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Dihapto Coordination of Carboxylic Acid Derivatives with an Asymmetric Rhenium π-Base: A New Mechanism for Amide Isomerization?

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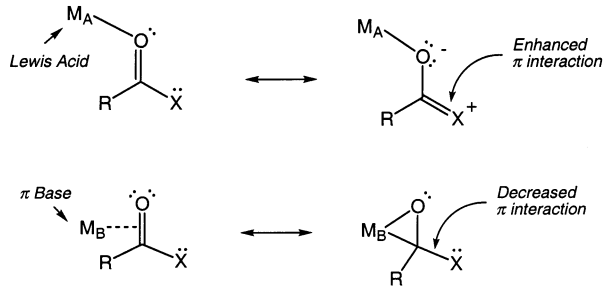
Abstract: The asymmetric π basic metal fragment {TpRe(CO)(MeIm)} (Tp = hydridotris(pyrazolyl)borate, MeIm = 1-methylimidazole) forms thermally stable complexes with ethyl acetate, acetic anhydride, *N*-methylsuccinimide, *N*-acetylpyrrole, and *N*-methylmaleimide in which the metal binds a carbonyl group in a π fashion. In all cases a single diastereomer is observed, indicating that one enantioface of the carbonyl is selectively coordinated. X-ray and NMR data for the compound TpRe(CO)(MeIm)(η^2-*N*-methylsuccinimide) indicate that metal coordination effectively removes the π interaction between the bound carbonyl and the nitrogen of the succinimide ring.

Introduction

The interaction of transition metals with esters and amides is a subject of intense interest for synthetic chemists as well as biochemists. The catalysis of nucleophilic substitution, conjugate addition,[1,2] and cycloaddition reactions,[3] as well as the induction of stereochemistry in these reactions,[4,5] is attributed to η^1-coordination of the carbonyl oxygen by a Lewis acidic transition metal.[6] This type of coordination is also thought to slow rates of isomerization of amides in biopolymers.[7] In contrast, dihapto coordination of an ester or amide carbonyl might be expected to have the opposite effect. Metal-to-ligand back-bonding should weaken or eliminate the electrophilic nature of the carbonyl carbon and minimize the π interaction with the neighboring N or O heteroatom (X). For example, while Lewis acidic metal catalysts typically decrease the rate of amide C−N rotation (i.e., amide isomerization), a π basic metal would be expected to accelerate this process.

Although η^2-aldehyde and -ketone complexes are well documented,[8−12] little is known about this mode of binding for amides, imides, or esters. An isolated example of such coordination is a report by Legzdins et al. of the complex (η^5-C_5Me_5)-W(NO)(PPh_3)(η^2-ethyl acetate),[13] but structural data were unavailable.



The fragment {TpRe(CO)(MeIm)} (Tp = hydridotris(pyrazolyl)borate; MeIm = 1-methylimidazole) has been shown to be a powerful π base that forms stable complexes with a wide range of arenes and aromatic heterocycles[14,15] in a manner similar to that of the pentaammineosmium(II) system.[16] Like its osmium analogue, {TpRe(CO)(MeIm)} also forms robust π complexes with olefins, ketones, and aldehydes.[17] In an effort to learn more about the structural and chemical properties of η^2-ester and -amide complexes, the precursor TpRe(CO)(MeIm)-(η^2-benzene) (**1**) was combined with a variety of carboxylic acid derivatives.

Results and Discussion

The complex TpRe(CO)(MeIm)(η^2-benzene) (**1**) is a convenient source of the π base {TpRe(CO)(MeIm)}.[14,15] Stirring **1**

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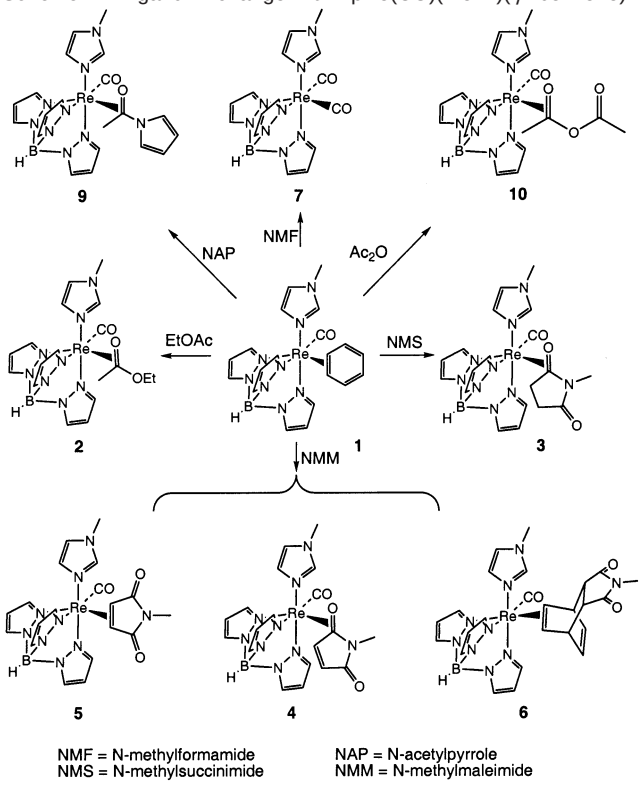
Scheme 1. Ligand Exchange with TpRe(CO)(MeIm)(η^2-benzene)



in EtOAc for 18 h at 22 °C generates a new complex assigned as TpRe(CO)(MeIm)(η^2-EtOAc) (**2**), which is isolated as a single diastereomer in 67% yield (Scheme 1).

Although the broad EtOAc ^{1}H NMR resonances in **2** at 25 °C indicate a fluxional process (i.e., an η^2 to η^1 to η^2 isomerization; vide infra), studies at −20 °C (acetone-d_6) reveal a single set of resolved signals including diastereotopic CH_2 resonances at δ 3.88 and 3.76 (J = 10 Hz), as well as CH_3 and acetate resonances at δ 1.18 and 0.91, respectively. In the ^{13}C NMR spectrum of **2** (−20 °C), the C═O resonance was observed at δ 118.9. The orientation shown in Figure 1, with the carbonyl oxygen oriented toward MeIm and the ester oxygen in quadrant A, was confirmed by nuclear Overhauser effect (NOE) studies. Irradiation of the acetate protons at −20 °C causes an enhancement with protons of pyrazolyl (pz) rings trans to CO and trans to MeIm (δ 7.15 and 8.28) as well as the diastereotopic methylene group. This observation is consistent with the depicted orientation shown in Figure 1 (note that the (CO)−OEt bond is now expected to be a free rotor (vide infra)). The shielding effects from the pz rings bordering quadrant B cause the unusual upfield shift of the signal for the acetyl protons.[14,15] The broadened signals of **2** at ambient temperature corresponding to the ethyl acetate ligand are thought to arise from an η^2 to η^2 diastereoisomerization mechanism (a "face-flip"). An oxygen inversion of the putative η^1 intermediate followed by a return to η^2-coordination would generate a coordination diastereomer of **2** in which the ester is bound on the opposite face of the carbonyl.

Further characterization of **2** includes an infrared absorption at 1801 cm^{-1} corresponding to the $\nu_{C\equiv O}$ and a broadened, chemically and electrochemically irreversible anodic wave with $E_{p,a}$(II/I) = 0.12 V (vs NHE; 100 mV/s). The ester complex **2** is stable for months under nitrogen as a solid, but in an acetone solution the solvent slowly displaces the ester ($t_{1/2} \sim 1$ week at 22 °C).

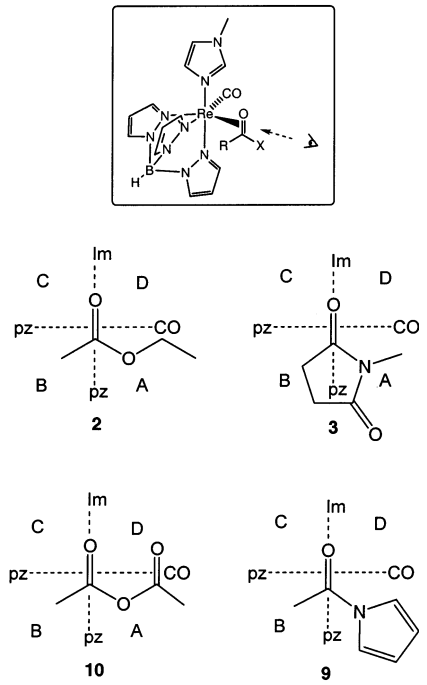


Figure 1. Orientation of dihapto-coordinated ligands on {TpRe(CO)(MeIm)}.

The *N*-methylsuccinimide (NMS) complex (**3**) (synthesized in a manner similar to **2**, but with THF as the solvent) also forms a single isomer. On the basis of NOE interactions that are similar to **2**, the imide ligand is oriented with the bound carbonyl oxygen toward MeIm and the nitrogen in quadrant A (see Figure 1). Key resonances from NMR data (acetone-d_6, 22 °C) include NMS methyl protons at δ 2.91 and unbound and bound carbonyl signals of NMS at δ 174.2 and 111.4 (^{13}C NMR), respectively. Infrared data show absorptions at $\nu_{C\equiv O}$ = 1807 cm^{-1} and $\nu_{C=O(unbound)}$ = 1667 cm^{-1}, and a cyclic voltammogram of **3** shows an irreversible anodic wave (Re(II/I)) at $E_{p,a}$ = 0.22 V, similar to that observed for η^2-ketone analogues.[17] The half-life for acetone substitution for **3** was determined to be 44 h (acetone-d_6, 22 °C), somewhat shorter than for its ester analogue (**2**) (vide supra).

To compare the binding rates of imides with alkenes, we repeated the coordination procedure with *N*-methylmaleimide (NMM). When NMM is combined with the benzene complex in THF, two linkage isomers of the maleimide complex are formed in a 2:1 ratio, corresponding to the η^2-*C*,*O*-NMM complex (**4**) and the η^2-*C*,*C*-NMM complex (**5**). This observation indicates that, while the C═C isomer is almost certain to be thermodynamically more stable, the η^2-imide mode is the kinetically preferred product (k_{CO}/k_{CC} = 2). Similarly, the π base pentaammineosmium(II) does not show a strong kinetic preference for binding ketones versus alkenes.[16] In addition to the two substitution products formed from the maleimide (**4**, **5**), a third product is formed (**6**, 40%) that is a result of the bound benzene of **1** undergoing a Diels−Alder cycloaddition with NMM. The latter reaction type has been investigated in detail and reported elsewhere.[18] These three compounds can be

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Table 1. IR Data ($\nu_{C=O}$) for Various η^2-Carbonyl Compounds and Unbound Ligands

compd	unbound $\nu_{C=O}$ (cm^{-1})	$\nu_{C=O}$ (cm^{-1})
3	1667	1807
4	1657	1821
5	1719, 1659	1833
9		1804
10	1704	1831
NMS[19]	1693	
NMM[19]	1697	
NMP	1675	
$(Ac)_2O$	1823, 1760	

efficiently separated by silica gel column chromatography. The orientation of the η^2-*C,O*-NMM linkage isomer (**4**) resembles that of the NMS adduct (see Figure 1). Characteristic properties of **4** include resonances for NMM at δ 3.00 (NMe), 5.25 (olefin), and 5.22 (olefin) in the ^{1}H NMR spectrum and ^{13}C signals at 169.1 (CO unbound), 107.7 (CO bound), 136.3 (olefin), and 122 (olefin). Infrared data for **4** indicate $\nu_{C\equiv O} = 1821$ cm^{-1} and $\nu_{C=O(unbound)} = 1657$ cm^{-1}, and a cyclic voltammogram (100 mV/s) reveals $E_{p,a}$(II/I) = 0.22 V. For the C═C bound linkage isomer (**5**), ^{1}H NMR resonances at δ 3.01 (NMe) and 3.69 (olefin) and 2.98 (olefin) were observed, as well as ^{13}C NMR signals at δ 184.8 and 184.1 (NMM carbonyls) and 54.4 and 52.0 (bound olefin). Infrared data for **5** show $\nu_{C\equiv O} = 1833$ cm^{-1}, indicating a more electron-deficient metal than for the η^2-*C,O*-bound isomer, and C═O stretching frequencies at 1719 and 1659 cm^{-1} corresponding to the maleimide carbonyls. Also indicative of a more electron-deficient metal is the reduction potential of **5**, for which $E_{1/2}$(II/I) = 0.67 V. Both **4** and **5** show no decomposition after 2 weeks in an acetone solution.

Infrared data for the imide ligands in complexes **3** and **4** support the isolation of the unbound amide group (Table 1). With the conjugation of one carbonyl effectively removed by coordination, the stretching frequencies of the unbound C═O in complexes **3** ($\nu_{CO} = 1667$ cm^{-1}) and **4** ($\nu_{CO} = 1657$ cm^{-1}) more closely resemble those of amides than they do imides.[19] In fact, complex **3** has a lower C═O stretching frequency than 1-methyl-2-pyrrolidinone (NMP; $\nu_{CO} = 1675$ cm^{-1}).

The structure of the succinimide complex was obtained from a single crystal of **3** (Figure 2). The X-ray data (Table 2, Figure 3) confirm the amide-like character of the uncoordinated carbonyl group that was suggested by the infrared data. Bond length comparisons between unbound[20] and bound succinimides are shown in Figure 3. The rhenium-coordinated carbon−oxygen bond of the coordinated NMS lengthens (+0.11 Å), as does the C−N bond adjacent to the metal (+0.10 Å). The latter value indicates a loss of π interaction between the nitrogen and the bound carbonyl. A shorter bond length (difference of 0.03 Å) for the opposite C−N bond of **3** is observed for the complex, a contraction consistent with an increase in amide character.

It is useful to compare crystal data of **3** with those of the more common η^1- amide carbonyls with Lewis acidic metals.[21] Although both coordination modes increase the C−O bond

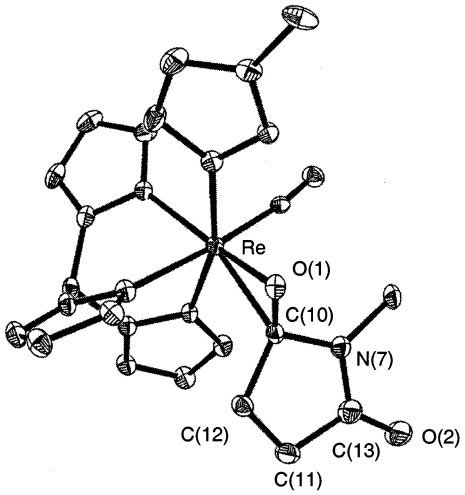

Figure 2. ORTEP diagram of TpRe(CO)(MeIm)(η^2-NMS) (**3**) (30% ellipsoids).

Table 2. Crystal Data for Compound **3**

empirical formula	$C_{19}H_{23}BN_9O_3Re$
fw	622.47
cryst dimens, mm	0.31 × 0.22 × 0.08
crystal system	monoclinic
space group	$P2_{1/n}$
a, Å	8.8399(4)
b, Å	23.919(1)
c, Å	10.4443(5)
β, deg	95.424(1)
V, Å^3	2198.5(2)
Z	4
D_{calcd}, mg m^{-3}	1.881
T, K	153(2)
μ, mm^{-1}	5.570
no. reflns	30 035
no. unique reflns	7937
final *R* factors	R1 = 0.0415, wR2 = 0.0958 [$I > 2\sigma(I)$]
goodness-of-fit on F^2	0.950

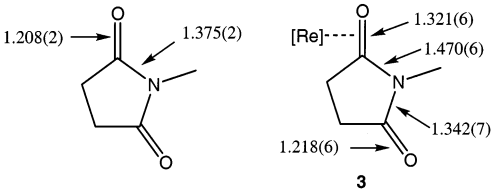

Figure 3. Bond distances for NMS and complexed NMS (**3**) (Å).

distance, η^2-coordination has a greater effect. Whereas η^1-coordination increases the bond length by ~0.02 Å, η^2-coordination for the imide produces an increase of more than 0.1 Å. Dihapto coordination in **3** also increases the C−N bond distance by ~0.1 Å, whereas Lewis acidic coordination to amides leads to a shortening of the adjacent C−N bond by several hundredths of an angstrom. In addition, whereas η^1-bound amide ligands are essentially planar, the bound carbonyl in **3** is bent 40° out of the plane defined by C−N−C (which also contains the methyl carbon and the unbound carbonyl oxygen ±1°), consistent with sp^3 hybridization for the bound amide carbon.

Attempts to isolate a simple η^2-amide complex of rhenium were unsuccessful. The reaction of TpRe(CO)(MeIm)(η^2-benzene) with *N*-methylformamide (NMF) yielded the amide decarbonylation product $TpRe(CO)_2(MeIm)$ (**7**), a result similar to that observed with pentaammineosmium(II).[22] A ^{1}H NMR

(19) Values reported are of strongest absorbance recorded by our methods (THF solution evaporated on HATR accessory). Although multiple absorbances for these systems are reported (see ref 20), they are in good agreement with our findings. The lowest absorbance observed was a low-energy shoulder off the strongest absorbance at ~1672 cm^{-1}.

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spectrum of **7** indicates an internal mirror plane, and its IR spectrum shows two CO signals. This compound can be generated directly (50−60%) by stirring **1** in THF under 25 psig of CO for 24 h. Reaction with acetamides, including *N*,*N*-dimethylacetamide (DMAc), yielded only small amounts of a compound that we assign as TpRe(CO)(MeIm)(N_2) (**8**) (resulting from the reaction being carried out under a nitrogen atmosphere) and an unidentified product similar to that obtained when **1** is allowed to stand in THF alone (THF complexation was not observed). Efforts to identify this paramagnetic complex were unsuccessful; however, the compound shows characteristics of a {TpRe^{II}(CO)} fragment including a featureless NMR spectrum and $\nu_{CO} = 1810$ cm^{-1}. The assignment of **8** as TpRe(CO)(MeIm)(N_2) is supported by a strong absorption in the infrared spectrum at 1996 cm^{-1}, consistent with an electron-rich rhenium(I) complex with a terminal dinitrogen ligand.[23] Complex **8** can be generated in higher yields (50−60%) by stirring **1** in THF under 25 psig of N_2 for 24 h.

To investigate the effect of η^2-coordination on amide isomerization (C−N rotation), an *N*,*N*-disubstituted amide was desired so that we could measure its proton NMR coalescence temperature on and off the metal. Given the difficulties associated with forming stable complexes of simple alkylated amides (vide supra), *N*-acetylpyrrole was chosen, an amide we reasoned would stand a better chance of forming a stable η^2-carbonyl complex given the involvement of the nitrogen lone pair with the heterocycle π system. The initial product resulting from the treatment of **1** with *N*-acetylpyrrole was a complex mixture containing the desired C−O complex **9** (62%), along with what we believe to be two isomers of a ring-bound linkage isomer. However, **9** is readily isolated in pure form through column chromatography. Key features in the NMR spectrum of **9** include unbound pyrrole peaks at δ 7.04 (t) and 5.95 (t), signals that are upfield of and sharper than those of the free ligand ($\delta \sim 7.5$ and 6.3). In addition, the complex shows an irreversible anodic wave at $E_{p,a} = 0.07$ V (100 mV/s), a result consistent with data from other η^2-carbonyl complexes reported herein.

Although the amide isomerization barrier for *N*-acetylpyrrole was previously examined by Bain and co-workers,[24] we wanted to measure this value under conditions identical to those used for the corresponding rhenium complex. Slow warming of a cooled acetone-d_6 solution of the pyrrole revealed a coalescence temperature of −59 °C, corresponding to a $\Delta G^{\ddagger}$ of 10.8 ± 0.5 kcal/mol. This value is similar to that reported earlier (12.4 ± 0.3 kcal/mol),[24] with any discrepancy being attributed to differences in solvent ($CDCl_3$ vs acetone) and experimental method.

In contrast to that observed for the free ligand, cooling a sample of the rhenium *N*-acetylpyrrole complex (**9**) to −85 °C (acetone-d_6) did not appreciably change either the line width or the splitting pattern of the pyrrole signals. Resonances for the α and β protons of the pyrrole ring still appeared as triplets.

While these observations are consistent with rapid rotation about the C−N bond at −85 °C, the inability to determine static chemical shifts prevented us from establishing a lower limit to the rotation barrier. Indeed it is possible, though highly improbable, that the chemical shifts for the two α protons and for the two β protons are nearly coincident at this temperature, which would give rise to a NMR spectrum consistent with that described above. However, these observations along with the observed upfield shift in the pyrrole ring protons as well as the crystallographic data presented for the η^2-imide **3** support the notion that η^2-coordination of an amide limits the interaction of the nitrogen lone pair with the carbonyl, thereby allowing for rapid isomerization of the amide C−N bond.

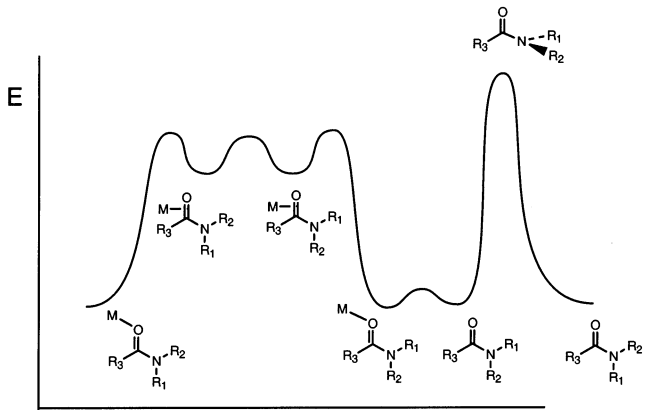

Figure 4. Reaction coordinate diagram for an amide isomerization catalyzed by η^2-coordination.

Although transition metals are generally observed to retard the rate of amide isomerization (i.e., C−N bond rotation), it has been demonstrated that a transition metal can catalyze the isomerization if it selectively binds nitrogen rather than oxygen.[7] Given the important role that amide isomerization plays in protein folding,[25] it is worth considering whether a protein rotamase could also function through an η^2-amide intermediate, at least in principle. Earlier studies showed the η^1 to η^2 isomerization barrier for acetone bound to osmium(II) to be about 12 kcal/mol (while η^2 to η^1 isomerization has an activation barrier of 17 kcal/mol).[26] Although transition metals typically present in biological systems vary considerably from rhenium and osmium, it is conceivable that even a first row transition metal could form a transient η^2-amide intermediate, provided that it was within about 10 kcal/mol of the O-bound form, which would assist in the isomerization of the C−N bond, a process that without a catalyst has an 18−22 kcal/mol barrier (Figure 4).[7]

Returning to O-acylated compounds, we attempted to form a stable complex with acetic anhydride, a compound considerably more electrophilic than aldehydes, ketones, esters, or amides. Treatment of a THF solution of **1** with an excess of acetic anhydride results in formation of a new complex **10**. The ^{1}H NMR of this material shows new sets of Tp and *N*-methylimidazole resonances, including a sharp singlet at δ 2.20 (3H), corresponding to the unbound acetyl, and a broad signal at δ 1.9 corresponding to the bound acetyl group. Reducing the temperature to −20 °C sharpens the latter signal into a well-defined peak that integrates to three protons. An infrared spectrum shows an absorption corresponding to Re−CO at 1831 cm^{-1}, 10 cm^{-1} higher than for *N*-methylmaleimide complex **4**. In addition, an absorption attributed to the unbound carbonyl group is present at 1704 cm^{-1}. This value is similar to what is

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observed for esters. Finally, a cyclic voltammogram of **10** shows an anodic wave at 0.26 V that compares well with that of the maleimide complex (**4**; 0.22 V). Unfortunately, our attempts to purify compound **10** either by chromatography or by reprecipitation resulted in decomposition to unknown paramagnetic materials. Based on electrochemical and NMR data, we estimate the purity of **10** to be 80%.

The highly π basic nature of the rhenium in {TpRe(CO)(MeIm)} is demonstrated by its ability to form stable π complexes with the carbonyl of an ester, imide, amide, and anhydride. Interestingly, for both the $\{(\eta^5\text{-}C_5Me_5)W(NO)(PPh_3)\}$[13] and the {TpRe(CO)(MeIm)} systems, ethyl acetate is actually more electron withdrawing as a π-bound ligand than is acetone, according to shifts in $N{\equiv}O^+$ or $C{\equiv}O$ stretching frequencies. This observation is surprising given that the π^* orbital of an ester is expected to be higher in energy than that for a ketone, and thus the back-bonding interaction is expected to be weaker. That the ester is able to withdraw more electron density than the ketone suggests that the inductive effect of the oxygen adjacent to the carbonyl on the σ bond is a greater factor than oxygen π donation once the carbonyl is bound by the metal. Crystallographic data (vide supra) support this notion in that the π orbital of the succinimide nitrogen in **3** is no longer aligned with the bound carbonyl π system. Similarly, X-ray data for a crystal of $[Os(NH_3)_5(\eta^2\text{-ethoxyethene})](OTf)_2$ shows that the methylene carbon of the ethoxy group lies well out of the plane defined by the oxygen and vinyl carbons.[27] Such a geometric arrangement rules out any significant π interaction between the oxygen and the vinyl group.[27] The stabilizing π interaction between the oxygen and carbonyl in an *uncoordinated* ester, however, renders it more difficult to bind than a ketone. Apparently, for simple amides, the nitrogen π donation is stabilizing to a degree where the metal cannot compensate for it. A similar feature is seen with other η^2-aromatic systems of rhenium and osmium.[16] For example, although benzene forms a much less stable complex than cyclohexene with {TpRe(CO)(MeIm)}, once bound, benzene is a better π acid and/or a worse σ donor due to the more conjugated π system.[14,15]

The stereoselective coordination of ethyl acetate, maleimide, and succinimide is somewhat surprising given our previous experience with prochiral ketones. For example, although the carbonyl oxygen selectively orients toward MeIm in ketones, esters, and imides alike,[17] methyl ethyl ketone is coordinated by {TpRe(CO)(MeIm)} at either face with equal affinity, putting the ethyl group in either quadrant A or B. In contrast, the esters and imides have a preference of at least 3 kcal/mol (22 °C) for placing the heteroatom in quadrant A (i.e., no other isomer was observed by NMR). The selective carbonyl coordinations in the imide complexes **3** and **4** and the anhydride **10** represent novel examples of desymmetrization.

The decreased stability of the η^2-NMS complex (**3**) compared to that of NMM (**4**) is likely due to the lower energy π^* orbitals in **4** as a consequence of the additional conjugation. The higher energy $\nu_{C\equiv O}$ observed for **4** supports this reasoning. When bound through the olefin, NMM is a stronger π acid than its carbonyl-bound linkage isomer (cf. **5**, $\nu_{C\equiv O} = 1833\ cm^{-1}$; **4**, $\nu_{C\equiv O} = 1821\ cm^{-1}$). In fact, NMM renders the rhenium more difficult to oxidize than does the benchmark π acid carbon monoxide (**5**, $E_{1/2} = 0.67$ V; **7**, $E_{1/2} = 0.45$ V). No linkage isomerization was observed (22 °C; 2 weeks) between carbonyl-bound (**4**) and olefin-bound (**5**) isomers in solution, a testament to the high kinetic stability of these compounds.

Conclusion

The π basic metal fragment {TpRe(CO)(MeIm)} forms stable complexes with esters, amides, imides, and anhydrides, offering unusual examples of dihapto-coordinated carboxylic acid derivatives. Coordination is accomplished with a high degree of stereocontrol. In all cases the bound carbonyl is orthogonal to the Re−CO bond, with the oxygen oriented toward the imidazole ligand and the other heteroatom directed toward the carbonyl. Crystallographic and variable temperature NMR data indicate that coordination effectively removes the carbonyl from conjugation with the heteroatom, and in this regard, the metal has the opposite effect on the physical and chemical properties of the carbonyl compared to η^1 complexes with Lewis acids.

Experimental Section

General Methods. NMR spectra (22 °C) were obtained on a 300 or 500 MHz Varian INOVA spectrometer. All chemical shifts are reported and are referenced relative to tetramethylsilane (TMS) utilizing residual ^1H or ^{13}C signals of the deuterated solvents as an internal standard. Coupling constants (*J*) are reported in hertz (Hz). Resonances in the ^1H NMR due to pyrazole ligands are listed by chemical shift and multiplicity only (all pyrazole coupling constants are 2 Hz). Variable temperature ^1H NMR spectra were acquired on a Varian Inova spectrometer operating at 500 MHz. Infrared spectra (IR) were recorded on a MIDAC Prospect Series (Model PRS) spectrometer as a glaze (evaporated THF) on a horizontal attenuated total reflectance (HATR) accessory (Pike Industries). Values were reproducible within $\pm 1\ cm^{-1}$. 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 tetrabutylammonium hexafluorophosphate (TBAH) electrolyte. 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 analyses (EA) were attempted on complexes **1**−**5** with a Perkin-Elmer 2400 Series II CHNS/O Analyzer. In most cases, the highly air sensitive nature of these materials prevented us from obtaining satisfactory results. In these cases purity was estimated from NMR, infrared, and electrochemical data. All synthetic reactions and electrochemical experiments were performed under a dry nitrogen atmosphere. Benzene, THF, and hexanes were purged with nitrogen and purified by passage through a column packed with activated alumina.[28] Other solvents, including ethyl acetate (EtOAc), were thoroughly degassed with nitrogen prior to use. Deuterated solvents were used as received from Cambridge Isotopes. Other reagents were used as received. Compound **1** and **6** have been reported previously. [14,15]

TpRe(CO)(MeIm)(η^2-EtOAc) (2). To a 100 mL round-bottom flask was added **1** (0.19 g, 0.32 mmol) and a stir bar. EtOAc (50 mL) was added, and the solution was stirred (18 h, 25 °C). The solvent volume was reduced by half under reduced pressure, and hexanes (40 mL) were added. The solvent volume was again reduced by half, and the suspension was filtered through a 30 mL medium frit. The yellow powder was washed with hexanes (2 × 15 mL) and dried in vacuo (0.13 g, 67%). ^1H NMR (acetone-d_6, 22 °C, δ): 8.30, 7.83, 7.78, 7.76,

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7.66, 7.18 (6H, 1:1:1:1:1:1, each a d, Tp 3,5), 6.24, 6.21, 6.14 (3H, 1:1:1, each a t, Tp 4), 7.79 (1H, br s, Im), 7.07, 6.41 (2H, 1:1, each a t, $J = 1.5$, Im), 3.86 (3H, s, MeIm), 3.85 (2H, br s, CH_2), 1.18 (3H, br s, CH_3), 0.97 (3H, br s, CO_2CH_3). ^{1}H NMR (acetone-d_6, −20 °C, δ), EtOAc resonances reported: 3.88 (1H, dq, $J = 10$, 7, CH_2), 3.76 (1H, dq, $J = 10$, 7, CH_2), 1.18 (3H, dd, $J = 7$,7, CH_3), 0.91 (3H, s, CO_2CH_3). ^{13}C NMR (acetone-d_6, 22 °C, δ): 199.1 (C≡O), 145.6, 145.2, 141.7, 140.8, 135.8 (2), 135.5 (Tp 3,5, Im), 131.2, 121.7 (Im), 107.3, 106.5, 105.7 (Tp 4), 55.9 (CH_2), 34.4 (MeIm), 26.1 (CO_2CH_3), 16.3 (CH_3). ^{13}C NMR (acetone-d_6, −20 °C, δ): 118.9 (C═O). IR (cm^{-1}): $\nu_{C\equiv O}$ = 1801 (vs), ν_{BH} = 2486 (w). CV: $E_{p,a}$ = 0.12 V (II/I) (br). Anal. Calcd for $C_{18}H_{24}BN_8O_3Re$: C, 36.18; H, 4.06; N, 18.76. Found: C, 35.74; H, 4.20; N, 19.19.

TpRe(CO)(MeIm)(η^2-N-methylsuccinimide) (3). To a 100 mL round-bottom flask was added **1** (0.17 g, 0.29 mmol), NMS (0.81 g, 7.2 mmol), and a stir bar. THF (25 mL) was added, and the solution was stirred (18 h, 25 °C). The solvent volume was reduced by half, and hexanes (50 mL) were added. The solvent volume was again reduced by half, and the suspension was filtered through a 30 mL medium frit. The precipitate was washed with hexanes (2 × 15 mL), dried in vacuo, and isolated as a yellow powder (0.11 g, 61%). ^{1}H NMR (acetone-d_6, 22 °C, δ): 7.84 (5H, overlapping Tp 3,5 and Im), 7.67 (2H, d, overlapping Tp 3,5), 7.29 (1H, d, Tp 3,5), 6.26, 6.23, 6.18 (3H, 1:1:1, each a t, Tp 4), 7.09, 6.36 (2H, 1:1, each a t, $J = 1.5$, Im), 3.86 (3H, s, MeIm), 2.91 (3H, s, NMe), 2.03 (2H, m, CH_2), 1.54 (1H, m, CH_2), 0.84 (1H, m, CH_2). ^{13}C NMR (CD_2Cl_2, 22 °C, δ): 198.1 (C≡O), 174.2 (C═O unbound), 145.3, 144.9, 141.6, 140.9, 136.2, 135.4, 135.3 (Tp 3,5, Im), 131.1, 121.0 (Im), 106.7, 106.5, 105.3 (Tp 4), 111.4 (C═O bound), 31.5 (MeIm), 30.8 (NMe), 34.8 (CH_2), 26.3 (CH_2). IR (cm^{-1}): $\nu_{C\equiv O}$ = 1807 (vs), ν_{BH} = 2486 (w), $\nu_{C=O(unbound)}$ = 1667 (s). CV: $E_{p,a}$ = 0.22 V (II/I). Estimated purity (NMR, IR, CV): >95%.

Synthesis of 4 and 5. These compounds were isolated along with a Diels−Alder cycloaddition product. The Diels−Alder cycloadduct has been isolated exclusively by other methods and reported elsewhere.[18] To a 100 mL round-bottom flask was added **1** (0.26 g, 0.44 mmol), NMM (0.81 g, 7.2 mmol), and a stir bar. THF (25 mL) was added, and the solution was brought to reflux and stirred (20 min). Upon cooling (25 °C), the solvent was removed under reduced pressure. The resulting residue was dissolved in CH_2Cl_2 (∼100 mL) and filtered through a medium frit. The filtrate was poured directly onto a silica gel column (20 cm × 2.5 cm). After eluting with CH_2Cl_2 to remove NMM, the complexes eluted with THF. First band (beige): NMM Diels−Alder product. Second band (beige): **5**. Third band (orange): **4**. The solutions of **4** and **5** were placed into separate round-bottom flasks each with a stir bar. The solvent volumes were decreased by 75% under reduced pressure, and hexanes were added to precipitate the products. Compound **4** was isolated as an orange powder (0.06 g, 22%; estimated purity (NMR, IR, CV): >90%); compound **5** was isolated as a beige powder (0.02 g, 8%; estimated purity (NMR, IR, CV): >95%).

TpRe(CO)(MeIm)(*C,O*-η^2-*N*-methylmaleimide) (4). ^{1}H NMR (acetone-d_6, 21 °C, δ): 7.90, 7.75, 7.66, 7.38, 7.22 (6H, 2:1:1:1:1, each a d, Tp 3,5), 6.29, 6.26, 6.15 (3H, 1:1:1, each a t, Tp 4), 7.94, 7.14, 6.38 (3H, 1:1:1, each a br t, Im), 5.25, 5.22 (2H, 1:1, each a d, $J = 6$, CH), 3.90 (3H, s, MeIm), 3.00 (3H, s, NMe). ^{13}C NMR (acetone-d_6, 22 °C, ***δ***): 196.6 (C≡O), 169.1(C═O unbound), 148.0, 145.8, 143.3, 142.7, 141.1, 136.6, 136.5, 136.3 (Tp 3,5, Im, olefin CH), 131.3 (Im), 122.2, 121.5 (Im, olefin CH), 107.8, 107.5, 106.3 (Tp 4), 107.7 (C═O bound), 34.6 (MeIm), 25.6 (NMe). IR: $\nu_{C\equiv O}$ = 1821 cm^{-1} (vs), ν_{BH} = 2488 cm^{-1} (w), $\nu_{C=O(unbound)}$ = 1657 cm^{-1} (s). CV: $E_{p,a}$ = 0.22 V (II/I), $E_{p,c}$ = −0.14 V.

TpRe(CO)(MeIm)(*C,C*-η^2-*N*-methylmaleimide) (5). ^{1}H NMR (acetone-d_6, 21 °C, ***δ***): 8.42, 7.94, 7.83, 7.78, 7.61, 7.38 (6H, 1:1:1:1:1:1, each a d, Tp 3,5), 6.36, 6.35, 6.17 (3H, 1:1:1, each a t, Tp 4), 7.73 (1H, br t, Im), 6.97, 5.91 (2H, 1:1, each a t, $J = 1.5$, Im), 3.82 (3H, s, MeIm), 3.01 (3H, s, NMe), 3.69 (1H, d, $J = 5$, olefin CH, toward Im), 2.98 (1H, d, $J = 5$, olefin CH, toward pz). ^{13}C NMR (CD_2Cl_2, 21 °C, ***δ***): 195.9 (C≡O), 184.8, 184.1(C═O), 145.7, 144.4, 142.0, 140.1, 136.2, 135.9, 135.1(Tp 3,5, Im), 130.7, 121.2 (Im), 106.8, 106.4, 106.3 (Tp 4), 54.4 (olefin CH, toward Im), 52.0 (olefin CH, toward pz), 34.7 (MeIm), 22.3 (NMe). IR: $\nu_{C\equiv O}$ = 1833 cm^{-1} (vs), ν_{BH} = 2488 cm^{-1} (w), $\nu_{C=O}$ = 1719 (m), 1659 cm^{-1} (vs). CV: $E_{1/2}$ = 0.67 V (II/I).

TpRe(CO)$_2$(MeIm) (7). This product was observed after stirring **1** (0.10 g, 0.17 mmol) in *N*-methylformamide (3 mL) for 16 h (precipitated with hexanes). Alternatively, this complex can be generated in higher yields (50−60%) by stirring **1** in THF under 25 psig of CO for 24 h. ^{1}H NMR (acetone-d_6, 21 °C, δ): 7.87, 7.73, 7.67, 7.45 (6H, 2:1:1:2, each a d, Tp 3,5), 6.24, 6.15 (3H, 2:1, each a t, Tp 4), 7.58 (1H, br t, Im), 7.06, 6.67 (2H, 1:1, each a t, $J = 1.5$, Im) 3.79 (3H, s, MeIm). ^{13}C NMR (acetone-d_6, 22 °C, δ): CO not observed; 146.8, 143.7 (2), 142.9, 136.0, 135.7 (2) (Tp 3,5, Im), 133.8 (Im), 122.3 (Im), 106.8, 106.7 (2) (Tp 4), 34.3 (MeIm). IR: ν_{CO} = 1888, 1799 cm^{-1} (each vs), ν_{BH} = 2495 cm^{-1} (w). CV: $E_{1/2}$ = 0.43 V (II/I).

TpRe(CO)(MeIm)(N$_2$) (8). This product was observed in small amounts (∼15%) after stirring **1** (0.10 g, 0.17 mmol) in *N*,*N*-dimethylacetamide (3 mL) under a nitrogen atmosphere for 16 h (precipitated with hexanes). Alternatively, this complex can be generated in higher yields (50−60%) by stirring **1** in THF under 25 psig of N_2 for 24 h. ^{1}H NMR (acetone-d_6, 22 °C, δ): 7.88, 7.84, 7.77, 7.68. 7.36, 7.35 (6H, 1:1:1:1:1:1, each a d (or fine dd with $J < 1$, Tp 3,5), 6.27, 6.20, 6.19 (3H, 1:1:1, each a t, Tp 4), 7.57 (1H, br t, Im), 7.12, 6.70 (2H, 1:1, each a t, $J = 1.5$, Im), 3.83 (3H, s, MeIm). ^{13}C NMR (acetone-d_6, 22 °C, δ), CO not observed: 145.2, 144.1, 142.0, 141.7, 136.0, 135.9, 135.6 (Tp 3,5, Im), 133.0 (Im), 122.4 (Im), 106.9, 106.7 (2) (Tp 4), 34.3 (MeIm). IR: $\nu_{N\equiv N}$ = 1996 cm^{-1} (vs), $\nu_{C\equiv O}$ = 1809 cm^{-1} (vs), ν_{BH} = 2485 cm^{-1} (w). CV: $E_{1/2}$ = 0.07 V (II/I).

TpRe(CO)(MeIm)(*C,O*-η^2-*N*-acetylpyrrole) (9). *N*-Acetylpyrrole was prepared according to the procedure reported by Bergman et al.[29] To a 100 mL round-bottom flask was added **1** (0.50 g, 0.85 mmol), *N*-acetylpyrrole (3.0 g, 27.5 mmol), and a stir bar. THF (25 mL) was added and the solution was stirred (18 h, 22 °C). Hexanes (300 mL) was added to produce a precipitate, which was dried in vacuo and isolated as a yellow powder (0.42 g, 80%). A solution of this product (50 mg, 0.08 mmol) in THF (1 mL) was loaded onto silica gel, and the elution of EtOAc yielded the product (31 mg, 62%, R_f = 0.72) after drying in vacuo. ^{1}H NMR (acetone-d_6, 22 °C, ***δ***): 8.04, 7.93, 7.84, 7.61, 7.41 (6H, 1:1:2:1:1, Tp 3, 5), 6.25, 6.23, 6.20 (3H, 1:1:1, each a t, Tp 4), 7.84, 7.09, 6.33 (3H, 1:1:1, each a t, MeIm), 7.04, 5.95 (4H, 1:1, each a t, $J = 2.0$, CH), 3.91 (3H, s, MeIm), 1.28 (3H, s, $COCH_3$). ^{13}C NMR (acetone-d_6, 22 °C, ***δ***): 197.1 (CO), 146.1, 145.6, 142.4, 141.3, 136.7, 136.0, 135.7, 131.1 (Tp 3, 5 and MeIm), 121.9 (MeIm), 118.0 (CH), 107.2, 106.9, 105.9 (Tp 4), 107.0 (CH), 34.5 (MeIm), 24.9 ($COCH_3$). ^{13}C NMR (acetone-d_6, −20 °C, δ): 98.3 (C═O). IR: ν_{CO} = 1804 cm^{-1} (vs), ν_{BH} = 2486 cm^{-1} (w). CV: $E_{p,a}$ = 0.07 V (II/I).

TpRe(CO)(MeIm)(η^2-acetic anhydride) (10). Acetic anhydride (0.6 g, 5.9 mmol) was added to a solution of **1** (0.050 mg, 0.085 mmol) in THF (0.67 mL) and stirred (18 h, 22 °C). The reaction mixture was added to hexanes (50 mL) to precipitate the product, which was dried in vacuo and isolated as a brown solid (0.042 mg, 72%). ^{1}H NMR (acetone-d_6, −20 °C, δ): 8.14, 7.98, 7.89, 7.85, 7.81, 7.25, 7.00 (6H, 1:1:1:1:1:2:1, Tp 3, 5 and MeIm), 6.30, 6.17, 5.98 (4H, 2:1:1, Tp 4 and MeIm), 3.82 (3H, s, MeIm), 2.20 (3H, s, $COCH_3$, unbound), 1.91 (3H, br s, $COCH_3$ bound). ^{13}C NMR (acetone-d_6, −20 °C, δ): 173.7 (C═O unbound), 146.5, 144.3, 143.8, 140.9, 136.3, 136.1, 135.6, 131.0 (Tp 3, 5 and MeIm), 121.6 (MeIm), 106.8 (2), 106.6 (Tp 4) 106.9 (C═O bound), 34.3 (MeIm), 22.3 ($COCH_3$ bound), 22.0 ($COCH_3$ unbound). IR: ν_{CO} = 1831 cm^{-1} (vs), ν_{CO} = 1704 cm^{-1} (s), ν_{BH} = 2486 cm^{-1} (w). CV: $E_{p,a}$ = 0.26 V (II/I).

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Rate Studies. For *N*-acetylpyrrole, a sample in acetone-d_6 was initially cooled to −85 °C. At this temperature, two resolved resonances were observed for the α-pyrrole protons (δ 7.44 and 7.40; $\Delta\nu = 19$ Hz). Spectra were acquired as the temperature of the sample was raised, with coalescence observed at −59 °C. For the *N*-acetylpyrrole complex **9**, no broadening or changes in coupling pattern were observed down to −85 °C.

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Supporting Information Available: Details of the X-ray diffraction study of **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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