers of the propene complex (**2**).

With an assessment of the steric interactions between a π-bound ligand and the {TpRe(CO)(MeIm)} system in hand, we are able to rationalize or predict the binding selectivities for arene and aromatic heterocycle complexes with this rhenium system. As an example, we consider the 1,2-dimethyl and 1,2,5-trimethylpyrrole ligands. One would predict based on the results herein that 1,2-dimethylpyrrole, where the rhenium will always bind the less hindered double bond, would orient the 1-methyl toward MeIm (quadrant D over A). 1,2,5-trimethylpyrrole, however, where the double bond coordinated to the metal is trisubstituted, should show the opposite selectivity. Orienting the 1-methyl toward quadrant A avoids placing a methyl group in quadrant C (analogous to 2-methyl-2-butene). These two complexes have been synthesized in their 3H protonated forms, and, as expected, the 1,2-dimethylpyrrole derivative favors 1-methyl toward MeIm (12:1) and 1,2,5-trimethylpyrrole favors 1-methyl toward pz (>19:1).[22]

Conclusion

A variety of olefins and carbonyl-containing ligands have been coordinated to the asymmetric metal fragment {TpRe(CO)(MeIm)}. Diastereomeric ratios have been determined on the basis of spectroscopic characterization as well as NOE data. From these data, quadrant C, defined by a pyrazole ring (*trans* to CO) and imidazole, was found to be highly sterically encumbered relative to the other three quadrants. The elucidation of the steric profile at the chiral metal coordination site allows the binding selectivity of other ligands to be predicted. Especially relevant are cases where barriers to isomerization are sufficiently low that coor-

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dination selectivity is under thermodynamic control such as the case with aromatic ligands.

Experimental Section

General Methods. NMR spectra were obtained on a 300 or 500 MHz Varian INOVA spectrometer. 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). Resonances in the ^{1}H NMR due to pyrazole ligands are listed by chemical shift and multiplicity only (all pyrazole coupling constants are 2 Hz). Infrared spectra (IR) were recorded on a MIDAC Prospect Series (model PRS) spectrometer (resolution ±4 cm^{-1}) as a glaze (evaporated THF) 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 −1.9 V with a glassy carbon working electrode, *N*,*N*-dimethylacetamide (DMAc) solvent, and tetrabutylammoniumhexaflurophosphate (TBAH) electrolyte (∼0.1 M). All potentials are reported versus NHE (normal hydrogen electrode) using cobaltocenium hexafluorophosphate ($E_{1/2}$ = −0.78 V) or ferrocene ($E_{1/2}$ = 0.55 V) as an internal standard. The peak to peak separation was less than 100 mV for all reversible couples. Elemental analysis (EA) was performed with a Perkin-Elmer 2400 Series II CHNS/O analyzer. EA was performed only for the representative olefin, ketone, and aldehyde complexes **9**, **12**, and **18**. Unless otherwise noted, all synthetic reactions were performed under a dry nitrogen atmosphere. CH_2Cl_2, benzene, THF (tetrahydrofuran), and hexanes were purged with nitrogen and purified by passage through a column packed with activated alumina.[23] Other solvents were thoroughly degassed with nitrogen prior to use. Deuterated solvents were used as received from Cambridge Isotopes. Other reagents were used as received. Compounds **1**[12] and **11**[3,4] have been previously reported. Purification of all compounds to remove trace Re(II) or free ligand impurities may be performed on silica gel (benzene, then ether, then THF).

TpRe(CO)(MeIm)(η^2-olefin) (2−10). For gases (**2**−**4**): To a 100 mL round-bottom Schlenk flask was added **11** (0.10 g, 0.17 mmol) and a stir bar. THF (20 mL) was added and the flask charged with the appropriate olefin (1 atm). The solution was stirred (20 h, 22 °C). Hexanes (75 mL) were added, 40 mL of solvent was removed under reduced pressure, and the suspension was filtered through a 30 mL medium frit. The precipitate was washed with hexanes (2 × 15 mL) and dried in vacuo. For liquids (**5**−**10**): To a 100 mL round-bottom flask was added **11** (0.10 g, 0.17 mmol) and a stir bar. THF (20 mL) and the appropriate olefin (5 mmol) were added. The solution was stirred (20 h, 22 °C). Hexanes (75 mL) were added, 40 mL of solvent was removed under reduced pressure, and the suspension was filtered through a 30 mL medium frit. The precipitate was washed with hexanes (2 × 15 mL) and dried in vacuo. Yields: 75−85%.

L = propene (2): light beige solid. ^{1}H NMR (acetone-d_6, 20 °C, δ), resonances reported for isomer A and B/D (1:1), bound propene resonances for rotamers B/D not observed (broad): 7.99, 7.85, 7.83, 7.76, 7.73, 7.72, 7.67, 7.55, 7.42, 7.23 (11H, 1:2:1:1:1:1:1:1:1:1:1, each a d (or fine dd with J < 1), Tp 3,5), 6.26, 6.18, 6.09, 6.07 (4H, 1:1:1:1, each a t, Tp 4), 6.27, 6.17 (2H, 1:1, each a broad s, Tp 4), 7.72, 7.47, 7.02, 6.74 (4H, 1:1:1:1, each a br t, Im), 6.95, 6.40 (2H, 1:1, each a t, J = 1.5, Im), 3.81 (3H, br s, MeIm, isomer B/D), 3.75 (3H, s, MeIm isomer A), 2.30, 2.12 (2H, 1:1, dd, J = 9, 2, propene geminal protons, isomer A), 2.18 (3H, d, J = 6, propene methyl, isomer A), 1.88 (1H, m, propene proton geminal to methyl, isomer A). ^{13}C NMR (acetone-d_6, −20 °C, δ); resonances reported for isomers A and D. Carbonyl not observed: 146.7, 145.5, 143.6, 143.1, 142.3, 142.1, 139.5, 139.0, 136.2, 135.9, 135.0, 134.9 (2), 132.1, 131.5, 129.0 (Tp 3,5, Im), 122.0, 121.8 (Im), 106.6, 106.4, 106.3 (3), 106.1 (Tp 4), 55.7, 51.4, 49.9, 48.9 (propene olefin), 34.1, 34.0 (NMe), 24.1, 23.6 (propene Me). ^{1}H NMR (acetone-d_6, −20 °C, δ); select resonances reported: 3.84, 3.77 (6H, 1:1, each a s, MeIm), 2.15, 1.97 (6H, 1:1, each a d, J = 6, propene Me), 0.81 (d, propene Me, Isomer B). IR: ν_{CO} 1781 cm^{-1} (vs), ν_{BH} 2469 cm^{-1} (w). CV: Two overlapping signals (isomer A and B/D) $E_{1/2}$ = 0.0 V (II/I).

L = *trans*-2-butene (3): light beige solid. ^{1}H NMR (acetone-d_6, 20 °C, δ), resonances reported for isomer AC and BD (1:1): 7.90, 7.87, 7.86, 7.82, 7.79, 7.77, 7.69, 7.68, 7.67, 7.62, 7.31, 7.09 (12H, 1:1:1:1:1:1:1:1:1:1:1:1, each a d (or fine dd with J < 1), Tp 3,5), 6.28, 6.24, 6.22, 6.19, 6.04, 6.03 (6H, 1:1:1:1:1:1, each a t, Tp 4), 7.81, 7.43, 6.61 (3H, 1:1:1, each a br t, Im), 7.05, 7.03, 6.88 (3H, 1:1:1, each a t, J = 1.5, Im), 3.83 (3H, s, MeIm, BD isomer), 3.79 (3H, s, MeIm, AC isomer), 2.91 (1H, dq, J = 9, 6, olefinic proton, quadrant A, BD isomer), 2.15 (1H, dq, J = 9, 6, olefinic proton, quadrant C, BD isomer), 2.32 (2H, br s, olefinic protons, quadrants B and D, AC isomer), 1.93 (3H, d, J = 6, Me, quadrant D, BD isomer), 0.79 (3H, d, J = 6, Me, quadrant B, BD isomer), 1.77 (6H, overlapping d, Me, quadrants A and C, AC isomer). ^{13}C NMR (acetone-d_6, 20 °C, δ): 199.7, 199.5 (CO), 146.7, 146.3, 144.3, 143.3, 143.2, 142.5, 142.4, 142.2, 136.4, 135.9, 135.2, 134.8, 134.6, 133.4, 132.4 (Tp 3,5, Im), 122.1, 121.9 (Im), 107.0, 106.2, 106.1, 105.9 (2), 105.8 (Tp 4), 58.3 (bound olefin, toward Im, BD isomer), 55.7 (bound olefin, toward pz, BD isomer), 54.3 (2) (bound olefin, AC isomer), 34.3 (NMe), 23.8 (Me, quadrant D, BD isomer), 22.4 (2) (Me, AC isomer), 18.2 (Me, quadrant B, BD isomer). IR: ν_{CO} 1781 cm^{-1} (vs), ν_{BH} 2484 cm^{-1} (w). CV: $E_{1/2}$ = 0.17 V (II/I) (BD isomer), $E_{1/2}$ = −0.26 V (II/I) (AC isomer).

L = 2-methylpropene (4): light beige solid. ^{1}H NMR (acetone-d_6, 20 °C, δ): 8.05, 7.84, 7.78, 7.70, 7.59, 7.16 (6H, 1:1:1:1:1:1, each a d (or fine dd with J < 1), Tp 3,5), 6.26, 6.22, 6.05 (3H, 1:1:1, each a t, Tp 4), 7.45 (1H, br t, Im), 6.96, 6.37 (2H, 1:1, each a t, J = 1.5, Im), 3.77 (3H, s, MeIm), 2.50 (1H, br s, 2-methylpropene geminal proton, quadrant D), 1.97 (1H, br s, 2-methylpropene geminal proton, quadrant C), 2.30 (3H, s, 2-methylpropene Me, quadrant A), 0.81 (3H, br s, 2-methylpropene Me, quadrant B). ^{13}C NMR (acetone-d_6, −20 °C, δ), carbonyl not observed: 144.8, 143.9, 142.3, 141.2, 136.5, 135.8, 134.7, 132.2 (Tp 3,5, Im), 121.5 (Im), 106.5, 106.3, 106.0 (Tp 4), 56.8, 55.2 (2-methylpropene olefin), 34.0 (NMe), 33.5 (2-methylpropene Me, quadrant A), 26.7 (2-methylpropene Me, quadrant B). ^{1}H NMR (acetone-d_6, −20 °C, δ), select resonances reported: 3.78 (3H, s, MeIm), 2.46 (1H, d, J = 1.5, 2-methylpropene geminal proton, quadrant D), 1.92 (1H, d, J = 1.5, 2-methylpropene geminal proton, quadrant C), 2.28 (3H, s, 2-methylpropene Me, quadrant A), 0.74 (3H, s, 2-methylpropene Me, quadrant B). IR: ν_{CO} 1780 cm^{-1} (vs), ν_{BH} 2479 cm^{-1} (w). CV: $E_{1/2}$ = −0.06 V (II/I), $E_{p,a}$ = 1.11 V (III/II).

L = 2-methyl-1-butene (5): light beige solid. ^{1}H NMR (acetone-d_6, 20 °C, δ), both isomers reported: 8.07, 8.04, 7.84, 7.77, 7.76, 7.70, 7.69, 7.58, 7.15 (12H, 1:1:2:1:1:1:1:3:1, each a d (or fine dd with J < 1), Tp 3,5), 6.26, 6.20, 6.04 (6H, 1:1:1, each a t, Tp 4), 7.58, 7.46, 7.44 (3H, 1:1:1, each a br t, Im), 6.96, 6.36, 6.34 (3H, 1:1:1, each a t, J = 1.5, Im), 3.77, (6H, 1:1, each a s, MeIm), 2.56, 2.43 (2H, 1:1, br s, olefinic protons, quadrant D, both isomers), 2.02, 1.90 (2H, 1:1, br s, olefinic protons, quadrant C, both isomers), 2.58, 2.22 (2H, 1:1, each a dq, J = 18, 6, CH_2, quadrant A), 1.11 (3H, dd, J = 6, 6, CH_3, quadrant A), 0.68 (3H, s, CH_3, quadrant B), 2.37 (3H, s, Me α to olefin, quadrant A), 0.81 (3H, s, Me α to olefin, quadrant B). Note: CH_2 in quadrant B not observed. ^{13}C NMR (acetone-

(23) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518−1520.

d_6, 21 °C, δ): 200.7, 200.5 (CO), 145.4 (2), 144.1, 142.5, 142.4, 141.3, 141.2, 136.5 (2), 135.9, 134.7, 132.7 (2) (Tp 3,5, Im), 129.1(2), 121.6(2) (Im), 106.4 (2), 106.3 (2), 106.2, 106.1 (Tp 4), 64.3 (quat. olefin), 54.4, 54.1 (=CH_2), 39.8 (CH_2, quadrant A), 34.2(2) (NMe), 33.0 (Me, α to olefin, quadrant A), 29.1 (CH_2, quadrant B), 22.1 (Me, α to olefin, quadrant B), 18.3 (CH_3, quadrant A), 16.2 (CH_3, quadrant B) IR: ν_{CO} 1781 cm^{-1} (vs), ν_{BH} 2477 cm^{-1} (w). CV: $E_{1/2} = -0.06$ V (II/I), $E_{p,a} = 1.12$ V (III/II).

L = 2-methyl-2-butene (6): light beige solid. ^{1}H NMR (acetone-d_6, 20 °C, δ), only isomer ABD reported: 8.04, 7.85, 7.84, 7.77, 7.63, 7.24 (6H, 1:1:1:1:1:1, each a d (or fine dd with $J < 1$), Tp 3,5), 6.31, 6.22, 6.00 (3H, 1:1:1, each a t, Tp 4), 7.77 (1H, br t, Im), 7.05, 6.87 (2H, 1:1, each a t, $J = 1.5$, Im), 3.83 (3H, s, MeIm), 2.17 (1H, q, $J = 6$, olefinic proton, quadrant C), 2.11 (3H, s, Me, quadrant A), 1.75 (3H, d, $J = 6$, Me, quadrant D), 0.71 (3H, s, Me, quadrant B). ^{13}C NMR (acetone-d_6, 20 °C, δ), only isomer ABD reported: 200.5 (CO), 145.1, 143.2, 142.1 (2), 136.4, 136.0, 134.7, 132.2 (Tp 3,5, Im), 121.8 (Im), 106.4, 106.1, 106.0 (Tp 4), 57.6 (2) (olefin), 34.3 (NMe), 28.6, 27.9 (Me, quadrant A and quadrant D), 20.5 (Me, quadrant B). IR: ν_{CO} 1778 cm^{-1} (vs), ν_{BH} 2471 cm^{-1} (w). CV: Isomer ABD $E_{1/2} = 0.07$ V (II/I), isomer ABC/ACD $E_{p,a} = -0.04$ V (II/I).

L = 2,3-dimethyl-2-butene (7): light beige solid. ^{1}H NMR (acetone-d_6, 22 °C, δ): 8.17, 8.01, 7.87, 7.81, 7.58, 7.03 (6H, 1:1:1:1:1:1, each a d (or fine dd with $J < 1$), Tp 3,5), 6.28, 6.26, 5.95 (3H, 1:1:1, each a t, Tp 4), 7.76, 6.97 (2H, 1:1, each a br t, Im), 7.10 (1H, t, $J = 1.7$, Im), 3.86 (3H, s, MeIm), 2.10 (3H, br s, Me, quadrant A), 1.97 (3H, br s, Me, quadrant D), 1.50 (3H, br s, Me, quadrant C), 0.84 (3H, br s, Me, quadrant B). ^{13}C NMR (acetone-d_6, 22 °C, δ), olefinic carbons not observed: 199.3 (CO), 145.6, 143.4, 142.6, 142.1, 136.9, 136.8, 134.3 (Tp 3,5, Im), 133.0, 121.8 (Im), 106.3, 106.0, 105.7 (Tp 4), 34.4 (NMe), 32.6, ~30, 26.9, 26.6 (Me, broad). IR: ν_{CO} 1777 cm^{-1} (vs), ν_{BH} 2470 cm^{-1} (w). CV: $E_{p,a} = 0.04$ V (II/I).

L = cyclopentene (8): light beige powder. ^{1}H NMR (acetone-d_6, 20 °C, δ): 8.03, 7.85, 7.72, 7.71, 7.64, 7.30 (6H, 1:1:1:1:1:1, each a d, Tp 3,5), 6.30, 6.17, 6.07 (3H, 1:1:1, each a t, Tp 4), 7.68, 6.99, 6.61 (3H, 1:1:1, each a br t, Im), 3.79 (3H, s, NMe), 3.10 (2H, m, cyclopentene), 2.99 (1H, dd, $J =$ 11, 6, cyclopentene), 2.61 (1H, dd, $J = 13$, 8, cyclopentene), 2.51 (1H, dd, $J = 6$, 5, cyclopentene), 2.31 (1H, dd, $J = 13$, 8, cyclopentene), 2.26 (1H, dd, $J = 20$, 10, cyclopentene), 1.44 (1H, dd, $J = 20$, 8, cyclopentene). ^{13}C NMR (acetone-d_6, 20 °C, δ): 200.4 (CO), 144.7, 143.1, 141.5, 139.8, 136.2, 135.8, 134.8 (Im, Tp 3,5), 131.7, 122.2 (Im), 106.4, 106.3, 106.2 (Tp 4), 66.4 (bound olefin, toward Im), 62.8 (bound olefin, toward pz), 35.9, 35.2, 23.7 (cyclopentene), 34.3 (MeIm). IR: ν_{CO} 1779 cm^{-1} (vs), ν_{BH} 2480 cm^{-1} (w) CV: $E_{1/2} = 0.00$ V (II/I), $E_{p,a} = 1.12$ V (III/II).

L = cyclohexene (9): light beige powder; bound at 1,2-position, 1 position in quadrant C. ^{1}H NMR (acetone-d_6, 20 °C, δ): 8.05, 7.84, 7.69, 7.74, 7.61, 7.37 (6H, 1:1:1:1:1:1, each a d, Tp 3,5), 6.30, 6.18, 6.05 (3H, 1:1:1, each a t, Tp 4), 7.76 (1H, br t, Im), 7.01 (1H, t, $J = 1.5$, Im), 6.72 (1H, t, $J = 1.5$, Im), 3.82 (3H, s, NMe), 2.65 (1H, td, $J = 2$, 6, cyclohexene), 2.78, 2.36, 2.24, 1.80, 1.33 (9H, 3:1:1:2:2, each a m, cyclohexene). ^{13}C NMR (CD_2Cl_2, 20 °C, δ): 200.1 (CO), 144.4, 142.5, 140.6, 138.7, 135.7, 135.6, 134.4 (Im, Tp 3,5), 131.9, 121.0 (Im) 105.9 (2), 105.8 (Tp 4), 57.5 (cyclohexene 1), 53.8 (cyclohexene 2), 31.0, 30.4, 24.8, 24.1 (cyclohexene 3, 4, 5, 6), 34.4 (MeIm). IR: ν_{CO} 1775 cm^{-1} (vs), ν_{BH} 2481 cm^{-1} (w). CV: $E_{1/2} = -0.05$ V (II/I). Anal. Calcd for $ReC_{20}H_{26}N_8BO$: C, 40.61; H, 4.44; N, 18.95. Found: C, 40.54; H, 4.43; N, 19.04.

L = 1,3-cyclohexadiene (10): off-white solid. ^{1}H NMR (acetone-d_6, 20 °C, δ), assignments were made considering olefin bound at 1,2 position; the two isomers (1:1) were distinguished by prime designations, with the 1,2 isomer placing the 1 position proton in quadrant C and the 1′,2′ isomer placing the 1′ position proton in quadrant B: 8.04, 7.87, 7.87, 7.83, 7.76, 7.69, 7.48, 7.30, 7.22 (9H, 1:1:1:1:1:1:1:1:1, each a d (or fine dd with $J < 1$), Tp 3,5), 7.71 (3H, three isochronous d, Tp 3,5), 7.71 (1H, buried Im), 7.55 (1H, br t, Im), 7.05, 7.01, 6.70, 6.59 (4H, 1:1:1:1, each a t, $J = 1.5$, Im), 6.32, 6.31, 6.21, 6.16, 6.07 (6H, 1:1:1:1:2, each a t, Tp 4), 3.82, 3.78 (6H, 1:1, each a s, MeIm), 6.47 (1H, ddd, $J = 10$, 6, 3, cyclohexadiene 3), 6.22 (1H, ddd, $J = 10$, 6, 3, cyclohexadiene 3′), 5.16 (1H, ddd, $J = 19$, 4, 2, cyclohexadiene 4), 5.13 (1H, ddd, $J = 19$, 4, 2, cyclohexadiene 4′), 3.16 (1H, tdd, $J = 14$, 7, 4, cyclohexadiene 6), 3.04 (1H, tdd, $J = 14$, 7, 4, cyclohexadiene 6′), 2.87 (1H, dd, $J = 9$, 5, cyclohexadiene 2′), 2.41 (1H, dd, $J = 9$, 5, cyclohexadiene 2), 2.80 (1H, br dt, $J = 9$, cyclohexadiene 1), 2.14 (1H, br dt, $J = 9$, cyclohexadiene 1′), 2.50 (2H, isochronous m, cyclohexadiene 5, 5′), 2.30 (1H, br ddt, $J = 14$, 7, cyclohexadiene 6′), 2.00 (1H, br ddt, $J = 14$, 7, cyclohexadiene 6), 1.80 (1H, br dt, $J = 18$, 6, cyclohexadiene 5′), 1.74 (1H, br dt, $J = 18$, 6, cyclohexadiene 5). ^{13}C NMR (acetone-d_6, 22 °C, δ), carbonyl not observed: 146.9, 144.9, 143.2, 143.0, 142.1, 141.8, 139.4, 139.3, 136.5, 136.4, 136.1 (3), 135.6, 135.0 (2) (Tp 3,5, Im, olefin 3, 3′), 132.4, 131.9 (Im), 122.4, 122.0 (Im), 119.4, 119.2 (olefin 4, 4′), 106.5, 106.4 (4), 106.3 (Tp 4), 60.0, 56.3, 51.7, 49.6 (olefin 1, 1′, 2, 2′), 34.3 (2) (NMe), 24.0 (2), 23.6 (2) (5,5′, 6,6′). IR: ν_{CO} 1788 cm^{-1} (vs), ν_{BH} 2478 cm^{-1} (w). CV: $E_{1/2} = 0.02$ V (II/I).

TpRe(CO)(MeIm)(η^2-ketone) (12−16). To a 100 mL round-bottom flask was added **11** (0.10 g, 0.17 mmol) and a stir bar. The appropriate ketone was added in enough volume to dissolve the solid (~10 mL). The solution was stirred (16 h, 22 °C). Hexanes (75 mL) were added, 40 mL of solvent was removed under reduced pressure, and the suspension was filtered on a 30 mL medium frit. The precipitate was washed with hexanes (2 × 15 mL) and dried in vacuo. Yields: 75−85%.

L = acetone (12): light yellow solid. ^{1}H NMR (acetone-d_6, 20 °C, δ): 8.13, 7.83, 7.75, 7.72, 7.38 (6H, 1:1:2:1:1, each a d (or fine dd with $J < 1$), Tp 3,5), 6.25, 6.22, 6.12 (3H, 1:1:1, each a t, Tp 4), 7.72 (1H, br t, Im), 6.98, 6.18 (2H, 1:1, each a t, $J = 1.5$, Im), 3.84 (3H, s, MeIm), 2.54 (3H, s, Me, quadrant A), 0.98 (3H, s, Me, quadrant B). ^{13}C NMR (acetone-d_6, 20 °C, δ): 199.8 (CO), 146.7, 145.4, 142.1, 141.5, 136.4, 135.8, 135.1 (Tp 3,5, Im), 130.8, 121.3 (Im), 107.0, 106.8, 105.4 (Tp 4), 92.0 (C=O), 34.3 (NMe), 34.0 (Me, quadrant A), 26.7 (Me, quadrant B). IR: ν_{CO} 1796 cm^{-1} (vs), ν_{BH} 2483 cm^{-1} (w). CV: $E_{p,a} = 0.19$ V (II/I). Anal. Calcd for $ReC_{17}H_{22}N_8BO_2$: C, 35.98; H, 3.91; N, 19.75. Found: C, 36.36; H, 4.23; N, 19.48.

L = methyl ethyl ketone (13): light yellow solid. ^{1}H NMR (acetone-d_6, 19 °C, δ): 8.14, 8.13, 7.84, 7.76, 7.75, 7.74, 7.73, 7.72, 7.70, 7.41 (12H, 1:1:2:1:1:1:1:1:1:2, each a d (or fine dd with $J < 1$), Tp 3,5), 6.23, 6.22, 6.21, 6.20, 6.14, 6.13 (6H, 1:1:1:1:1:1, each a t, Tp 4), 7.7 (2H, br t, 2 isochronous Im), 6.98 (2H, br t, 2 isochronous Im), 6.19, 6.15 (2H, 1:1, each a t, $J = 1.5$, Im), 3.84, 3.83 (6H, 1:1, s, MeIm), 2.59 (3H, s, Me, quadrant A), 1.01 (3H, s, Me, quadrant B), 1.15 (3H, t, $J =$ 2.5, ethyl CH_3, quadrant A), 0.75 (3H, t, $J = 2.5$, ethyl CH_3, quadrant B), 2.71, 2.67 (2H, 1:1, each a dq, $J = 16$, 8, CH_2, quadrant A), 1.03, 0.51 (2H, 1:1, each a dq, $J = 16$, 8, CH_2, quadrant B). ^{13}C NMR (acetone-d_6, 19 °C, δ), one isomer reported, CO not observed: 146.7, 145.7, 142.7, 141.2, 136.3, 135.8, 135.2 (Tp 3,5, Im), 130.8, 121.3 (Im), 107.0, 106.6, 105.5 (Tp 4), 95.7 (C=O), 34.3 (NMe), 33.0 (Me, quadrant A), 29.8 (CH_2, quadrant B), 14.2 (ethyl CH_3, quadrant B). IR: ν_{CO} 1797 cm^{-1} (vs), ν_{BH} 2484 cm^{-1} (w). CV: $E_{p,a} = 0.11$ V (II/I).

L = 3-pentanone (14): beige solid. ^{1}H NMR (acetone-d_6, 20 °C, δ): 8.18, 7.83, 7.75, 7.72, 7.69, 7.48 (6H, 1:1:1:1:1:1, each a d (or fine dd with $J < 1$), Tp 3,5), 6.21, 6.20, 6.13 (3H, 1:1:1, each a t, Tp 4), 7.67 (1H, br t, Im), 6.98, 6.15 (2H, 1:1, each a t, $J = 1.5$, Im), 3.83 (3H, s, MeIm), 3.30, 2.73 (2H, 1:1, each a dq, $J = 16$, 8, CH_2, quadrant A), 1.18, 0.67 (2H, 1:1, each a dq, $J = 16$, 8, CH_2, quadrant B), 1.17 (3H, t, $J = 8$, CH_3, quadrant A), 0.69 (3H, t, $J = 8$, CH_3, quadrant B). ^{13}C NMR (acetone-d_6, 20 °C, δ), carbonyl not observed: 146.7, 146.4,

141.9, 141.4, 136.4, 135.7, 135.1 (Tp 3,5, Im), 130.9, 121.3 (Im), 107.0, 106.5, 105.4 (Tp 4), 98.8 (C═O), 34.3 (NMe), 36.5 (CH_2, quadrant A), 32.4 (CH_2, quadrant B), 14.7 (CH_3, quadrant A), 13.1 (CH_3, quadrant B). IR: ν_{CO} 1796 cm^{-1} (vs), ν_{BH} 2483 cm^{-1} (w). CV: $E_{p,a} = 0.18$ V (II/I).

L = methyl isopropyl ketone (15): beige solid. Two isomers: isopropyl group in quadrant A (isomer A) and isopropyl group in quadrant B (isomer B) (1.8:1). ^{1}H NMR (acetone-d_6, 20 °C, δ) isomer A: 8.23, 7.85, 7.76, 7.74, 7.63, 7.69 (6H, 1:1:1:1:1:1, each a d (or fine dd with $J < 1$), Tp 3,5), 6.21, 6.19, 6.14 (3H, 1:1:1, each a t, Tp 4), 7.55 (1H, br t, Im), 6.94, 6.07 (2H, 1:1, each a t, $J = 1.5$, Im), 3.80 (3H, s, MeIm), 2.49 (1H, qq, $J = 8, 8$, CH), 1.45 (3H, d, $J = 8$, CH_3), 1.22 (3H, d, $J = 8$, CH_3), 1.17 (3H, s, $COCH_3$). Isomer B: 8.23, 7.76, 7.56, 7.36 (6H, 1:3:1:1, each a d (or fine dd with $J < 1$), Tp 3,5), 6.15 (3H, three isochronous t, Tp 4), 7.76 (1H, br t, Im), 6.98, 6.12 (2H, 1:1, each a t, $J = 1.5$, Im), 3.84 (3H, s, MeIm), 2.55 (3H, s, $COCH_3$), 1.14 (1H, qq, $J = 8, 8$, CH), 0.82 (3H, d, $J = 8$, CH_3), 0.17 (3H, d, $J = 8$, CH_3). ^{13}C NMR (acetone-d_6, 20 °C, δ), both isomers reported: 203.3 (CO), 148.8, 147.9, 147.2, 145.9, 142.5, 141.8 (2), 141.5, 137.2, 136.4, 135.7, 135.4 (2), 135.1, (Tp 3,5, Im), 130.8 (2), 121.2 (2) (Im), 107.1, 106.7, 106.4 (2), 105.6, 105.4 (Tp 4), 97.5 (C═O, isomer A), 97.1 (C═O, isomer B), 45.0 (CH, isomer A), 37.1 (CH, isomer B), 34.3 (2) (NMe), 26.1 ($COCH_3$, isomer B), 25.0 (CH_3, isomer A), 24.8 ($COCH_3$, isomer A), 21.8 (CH_3, isomer A), 19.7 (2) (CH_3, isomer B). IR: ν_{CO} 1798 cm^{-1} (vs), ν_{BH} 2481 cm^{-1} (w). CV: $E_{p,a} = 0.02$ V (II/I).

L = cyclohexanone (16): beige solid. ^{1}H NMR (acetone-d_6, 20 °C, δ): 8.13, 7.82, 7.75, 7.73, 7.69, 7.45 (6H, 1:1:1:1:1:1, each a d (or fine dd with $J < 1$), Tp 3,5), 6.25, 6.19, 6.13 (3H, 1:1:1, each a t, Tp 4), 7.74 (1H, br t, Im), 6.98, 6.18 (2H, 1:1, each a t, $J = 1.5$, Im), 3.82 (3H, s, MeIm), 2.68 (1H, td, $J = 13, 5, \alpha$, toward metal, quadrant A), 2.40 (1H, br d, $J = 13, \alpha$, away from metal, quadrant A), 1.06 (1H, br d, $J = 13, \alpha$, toward metal, quadrant B), 0.47 (1H, td, $J = 13, 5, \alpha$, away from metal, quadrant B), 1.94 (1H, br d, $J = 10$, CH_2), 1.77 (2H, m, CH_2), 1.44 (2H, m, CH_2), 1.27 (1H, tt, $J = 12, 4$, CH_2). ^{13}C NMR (acetone-d_6, 20 °C, δ): 200.3 (CO), 146.6, 145.5, 142.3, 141.5, 136.4, 135.7, 135.1 (Tp 3,5, Im), 130.9, 121.3 (Im), 107.0, 106.8, 105.5 (Tp 4), 98.9 (C═O), 44.4 (α, quadrant A), 37.3 (α, quadrant B), 32.6, 31.4, 27.5 (CH_2), 34.3 (NMe). IR: ν_{CO} 1799 cm^{-1} (vs), ν_{BH} 2476 cm^{-1} (w). CV: $E_{p,a} = 0.12$ V (II/I).

TpRe(CO)(MeIm)(η^2-formaldehyde) (17). To a 100 mL round-bottom flask was added **11** (0.10 g, 0.17 mmol) and a stir bar. Formaldehyde (1 mL (aq), 37% by wt) and THF (20 mL) were added. The solution was stirred (16 h, 22 °C) and the solvent removed in vacuo. Et_2O (3 × 30 mL) was added to the residue and filtered through Celite. The filtrate was poured onto a silica column, eluted with 1:1 Et_2O/THF, then THF to isolate a pale yellow band. The solvent was removed in vacuo, the precipitate was redissolved in minimal THF and precipitated with hexanes (50 mL), and the suspension was filtered on a 30 mL medium frit. The precipitate was washed with hexanes (2 × 15 mL) and dried in vacuo, resulting in a light beige solid. Yield: 30−40%. ^{1}H NMR (acetone-d_6, 20 °C, δ): 7.98, 7.89, 7.80, 7.77, 7.68, 7.38 (6H, 1:1:1:1:1:1, each a d (or fine dd with $J < 1$), Tp 3,5), 6.27, 6.20, 6.15 (3H, 1:1:1, each a t, Tp 4), 7.76, 7.00, 6.30 (3H, 1:1:1, each a t, $J = 1.5$, Im), 3.82 (3H, s, MeIm), 5.07 (1H, br d, $J = 17$, formaldehyde, quadrant A), 3.43 (1H, br d, $J = 17$, formaldehyde, quadrant B). ^{1}H NMR (acetone-d_6, −20 °C, δ), Select resonances reported: 5.04 (1H, d, $J = 17$, formaldehyde, quadrant A), 3.36 (1H, d, $J = 17$, formaldehyde, quadrant B), 3.82 (3H, s, NMe). ^{13}C NMR (acetone-d_6, 20 °C, δ): 197.0 (CO), 147.0, 146.7, 142.7, 139.7, 136.1, 135.5 (2) (Tp 3,5, Im), 131.2, 121.6 (Im), 107.3, 107.0, 105.8 (Tp 4), 80.9 (C═O), 34.4 (NMe). IR: ν_{CO} 1804 cm^{-1} (vs), ν_{BH} 2487 cm^{-1} (w). CV: $E_{p,a} = 0.23$ V (II/I).

TpRe(CO)(MeIm)(η^2-acetaldehyde) (18). To a 100 mL round-bottom flask was added **11** (0.10 g, 0.17 mmol) and a stir bar. Acetaldehyde (0.25 mL, 4.5 mmol) and THF (20 mL) were added. The solution was stirred (16 h, 22 °C). Hexanes (75 mL) were added, 40 mL of solvent was removed under reduced pressure, and the suspension was filtered on a 30 mL medium frit. The product was further purified by passage through silica (Et_2O/THF, then THF), resulting in a light beige solid. Yield: 55−65%. A ratio of 4:1 was observed for isomer A:B. ^{1}H NMR (acetone-d_6, 20 °C, δ), isomer A: 7.96, 7.82, 7.77, 7.76, 7.70, 7.28 (6H, 1:1:1:1:1:1, each a d (or fine dd with $J < 1$), Tp 3,5), 6.25, 6.20, 6.12 (3H, 1:1:1, each a t, Tp 4), 7.37 (1H, br t, Im), 6.98, 6.37 (2H, 1:1, each a t, $J = 1.5$, Im), 3.81 (3H, s, MeIm), 3.92 (1H, q, $J = 4$, acetaldehyde), 2.58 (3H, d, $J = 4$, acetaldehyde). ^{1}H NMR (acetone-d_6, −20 °C, δ), select isomer B resonances reported: 5.61 (1H, q, $J = 4$, acetaldehyde), 1.09 (3H, d, $J = 4$, acetaldehyde), 3.84 (3H, s, NMe). ^{13}C NMR (acetone-d_6, −20 °C, δ), isomer A: no carbonyl observed; 146.3, 145.2, 142.6, 139.6, 136.1, 135.9, 135.5 (Tp 3,5, Im), 130.7, 121.4 (Im), 107.1, 106.6, 105.7 (Tp 4), 87.8 (C═O), 34.2 (NMe), 25.6 (CH_3). Select resonances for isomer B: 86.8 (C═O). IR: ν_{CO} 1790 cm^{-1} (vs), ν_{BH} 2482 cm^{-1} (w). CV: $E_{p,a} = 0.12$ V (II/I). Anal. Calcd for $ReC_{16}H_{20}N_8BO_2$: C, 34.73; H, 3.64; N, 20.25. Found: C, 34.55; H, 3.33; N, 20.36

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