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Reactions of TpRe(CO)$_2$(THF) with Aromatic Molecules (Tp = Hydridotris(pyrazolyl)borate)

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Abstract: The complex TpRe(CO)$_2$(THF) (**3**) (Tp = hydridotris(pyrazolyl)borate) reacts with a variety of aromatic molecules to form stable binuclear complexes of the form {TpRe(CO)$_2$}$_2$(μ-η^2-$\eta^{2\prime}$-L), where L = furan (**6**), *N*-methylpyrrole (**7**), or naphthalene (**8**). With thiophene, the TpRe(CO)$_2$ fragment yields the sulfur-bound mononuclear complex TpRe(CO)$_2$(η^1-thiophene) (**5**). In the absence of a suitable ligand, complex **3** reacts under a nitrogen atmosphere to form Tp(CO)$_2$Re(μ-N$_2$)Re(CO)$_2$Tp (**9**). An X-ray diffraction study of a single crystal of **9** provides geometric details.

Introduction

The coordination of an aromatic molecule by a transition metal has a profound impact on its reactivity. While numerous examples have been reported in which the aromatic ligand serves as a six-electron donor, examples of complexes showing lower coordination modes (e.g., η^2) are scarce. Not only is the latter class of compounds important from a synthetic perspective (vide infra), but it offers insight into the mechanism(s) of C−H activation for aromatic molecules.[1,2] The dearth of dihapto π-bound aromatic complexes is in part a direct result of the stringent electronic requirements. To stabilize the metal−aromatic bond, the metal must be a potent π-base. However, the electron-rich nature of the transition metal makes it highly prone to oxidative addition reactions.[2] Thus, a demarcation of electronic boundaries is set by the extremes of the metal's incapability of binding the aromatic (too electron deficient) and oxidative addition of the aromatic becoming problematic (too electron rich).

The pentaammineosmium(II) system [(NH$_3$)$_5$Os]$^{2+}$ (**1**) is a notable exception to the generally fragile nature of η^2-aromatic complexes. Fragment **1** forms thermally robust complexes with arenes as well as aromatic heterocycles.[3] The π-basic nature of **1** activates dihapto-coordinated ligands toward electrophilic attack, and this feature has been exploited in a broad array of organic transformations.[4] While we continue to seek novel synthetic applications of complex **1**, the inability to easily adjust the ligand set of this metal while preserving its aromatic binding characteristics has prompted an intense exploration for a more flexible surrogate.[5−11]

Other examples of characterized η^2-arene complexes include Cp*(NO)Ru(η^2-naphthalene),[12] [Cp(CO)(NO)Re(η^2-arene)]$^+$,[13] Cp*Rh(η^2-arene),[14] (R$_3$P)$_2$Ni(η^2-anthracene),[15] and a samarium dimer in which a phenyl group pendant to the hydrocarbon bridge is η^2-coordinated to one of the metal centers.[16] In addition, a handful of η^2-aromatic heterocycle complexes have been reported including (silox)$_3$M((η^2-*N*,*C*-pyridine) (silox = ^{t}Bu$_3$SiO; M = Ta, Nb),[17] η^2-selenophene complexes of Cp*Re(CO)$_2$ (Cp* = pentamethylcyclopentadienyl),[18a,b] and an η^2-benzothiophene complex of the Cp*Re(CO)$_2$ fragment in equilibrium with its sulfur-bound isomer.[18c] Most pertinent from our perspective was a report by Orpen et al. on the photolysis of Cp*Re(CO)$_3$ in benzene solution.[19] In this report, the complex Cp*Re(CO)$_2$(η^2-C$_6$H$_6$) was postulated as an intermediate in the formation of Cp*(CO)$_2$Re(μ-1,2-η^2-3,4-η^2-C$_6$H$_6$)Re(CO)$_2$Cp*. Although the latter was formed in low yield (5%),

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(2) For examples of C−H bond activation of aromatics, see: (a) Arndtsen, B. A.; Bergman, R. G. *Science* **1995**, *270*, 1970. (b) Chin, R. M.; Dong, L.; Duckett, S. B.; Jones, W. D. *Organometallics* **1992**, *11*, 871. (c) Chin, R. M.; Dong, L.; Duckett, S. B.; Partridge, M. G.; Jones, W. D.; Perutz, R. N. *J. Am. Chem. Soc.* **1993**, *115*, 7685. (d) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1984**, *106*, 1650. (e) Werner, R.; Werner, H. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 793. (f) Green, M. A.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1981**, *103*, 695. (g) Jones, W. D.; Hessell, E. T. *J. Am. Chem. Soc.* **1992**, *114*, 6087.

(3) Fragment **1** is the only known metal system that forms thermally stable η^2-complexes with arenes, pyrroles, furans, and thiophenes.

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(5) For example, the inability to alter the pentaammine ligand set has placed restrictions on the ability to perform enantioselective reactions, the acidic ammonia ligands limit the range of nucleophiles accessible for dearomatization reaction sequences, and the dicationic nature of **1** restricts the solvent environments and purification techiniques available for use.

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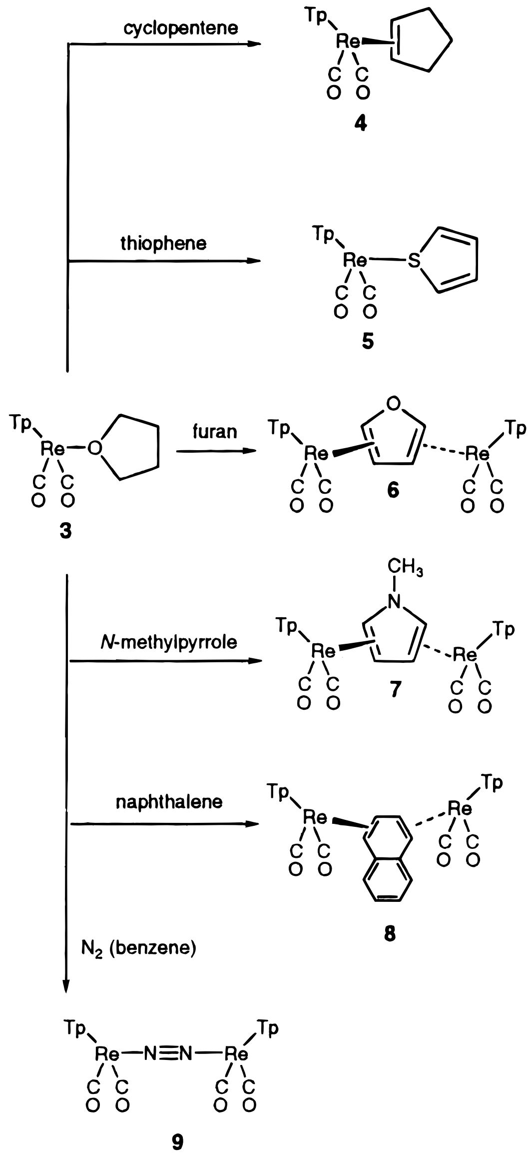
this thermally stable material is isoelectronic to the complex $\{Os(NH_3)_5\}_2(\mu\text{-}1,2\text{-}\eta^2\text{-}3,4\text{-}\eta^2\text{-}C_6H_6)$ prepared by Taube and Harman.[20] We reasoned that by replacing the Cp* with Tp, a ligand purported to have stronger σ-donor abilities[21] and to be more predisposed to supporting complexes of octahedral geometry than its carbon counterpart,[22] a more stable class of mononuclear η^2-arene complexes would result.

Results

Recently, transition metal chemistry with hydridotris(pyrazolyl)borate ligands has attracted considerable attention.[23,24] Moret et al. have reported that the tetrahydrofuran (THF) ligand of $TpRe(CO)_2(THF)$ (**3**) (Tp = hydridotris(pyrazolyl)borate) is labile, and the facile dissociation of the cyclic ether ligand allowed access to complexes of the type $TpRe(CO)_2(L)$ (L = PPh_3, CH_3CN, pyridine, and PMe_2Ph).[25] To establish a benchmark for spectroscopic reference, the coordination of a nonaromatic hydrocarbon was attempted first. Reaction of $TpRe(CO)_2(THF)$ (**3**) with an excess of cyclopentene in benzene produces the compound $TpRe(CO)_2(\eta^2\text{-cyclopentene})$ (**4**) in 66% isolated yield (Scheme 1). The disappearance of CO stretching frequencies for **3** (1907, 1823 cm^{-1} in C_6H_6) and incipient stretching frequencies at 1954 and 1866 cm^{-1} are consistent with the replacement of the THF ligand with the moderately π-acidic cyclopentene ligand. A cyclic voltammogram of **4** taken in DMA shows a reversible oxidation wave at $E_{1/2} = 1.08$ V (vs NHE).[26] The 0.66 V increase for the Re^{II}/Re^{I} couple of **4** compared to **3** reflects the stabilization of the lower oxidation state for the latter compound due to π back-bonding. The better σ-donor properties of THF compared to the olefin would also be consistent with these electrochemical observations. A mirror plane of symmetry which bisects the Tp, CO, and η^2-cyclopentene ligands is implicated by the ^1H and ^{13}C NMR spectra of **4**. Thus, 2:1 patterns are detected for the Tp proton resonances, and four distinct cyclopentene proton resonances are evident in the ^1H NMR spectrum, and a single carbonyl resonance and three unique cyclopentene carbon resonances are observed in the ^{13}C NMR spectrum. The bound cyclopentene carbons are equivalent and resonate as a doublet (J_{CH} = 164 Hz) at 71.8 ppm in the ^{13}C NMR spectrum. These data are consistent with η^2-bonding in d^6 dicarbonyl complexes of C_s symmetry (Scheme 2).[27] A CD_2Cl_2 solution of **4** shows no signs of decomposition after several days.

Scheme 1. Reactions of $TpRe(CO)_2(THF)$ (**3**) with Unsaturated Compounds[a]



[a] Reactions were performed under an atmosphere of argon, except for the synthesis of **9**.

Reaction of **3** with thiophene results in the displacement of the THF ligand with the sulfur heterocycle (79% yield, Scheme 1). In this case, spectroscopic and electrochemical features are

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(20) Harman, W. D.; Taube, H. *J. Am. Chem. Soc.* **1987**, *109*, 1883.

(21) There are conflicting reports in the literature concerning the donating ability of Tp relative to cyclopentadienyl ligands. See, for example: (a) Curtis, M. D.; Shiu, K.-B.; Butler, W. M.; Huffman, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 3335. (b) Sun, N.-Y.; Simpson, S. J. *J. Organomet. Chem.* **1992**, *434*, 341.

(22) It has been suggested that the localized facial bonding of the Tp ligand polarizes the metal d-orbitals into a preferred octahedral geometry: (a) Curtis, M. D.; Shiu, K.-B.; Butler, W. M. *J. Am. Chem. Soc.* **1986**, *108*, 1550. (b) Curtis, M. D.; Shiu, K. *Inorg. Chem.* **1985**, *24*, 1213. (c) Gelabert, R.; Moreno, M.; Lluch, J. M.; Lledós, A. *Organometallics* **1997**, *16*, 3805. (d) Oldham, W. J., Jr.; Hinkle, A. S.; Heinekey, D. M. *J. Am. Chem. Soc.* **1997**, *119*, 11028.

(23) For recent reviews of hydridotris(pyrazolyl)borate ligands, see: (a) Kitajima, N.; Tolman, W. D. *Prog. Inorg. Chem.* **1995**, *43*, 419. (b) Trofimenko, S. *Chem. Rev.* **1993**, *93*, 943. (c) Trofimenko, S. *Prog. Inorg. Chem.* **1986**, *34*, 115.

(24) For a representative list of recent chemistry with tris(pyrazolyl)borate ligands, see: (a) Bromberg, S. E.; Yang, H.; Asplund, M. C.; Lian, T.; McNamara, B. K.; Kotz, K. T.; Yeston, J. S.; Wilkens, W.; Frei, H.; Bergman, R. G.; Harris, C. B. *Science* **1997**, *278*, 260. (b) Katayama, H.; Yamamura, K.; Miyaki, Y.; Ozawa, F. *Organometallics* **1997**, *16*, 4497. (c) Bohanna, C.; Esteruelas, M. A.; Gómez, A. V.; López, A. M.; Martínez, M.-P. *Organometallics* **1997**, *16*, 4464. (d) Trimmel, G.; Slugovc, C.; Wiede, P.; Mereiter, K.; Sapunov, V. N.; Schmid, R.; Kirchner, K. *Inorg. Chem.* **1997**, *36*, 1076. (e) Wick, D. D.; Jones, W. D. *Inorg. Chem.* **1997**, *36*, 2723. (f) Keyes, M. C.; Young, V. G., Jr.; Tolman, W. B. *Organometallics* **1996**, *15*, 4133. (g) Gunnoe, T. B.; White, P. S.; Templeton, J. L.; Casarrubios, L. *J. Am. Chem. Soc.* **1997**, *119*, 3171. (h) O'Reilly, S. A.; White, P. S.; Templeton, J. L. *J. Am. Chem. Soc.* **1996**, *118*, 5684. (i) Paneque, M.; Taboada, S.; Carmona, E. *Organometallics* **1996**, *15*, 2678. (j) Chen, Y.-Z.; Chan, W. C.; Lau, C. P.; Chu, H. S.; Lee, H. L.; Jia, G. *Organometallics* **1997**, *16*, 1241. (k) Chan, W.-C.; Lau, C.-R.; Chen, Y.-Z.; Fang, Y.-Q.; Ng, S.-M.; Jia, G. *Organometallics* **1997**, *16*, 34. (l) Oldham, Jr., W. J.; Heinekey, D. M. *Organometallics* **1997**, *16*, 467. (m) Chowdhury, S. K.; Nandi, M.; Joshi, V. S.; Sarkar, A. *Organometallics* **1997**, *16*, 1806. (n) Brown, S. N.; Mayer, J. M. *J. Am. Chem. Soc.* **1996**, *118*, 12119. (o) Woodworth, B. E.; White, P. S.; Templeton, J. L. *J. Am. Chem. Soc.* **1997**, *119*, 828. (p) Wick, D. D.; Goldberg, K. I. *J. Am. Chem. Soc.* **1997**, *119*, 10235.

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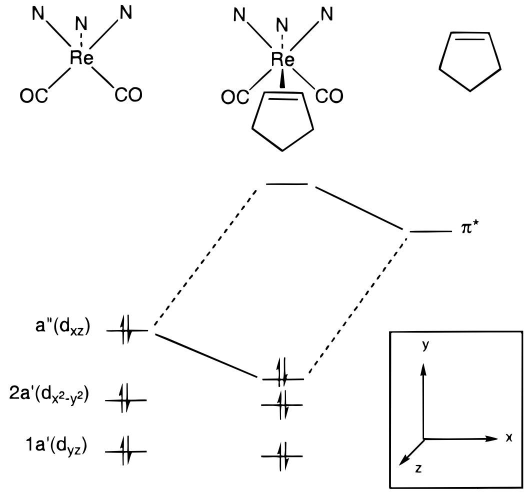
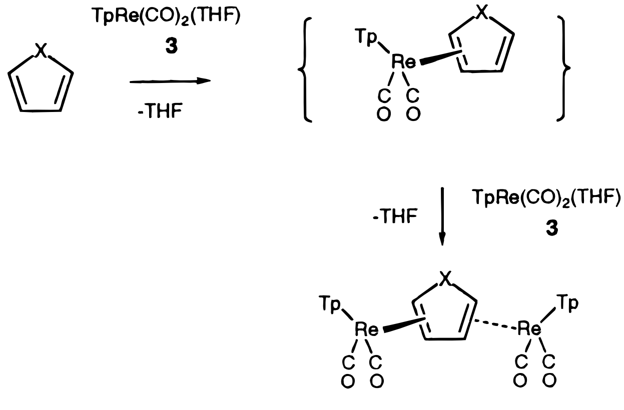
(26) For comparison, the related complex $[(dien)Re(PF_3)(PPh_3)(\text{cyclopentene})][OTf]$ (dien = diethylenetriamine) shows a reversible oxidation wave at 0.51 V (CH_3CN): Brooks, B. C.; Chin, M.; Harman, W. D. Submitted for publication.

(27) See, for example: (a) Schilling, B. E. R.; Hoffmann, R.; Lichtenberger, D. L. *J. Am. Chem. Soc.* **1979**, *101*, 585. (b) Schilling, B. E. R.; Hoffmann, R.; Faller, J. W. *J. Am. Chem. Soc.* **1979**, *101*, 592.

Scheme 2. Qualitative Molecular Orbital Diagram for TpRe(CO)$_2$(η^2-cyclopentene) (**4**) Demonstrating the Electronically Preferred Orientation of the Cylcopentene Ligand



Scheme 3. Proposed Route for the Formation of the Heterocycle-Bridged Complexes **6** and **7**

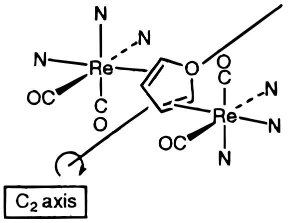


6 (X = O)
7 (X = NCH$_3$)

inconsistent with dihapto binding. The thiophene proton resonances (7.42, 7.22 ppm) remain degenerate (2H) and are shifted downfield relative to free thiophene (7.37, 7.14 ppm), the thiophene carbons resonate at 136.9 and 130.8 ppm in the ^{13}C NMR spectrum of **5**, and the IR spectrum of **5** reveals CO stretching frequencies at 1930 and 1852 cm^{-1}. The cyclic voltammogram of **5** reveals a reversible oxidation wave at $E_{1/2} = 0.82$ V (CH$_2$Cl$_2$; cf. 1.08 V for **4**) for the (II/I) couple. Complex **5** decomposes in solution (CD$_2$Cl$_2$; $t_{1/2} \sim 10$ h at room temperature) with concomitant appearance of resonances for free thiophene. In addition to the above data, the 2:1 pattern for the Tp ligand in the ^{1}H NMR spectrum of **5** as well as equivalent carbonyl ligands in the ^{13}C NMR spectrum support the conclusion that the thiophene ligand is bound through sulfur. Evidence for the existence of an η^2-bound isomer has not been found (complex **5** is >95% sulfur-bound as determined by NMR and IR spectroscopy).

In contrast to that observed for thiophene, when a benzene solution of **3** is treated with an excess of furan a binuclear species, Tp(CO)$_2$Re(μ-2,3-η^2-4,5-η^2-furan)Re(CO)$_2$Tp (**6**), precipitates from solution (Schemes 1 and 3) over a period of 4 h.[28] Complex **6** is isolated in 58% yield and is characterized by $\nu_{CO} = 1952$ and 1852 cm^{-1} in the IR spectrum, resonances at 6.12 and 5.11 ppm (each a doublet) for the bound furan α- and β-protons (respectively) in the ^{1}H NMR spectrum, and upfield chemical shifts for the bound furan carbons in the ^{13}C NMR spectrum (103.4 and 65.3 ppm, each a doublet). The ^{1}H and ^{13}C NMR spectra of **6** indicate that the two rhenium environments are equivalent. The sterically most feasible structure is one in which the two metal centers are bound to opposite faces of the aromatic ligand. Thus, a C_2 axis of symmetry likely bisects the furan bridge (Scheme 4). A CD$_2$Cl$_2$ solution of **6** shows that the furan binuclear complex is unchanged after a period of days. A cyclic voltammogram of **6** recorded in CH$_2$Cl$_2$ shows a quasi-reversible oxidation wave at $E_{1/2} = 0.98$ V and a second irreversible oxidation peak at $E_{p,a} = 1.25$ V.

Scheme 4. Proposed Geometry of TpRe(CO)$_2$(μ-2,3-η^2-4,5-η^2-furan)Re(CO)$_2$Tp (**6**) with the Two Rhenium Environments Equivalent by a C_2 Axis of Rotation



The reaction that forms **6** was repeated in neat furan to suppress the formation of binuclear complexes. After 2 h, hexane was added effecting the precipitation of the metal complexes. A ^{1}H NMR spectrum of the resulting solid material indicated the presence of a combination of components, none of which were the starting material. Resonances for the dimer **6** were present, as well as four broad peaks at 8.32, 7.04, 6.79, and 5.68 ppm. We tentatively attribute these broad resonances to the putative monomeric intermediate TpRe(CO)$_2$(η^2-furan). A fluxional process would account for the observed line broadening of these signals. ^{1}H NMR spectra (CD$_2$Cl$_2$) recorded over time reveal that these peaks disappear after 2 to 3 h accompanied by the appearance of resonances for free furan. In addition, the appearance of a third uncharacterized product is observed, and this product is ascribed to the reaction of TpRe(CO)$_2$ with CD$_2$Cl$_2$.[29] Apparently, reaction of the {TpRe(CO)$_2$} fragment with the deuterated solvent is kinetically competitive with the reaction with TpRe(CO)$_2$(η^2-furan) to form **6**.

Similar to what is observed for the reaction of **3** with furan, a benzene solution of TpRe(CO)$_2$(THF) and excess *N*-methylpyrrole produces a yellow precipitate which is characterized as the *N*-methylpyrrole bridged complex Tp(CO)$_2$Re(μ-2,3-η^2-4,5-η^2-*N*-methylpyrrole)Re(CO)$_2$Tp (**7**) (Schemes 1 and 3, 35% yield). Spectroscopic and electrochemical properties of **7** are similar to those of **6**. The pyrrole ring protons resonate as doublets at 6.85 and 4.55 ppm in the ^{1}H NMR spectrum, substantially shifted upfield from those of the free ligand. The methyl group of the bound heterocycle resonates as a singlet at 3.84 ppm. A C_2 axis of symmetry is inferred from equivalent rhenium environments, and the lack of mirror symmetry in the bimetallic complex is confirmed by six downfield doublets and three distinct triplets from 6.27 to 6.17 ppm for the chemically inequivalent Tp rings. The ^{13}C NMR spectrum shows resonances for the bound pyrrole carbons at 100.7 and 67.8 ppm.

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[28] The binuclear complex [((NH$_3$)$_5$Ru)$_2$(μ-2,3-η^2-4,5-η^2-furan)][OTf]$_4$ has been reported: Chen, H. "Activation of Olefins and Furans with Pentaammineosmium(II)," Ph.D. Dissertation, University of Virginia, 1997.

[29] Independent reaction of TpRe(CO)$_2$(THF) in neat CD$_2$Cl$_2$ confirms this assignment.

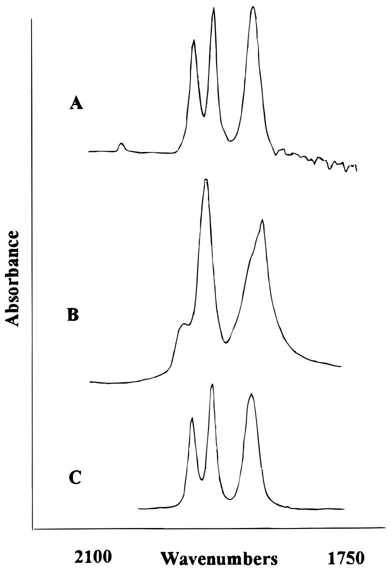

Figure 1. Various IR spectra of Tp(CO)$_2$Re(μ-N$_2$)Re(CO)$_2$Tp (**9**): (**A**) methylene chloride solution of crude product; (**B**) KBr pellet of a crystalline sample; (**C**) methylene chloride solution of the same crystalline sample.

Carbonyl stretching frequencies at 1931 and 1846 cm^{-1} are observed in the IR spectrum of complex **7**. Similar to complex **6**, the cyclic voltammogram of **7** exhibits a quasi-reversible oxidation wave at $E_{1/2} = 0.61$ V and an irreversible oxidation peak at $E_{1/2} = 0.89$ V. The decomposition of **7** in CD$_2$Cl$_2$ is accompanied by the appearance of resonances for free *N*-methylpyrrole ($t_{1/2} \sim 6.5$ h).

Tp(CO)$_2$Re(μ-1,2-η^2-3,4-η^2-naphthalene)Re(CO)$_2$Tp (**8**) is isolated in 44% yield from the reaction of TpRe(CO)$_2$(THF) with excess naphthalene in benzene (Scheme 1). The ^{1}H and ^{13}C NMR spectra of **8** confirm the formation of a bimetallic species in which two rhenium metal centers are bound to a single ring of the hydrocarbon. Like the other binuclear species reported above, we attribute the equivalent metal environments to a C_2 axis of symmetry which lies in the plane of the naphthalene rings and is orthogonal to its ring juncture. Consistent with this assertion is the observation of four unique proton resonances for bound naphthalene in the ^{1}H NMR spectrum (7.31, 7.24, 5.47, and 4.38 ppm) and five resonances in the ^{13}C NMR spectrum (129.1, 128.7, 125.7, 68.3, and 64.8 ppm). The ^{1}H NMR resonances for the uncoordinated portion of the naphthalene ligand exhibit a classic AA′BB′ pattern.[30] The IR spectrum of **8** reveals CO stretching frequencies at 1952 and 1871 cm^{-1}, and the cyclic voltammogram of **8** has a quasi-reversible oxidation couple at $E_{1/2} = 0.91$ V. A second oxidation wave ($E_{p,a} = 1.41$ V) is observed with a peak separation of 0.46 V.

The ability of the TpRe(CO)$_2$ fragment to bind cyclopentene, furan, *N*-methylpyrrole, and naphthalene in a dihapto-coordination mode prompted an exploration of the reaction of **3** in neat benzene. Under a dinitrogen atmosphere, stirring complex **3** in benzene yields the dinitrogen-bridged bimetallic complex Tp(CO)$_2$Re(μ-N$_2$)Re(CO)$_2$Tp (**9**) in 65% isolated yield.[31] Complex **9** has been characterized by ^{1}H, ^{13}C, and IR spectra, cyclic voltammetry, and X-ray crystallography (vide infra). As expected, the two rhenium environments are equivalent in solution and the solid state. In addition, a mirror plane of symmetry which is parallel to the Re−N$_2$−Re bond axis bisects the Tp ligands and the OC−Re−CO angles. The IR spectrum of a solid sample of **9** exhibits a CO stretching pattern consisting of *three* absorptions (1957, 1931, 1848 cm^{-1} in CH$_2$Cl$_2$, Figure 1, spectrum A, vide infra).

Table 1. Selected Crystallographic Data and Collection Parameters for Tp(CO)$_2$Re(μ-N$_2$)Re(CO)$_2$Tp·CH$_2$Cl$_2$ (**9**)

formula	C$_{23}$H$_{20}$N$_{14}$O$_4$B$_2$Cl$_2$Re$_2$
mol wt	1021.44
crystal	brown prism
cryst dimens, mm	0.28 × 0.31 × 0.43
cryst syst	monoclinic
space group	$P2_1/c$ (No. 14)
a, Å	7.675(2)
b, Å	13.090(4)
c, Å	16.567(6)
β, deg	96.80(3)
V, Å^3	1653(1)
Z	2
D_{calcd}, g cm^{-3}	2.05
μ(MoKα), cm^{-1}	75.36
absorption corrections	ψ scans (trans. factors 0.53−1.00)
temp, °C	−100
2θ max, deg	46
total no. reflections	2683
unique reflections	2427
R	0.040
R_w	0.054

The cyclic voltammogram of **9** shows a reversible couple with $E_{1/2} = 0.90$ V and an anodic wave at $E_{p,a} = 1.55$ V (NHE). The first oxidation peak (0.90 V) is fully reversible only if the scan direction is reversed prior to the second oxidation (1.55 V). When complex **3** is allowed to stand in benzene solution under argon, no reaction occurs even at elevated temperatures (65 °C/2 weeks).

X-ray Structure of Tp(CO)$_2$Re(μ-N$_2$)Re(CO)$_2$Tp (9). A single-crystal X-ray diffraction study confirmed the identity of Tp(CO)$_2$Re(μ-N$_2$)Re(CO)$_2$Tp (**9**). Collection data and parameters are summarized in Table 1, selected bond distances and angles are presented in Table 2, and an ORTEP diagram is shown in Figure 2. A search of the Cambridge Crystallographic Database revealed no other structurally characterized dinitrogen-bridged dirhenium complexes. However, solid-state structures of rhenium dinitrogen monomers have been reported.[32] Each rhenium center is in a slightly distorted octahedral environment, and the Tp ligands are in an anti orientation. A mirror plane of symmetry containing both metal centers and the unique pyrazolyl ring of each Tp ligand bisects both OC−Re−CO angles. The two equivalent metal environments are related by a C_2 axis of rotation which bisects the dinitrogen bridge and lies orthogonal to the mirror plane. Bond distances from the Tp ligands to the rhenium centers (Re−N 2.1 Å) are similar to other Tp−Re complexes.[23n,24,33] The Re−N−N−Re linkage is nearly linear (Re−N−N angle = 176(1)°) with a nitrogen−nitrogen bond distance of 1.15(2) Å. The dinitrogen bond length lies on the low end of other reported structures and is only

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[30] Friebolin, H. *Basic One and Two-Dimensional NMR Spectroscopy*, 2nd ed.; VCH Publishers: New York, 1993; p 122.

[31] (a) For a substantial list of dinitrogen-bridged metal binuclear complexes, see ref 9 in Laplaza, C. E.; Johnson, M. J. A.; Peters, J. C.; Odom, A. L.; Kim, E.; Cummins, C. C.; George, G. N.; Pickering, I. J. *J. Am. Chem. Soc.* **1996**, *118*, 8623. (b) Also, see Hidai, M.; Mizobe, Y. *Chem. Rev.* **1995**, *95*, 1115.

[32] (a) Pombeiro, A. J. L.; Hitchcock, P. B.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1987**, 319. (b) Davis, B. R.; Ibers, J. A. *Inorg. Chem.* **1971**, *10*, 578. (c) Carvalho, M. F. N. N.; Pombeiro, A. J. L.; Schubert, U.; Orama, O.; Pickett, C. J.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1985**, 2079. (d) The structure of Cp−Me(CO)$_2$Mn(μ-N$_2$)Mn(CO)$_2$Cp−Me has been reported: Weidenhammer, V. K.; Herrmann, W. A.; Ziegler, M. L. *Z. Anorg. Allg. Chem.* **1979**, *457*, 183.

[33] Brown, S. N.; Mayer, J. M. *Organometallics* **1995**, *14*, 2951.

Table 2. Selected Bond Distances (Å) and Angles (deg) for Tp(CO)$_2$Re(μ-N$_2$)Re(CO)$_2$Tp (**9**)

Re−N1	2.17(1)	Re−C10	1.91(2)
Re−N3	2.12(1)	Re−C11	1.90(2)
Re−N5	2.15(1)	C10−O1	1.15(2)
Re−N7	1.98(1)	C11−O2	1.16(2)
N7−N7*	1.15(2)		
N1−Re−N3	83.7(4)	N5−Re−N7	87.5(4)
N1−Re−N5	82.0(4)	N5−Re−C10	96.2(5)
N1−Re−N7	91.2(5)	N5−Re−C11	174.5(5)
N1−Re−C10	176.7(5)	N7−Re−C10	91.5(6)
N1−Re−C11	92.7(5)	N7−Re−C11	93.9(6)
N3−Re−N5	84.3(4)	C10−Re−C11	89.1(6)
N3−Re−N7	170.8(4)	Re−N7−N7*	176(1)
N3−Re−C10	93.4(5)	Re−C10−O1	178(1)
N3−Re−C11	93.9(5)	Re−C11−O2	177(1)

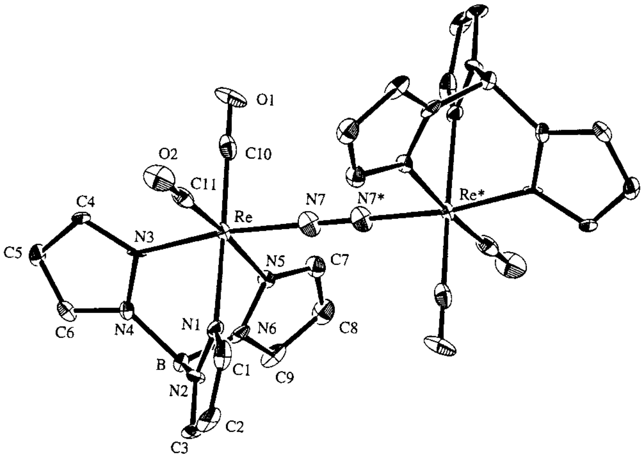

Figure 2. ORTEP diagram for the complex Tp(CO)$_2$Re(μ-N$_2$)Re(CO)$_2$-Tp (**9**) (solvent molecules omitted for clarity).

slightly elongated compared to free dinitrogen (1.098 Å).[34,35] Thus, the bridging dinitrogen unit is only slightly reduced upon coordination to the TpRe(CO)$_2$ fragments, and the Re(μ-N$_2$)Re moiety is best described as possessing a Re−N single bond and a N−N triple bond.

The solid-state structure of Tp′(CO)$_2$Tc(μ-N$_2$)Tc(CO)$_2$Tp′ (Tp′ = hydridotris(3,5-dimethylpyrazolyl)borate) has been reported.[36] Although the Tc−N−N bond angle (174.0 °) and N−N bond distance (1.160 Å) of this complex are comparable with complex **9**, the two congeners crystallize with different conformations. The pyrazolylborate ligands of **9** are in an anti orientation, while the technetium dimer displays a structure in which one of the metal fragments is rotated 90° compared to **9**. The implications of this observation are discussed below.

Discussion

To our knowledge, complexes **6** and **7** represent the only examples reported in the literature[28] of heterocycle-bridged binuclear species not involving coordination of the heteroatom. Angelici et al. have reported a μ-Se,η^2 binuclear selenophene complex of rhenium,[18a,b] and numerous examples exist of μ-*N*,*N*-pyrazine binuclear species.[37] Although not unprecedented, binuclear complexes of aromatic hydrocarbons are equally rare. Orpen et al. have reported the isolation of Cp*(CO)$_2$Re(μ-1,2-η^2-3,4-η^2-C$_6$H$_6$)Re(CO)$_2$Cp*,[19] and Jones et al. have prepared a binuclear naphthalene rhodium complex similar to **8**.[38] In addition, binuclear complexes of naphthalene and benzene have been synthesized that incorporate pentaammineosmium(II).[20,39]

The pyrazolyl borate ligand apparently deters the formation of CO-bridged dimeric complexes and oxidative addition products characteristic of electron-rich metal systems by enforcing the octahedral geometry. Thus, while Cp*(CO)$_2$Re(μ-1,2-η^2-3,4-η^2-C$_6$H$_6$)Re(CO)$_2$Cp* was a minor product amid the formation of, inter alia, CO-bridged rhenium binuclear complexes,[19] complexes **6**−**8** form in reasonable yields (35−58%) while products due to CO-bridging or oxidative addition were undetected.

Only in the case of thiophene was a mononuclear heterocyclic complex stable enough to be isolated. In contrast to that observed for the pentaammineosmium(II) system,[40] thiophene is coordinated by {TpRe(CO)$_2$} at the heteroatom. In contrast to the heteroatoms of pyrrole or furan, sulfur can participate directly with π symmetry orbitals of the metal. Correspondingly, several examples have been reported of *S*-bound thiophene complexes, while pentaammineosmium(II) remains the only known transition metal system that favors dihapto coordination.[40]

Given that {TpRe(CO)$_2$} shares with {Os(NH$_3$)$_5$}$^{2+}$ the unusual ability to form stable η^2-bound complexes with aromatic ligands, a direct comparison of spectroscopic and electrochemical properties is warranted. These data suggest that despite its high cationic charge, the osmium system is considerably more electron-rich than this isoelectronic rhenium analogue. Electrochemical data enforce this hypothesis. Whereas most olefinic complexes of pentaammineosmium(II) show d^5/d^6 reduction potentials near 0.5 V,[41] compound **4** has a potential more than 0.5 V positive of this value (Table 3), indicative of its greater resistance to oxidation. Furthermore, whereas the THF complex **3** and *S*-bound thiophene complex **5** show d^5/d^6 reduction potentials of 0.42 and 0.82 V, respectively, the osmium analogues are estimated to be shifted nearly 1 V more negative.[42] The above observations make a strong argument that, although the oxidation state and charge of the rhenium system is lower, the CO ligands more than compensate for this and render the group 7 analogue a less potent π-base.

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(34) See, for example: (a) Churchill, M. R.; Li, Y. *J. Organomet. Chem.* **1986**, *301*, 49. (b) Churchill, M. R.; Li, Y.-J.; Theopold, K. H.; Schrock, R. R. *Inorg. Chem.* **1984**, *23*, 4472. (c) Luo, X.-L.; Kubas, G. J.; Burns, C. J.; Butcher, R. J.; Bryan, J. C. *Inorg. Chem.* **1995**, *34*, 6538. (d) Schrock, R. R.; Kolodziej, R. M.; Liu, A. H.; Davis, W. M.; Vale, M. G. *J. Am. Chem. Soc.* **1990**, *112*, 4338. (e) Shih, K.-Y.; Schrock, R. R.; Kempe, R. *J. Am. Chem. Soc.* **1994**, *116*, 8804 and references therein.

(35) Wilkinson, P. G.; Houk, N. B. *J. Chem. Phys.* **1956**, *24*, 528.

(36) (a) Joachim, J. E.; Apostolidis, C.; Kanellakopulos, B.; Maier, R.; Meyer, D.; Rebizant, J.; Ziegler, M. L. *J. Organomet. Chem.* **1993**, *455*, 137. (b) Analogous to complex **9**, Tp′(CO)$_2$Tc(μ-N$_2$)Tc(CO)$_2$Tp′ displays three CO stretching frequencies: 1964, 1941, and 1899 cm^{-1}.

(37) For representative examples from an extensive area of literature, see: (a) Wlodarczyk, A.; Doyle, G. A.; Maher, J. P.; McCleverty, J. A.; Ward, M. D. *Chem. Commun.* **1997**, 769. (b) Caruso, F.; Giomini, M.; Giuliani, A. M.; Rivarola, E. *J. Organomet. Chem.* **1996**, *506*, 67. (c) George, M. W.; Johnson, F. P. A.; Turner, J. J.; Westwell, J. R. *J. Chem. Soc., Dalton Trans.* **1995**, 2711. (d) Lay, P. A.; Magnuson, R. H.; Taube, H. *Inorg. Chem.* **1988**, *27*, 2364. (e) Steed, J. W.; Tocher, D. A. *J. Organomet. Chem.* **1991**, *412*, C34. (f) Julve, M.; Verdaguer, M.; Faus, J.; Tinti, F.; Moratal, J.; Monge, A.; Gutiérrez-Puebla, E. *Inorg. Chem.* **1987**, *26*, 3520.

(38) (a) Chin, R. M.; Dong, L.; Duckett, S. B.; Jones, W. D. *Organometallics* **1992**, *11*, 871.

(39) Harman, W. D.; Taube, H. *J. Am. Chem. Soc.* **1988**, *110*, 7555.

(40) (a) Cordone, R.; Harman, W. D.; Taube, H. *J. Am. Chem. Soc.* **1989**, *111*, 5969. (b) Spera, M. L.; Harman, W. D. *Organometallics* **1995**, *14*, 1559. (c) Spera, M. L.; Harman, W. D. *J. Am. Chem. Soc.* **1997**, *119*, 8843. (d) For an η^2-benzothiophene complex, see: Robertson, M. J.; Day, C. L.; Jacobson, R. A.; Angelici, R. J. *Organometallics* **1994**, *13*, 179.

(41) Chen, H.; Harman, W. D. *J. Am. Chem. Soc.* **1996**, *118*, 5672.

(42) (a) The d^5/d^6 reduction potential for [(NH$_3$)$_5$Os(H$_2$O)]$^{2+}$ is −0.73 V: Gulens, J.; Page, J. A. *J. Electroanal. Chem.* **1974**, *65*, 239. (b) The reduction potential for the sulfur bound complex [(NH$_3$)$_5$Os(η^1-tetrahydrothiophene)]$^{2+}$ is 0.01 V: Spera, M. L. “Elementary Transformations of Dihapto-Coordinated Thiophene Complexes of Pentaammineosmium(II),” Ph.D. Dissertation, University of Virginia, 1997.

Table 3. Selected Data for Complexes 3−9

complex	IR (νCO)[a]	$E_{1/2}$ (II/I)[b],v
TpRe(CO)$_2$(THF) (**3**)	1901, 1811[c]	0.42
TpRe(CO)$_2$(η^2-cyclopentene) (**4**)	1958, 1869	1.08
TpRe(CO)$_2$(η^1-thiophene) (**5**)	1927, 1846	0.82[e]
[Tp(CO)$_2$Re]2[μ-η^2,$\eta^{2'}$-furan] (**6**)	1952, 1872	0.98, 1.25[d,e]
[Tp(CO)$_2$Re]2[μ-η^2,$\eta^{2'}$-*N*-methylpyrrole] (**7**)	1931, 1846	0.61, 0.89[d]
[Tp(CO)$_2$Re]2[μ−η2,η2′-naphthalene] (**8**)	1952, 1871	0.91, 1.41[d]
[Tp(CO)$_2$Re][μ-N2] (**9**)	1956,1924, 1849[f]	0.90, 1.55[d]

[a] In CH_2Cl_2, cm^{-1}. [b] vs NHE, in DMA. [c] See ref 24. [d] Reported for $E_{p,a}$. [e] In CH_2Cl_2. [f] KBr pellet.

Interestingly, the first oxidation peak for the *N*-methylpyrrole complex **7** is considerably more negative than the other η^2-bound binuclear species and is even negative of the couple for the σ-bound thiophene complex **5**. As expected, the CO stretching frequencies of complexes with η^2-bound ligands (**4**, **6**−**8**) are higher compared to the σ-bound THF (**3**) and thiophene (**5**) complexes, but for the *N*-methylpyrrole complex **7** the CO stretching frequencies (1931, 1846 cm^{-1}) are considerably lower in energy than the other aromatic-bridged binuclear complexes and are only slightly higher than the thiophene complex **5**. These effects indicate that even in its fully complexed form the nitrogen atom effectively increases the electron donor ability of the pyrrole ligand relative to furan or naphthalene.

As mentioned above, the IR spectrum of the dinitrogen-bridged dimer **9** exhibits three CO stretching frequencies (Figure 1, spectrum A). The low-energy absorption is clearly broader than the other two absorptions. Of note, the aromatic-bridged bimetallic complexes **6**−**8** display only two CO stretching frequencies in their IR spectra. The three CO absorptions for **9** are ascribed to two possibilities. Although crystallographic data indicate that the two Tp ligands for **9** are in an anti orientation (C_{2h} symmetry), it is possible that a rotational conformer coexists in solution. If only local C_s symmetry is considered, each rotamer would be expected to yield two CO stretching absorptions (symmetric and asymmetric stretches). If the two low-energy absorptions partially overlap, an appropriate ratio of the conformers could explain the observation of three CO stretching absorptions. A second explanation is that only the syn rotational isomer (C_{2v} symmetry) is present and intramolecular vibronic coupling accounts for the three CO absorptions (A_1, B_1, B_2).[43] However, to our knowledge no definitive examples of vibronic coupling in systems without direct metal−metal bonds have been reported. In addition, it is unlikely that the syn isomer would be the thermodynamically preferred rotational conformation. The ability of **9** to access different rotational conformations is supported by the solid-state structure of Tp′(CO)$_2$Tc(μ-N$_2$)Tc(CO)$_2$Tp′ (vide supra).[36] The presence of orthogonal π* orbitals on the dinitrogen bridge likely results in a low electronic contribution to the barrier of metal rotation, and given the distance between the Tp ligands, steric inhibition of rotation is also likely to be minimal. Therefore, the barrier to rotation for the dimer **9** should be small, and complex **9** should have kinetic access to different rotational conformations. An IR spectrum of crystals of **9** (KBr) reveals a change from the solution spectrum (Figure 1, spectrum B).[44] In this spectrum the intensity of the high-energy stretch decreases, and a shoulder can be observed on the low-energy CO absorption. When the crystalline sample is redissolved in methylene chloride, a spectrum identical with the original solution spectrum is acquired (Figure 1, spectrum C). Thus, the three CO absorptions present in the solution IR spectrum of **9** are most likely a superposition of the absorptions of more than one rotamer.

Finally, it is interesting to note that the separation of $E_{p,a}$ for the Re^{I}Re^I/Re^{II}Re^I and Re^{I}Re^{II}/Re^{II}Re^{II} oxidations is about 0.20 V for the two heterocyclic complexes (**6** and **7**), whereas for the hydrocarbon bridged complex **8**, the separation approaches 0.5 V.[45,46] Although it is tempting to suggest that this is indicative of a considerably higher level of communication between the rhenium centers for the latter,[47] we cannot make such a statement without an accurate estimate of $E°$ for the second oxidation wave. It is possible that chemical reactions coupled with the second oxidation ($E_rE_rC_i$) have vastly different rates for **8** compared to **7** or **6**, causing the separation between anodic peaks to be different from the separation of formal reduction potentials.

Conclusion

The ability of the {TpRe(CO)$_2$} fragment to bind aromatic compounds has been demonstrated by the unprecedented formation of binuclear complexes **6**, **7**, and **8**. Spectroscopic evidence suggests that the furan-bridged complex **6** is formed via a transient η^2-furan monomeric complex, and it is reasonable to assume that a similar pathway is operative for the production of **7** and **8**. Thus, while the TpRe(CO)$_2$ moiety can bind aromatic compounds, the presence of two carbonyl ligands significantly reduces the electron density at the metal center and decreases the metal dπ to π* component of metal−aromatic

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(43) See, for example: (a) Casey, C. P.; Konings, M. S.; Marder, S. R. *Polyhedron* **1988**, *7*, 881. (b) Joshi, K. K.; Mills, O. S.; Pauson, P. L.; Shaw, B. W. Stubbs, W. H. *J. Chem. Soc., Chem. Commun.* **1965**, 181. (c) Casey, C. P.; Meszaros, M. W.; Fagan, P. J.; Bly, R. K.; Marder, S. R.; Austin, E. A. *J. Am. Chem. Soc.* **1986**, *108*, 4043.

(44) From the present data, it is impossible to determine the structure of the second conformer or which conformation is dominant. It should be noted that an IR spectrum of a fine powder of **9** yields a spectrum identical with that of a crystalline sample.

(45) The peak-to-peak separations were measured between the apexes of the two anodic waves ($E_{p,a}2 - E_{p,a}1$).

(46) Astruc, D. In *Electron Transfer and Radical Processes in Transition-Metal Chemistry*; VCH Publishers: New York, 1995; p 42.

(47) For a representative sampling of intermetal (intramolecular) electronic communication through bridges, see: (a) Beck, W.; Niemer, B.; Wieser, M. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 923. (b) Geiger, W. E.; Connelly, N. G. *Adv. Organomet. Chem.* **1985**, *24*, 87. (c) Richardson, D. E.; Taube, H. *J. Am. Chem. Soc.* **1983**, *105*, 40. (d) Richardson, D. E.; Taube, H. *Inorg. Chem.* **1981**, *20*, 1278. (e) Richardson, D. E.; Sen, J. P.; Buhr, J. D.; Taube, H. *Inorg. Chem.* **1982**, *21*, 3136. (f) Astruc, D. *Acc. Chem. Res.* **1997**, *30*, 383. (g) Atwood, C. G.; Geiger, W. E.; Rheingold, A. L. *J. Am. Chem. Soc.* **1993**, *115*, 5310. (h) Richardson, D. E.; Taube, H. *Coord. Chem. Rev.* **1984**, *60*, 107. (i) Brady, M.; Weng, W.; Gladysz, J. A. *J. Chem. Soc., Chem. Commun.* **1994**, 2655. (j) Brady, M.; Weng, W.; Zhou, Y.; Seyler, J. W.; Amoroso, A. J.; Arif, A. M.; Böhme, M.; Frenking, G.; Gladysz, J. A. *J. Am. Chem. Soc.* **1997**, *119*, 775. (k) Chin, T. T.; Geiger, W. E.; Rheingold, A. L. *J. Am. Chem. Soc.* **1996**, *118*, 5002. (l) Coat, F.; Lapinte, C. *Organometallics* **1996**, *15*, 477. (m) Etzenhouser, B. A.; Cavanaugh, M. D.; Spurgeon, H. N.; Sponsler, M. B. *J. Am. Chem. Soc.* **1994**, *116*, 2221. (n) Geiger, W. E.; Order, Jr., N. V.; Pierce, D. T.; Bitterwolf, T. E.; Rheingold, A. L.; Chasteen, N. D. *Organometallics* **1991**, *10*, 2403. (o) Narvor, N. L.; Lapinte, C. *J. Chem. Soc., Chem. Commun.* **1993**, 357. (p) Creutz, C.; Taube, H. *J. Am. Chem. Soc.* **1973**, *95*, 1086. (q) Creutz, C.; Taube, H. *J. Am. Chem. Soc.* **1969**, *91*, 3988.

bonding. As a result, the rate of dissociation of the aromatic ligand is significant in the putative monomeric complexes, and the thermodynamically more stable binuclear complexes are isolated.

Experimental Section

General Methods. Unless otherwise noted, all reactions were performed under a dry nitrogen atmosphere in a Vacuum Atmospheres Co. glovebox. ^{1}H and ^{13}C NMR spectra were recorded on a General Electric GN-300 or Varian INOVA-300 spectrometer at room temperature. All chemical shifts are reported in parts per million (ppm) and are referenced to residual ^{1}H signals and to the ^{13}C signals of the deuterated solvents. Coupling constants are reported in hertz (Hz). Peaks in the ^{1}H NMR due to the pyrazole ligands are listed by chemical shift and multiplicity only (all coupling constants are 2 Hz). Infrared spectra were recorded on a MIDAC Prospect Series (Model PRS) spectrometer. Photolyses were performed in a quartz reaction vessel using a water-cooled Hanovia mercury arc lamp. During photolysis, the reaction solutions were cooled by pumping antifreeze at 0 °C (Fisher Scientific Refrigerated Circulator, Model 900) through a cold finger which was submersed in the reaction solution. Electrochemical experiments were performed under a nitrogen atmosphere using a PAR Model 362 potentiostat driven by a PAR Model 175 universal programmer. Cyclic voltammograms were recorded (Kipp and Zonen BD90 XY recorder) in a standard three-electrode cell from +2.20 to −1.50 V with a glassy carbon working electrode. All potentials are reported vs NHE (normal hydrogen electrode) using cobaltocenium hexafluorophosphate ($E_{1/2} = -0.78$ V) as internal standard. The peak-to-peak separation ($E_{p,a} - E_{p,c}$) was between 70 and 100 mV for all reversible couples. Elemental analyses were obtained on a Perkin-Elmer PE−2400 Series II CHN analyzer. All distillations were performed under a nitrogen atmosphere. Benzene and diethyl ether were distilled from Na/benzophenone ketyl, methanol was distilled from Mg(OMe)$_2$ (freshly prepared from Mg activated by iodine), and DMA was distilled from CaH$_2$. Methylene chloride, hexanes, and THF were purified by passage through a column packed with activated alumina.[48] All solvents were thoroughly purged with nitrogen prior to use, unless otherwise noted. Deuterated solvents were deoxygenated by repeated freeze−pump−thaw cycles.

TpRe(CO)$_3$ (**2**) and TpRe(CO)$_2$(THF) (**3**) have been previously reported in the literature.[25] KTp was prepared according to a published procedure.[49] *N*-Methylpyrrole and thiophene were distilled under a dinitrogen atmosphere from CaH$_2$. All other reagents were used as purchased from commercial sources.

TpRe(CO)$_3$ (1). The following procedure is a modification of a literature preparation.[25] In a typical reaction, Re(CO)$_5$Cl (3.0524 g, 8.44 mmol) and KTp (7.448 g, 29.5 mmol, 3.5 equiv) were dissolved in THF (500 mL). The solution was stirred for a period of approximately 36 h, during which time a precipitate formed and the solution color changed from colorless to pale yellow (Note: the appearance of TpRe(CO)$_3$ can be followed by IR spectroscopy.) The solution was vacuum filtered to remove the precipitate (presumably KCl), and the solvent was removed from the filtrate under reduced pressure. The resulting yellow oil was washed with MeOH (5 × 30 mL) and hexanes (5 × 30 mL). The resulting white solid was collected and dried in vacuo (2.3392 g, 57% yield).

TpRe(CO)$_2$(THF) (3). The following procedure is a slight modification of a previously reported preparation.[25] In a representative reaction, TpRe(CO)$_3$ (**2**) (1.5487 g, 3.2 mmol) was dissolved in THF (approximately 200 mL). (Note: the reaction was performed in a quartz vessel.) The solution was cooled using antifreeze (0 °C) circulated through a coldfinger. The colorless solution was irradiated for approximately 15 h, during which time a color change to yellow was noted. The solvent was evaporated to approximately 25 mL under reduced pressure. Addition of MeOH (100 mL) resulted in the precipitation of a yellow solid. The solid was collected by vacuum filtration and washed with MeOH (3 × 15 mL) and hexanes (5 × 30 mL). Drying under vacuum allowed isolation of a yellow powder (1.2764 g, 76% yield). IR (KBr) and NMR spectroscopic data have previously been reported.[25] IR (CH$_2$Cl$_2$): $\nu_{CO} = 1901$, 1811 cm^{-1}. CV (DMA, TBAH, 100 mV/s) (TBAH = tetrabutylammonium hexafluorophosphate): $E_{1/2} = 0.42$ V.

TpRe(CO)$_2$(η^2-cyclopentene) (4). A flask was charged with TpRe(CO)$_2$(THF) (**3**) (0.4700 g, 0.89 mmol) and cyclopentene (0.4 mL, 4.5 mmol). Benzene (175 mL) was added to the reaction flask to achieve total dissolution, and the solution was stirred for 3 h (the dissipation of **3** was followed by infrared spectroscopy). Benzene was removed under reduced pressure, and the resulting product was washed with hexanes (5 × 15 mL). The yellow product was dried in vacuo (0.3067 g, 66% yield). IR (KBr): $\nu_{CO} = 1940$, 1847 cm^{-1}; (CH$_2$Cl$_2$) $\nu_{CO} = 1958$, 1869 cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$, δ): 7.99, 7.97, 7.69, 7.62 (6H, 1:2:2:1, each a d, Tp C*H*), 6.27, 6.23 (3H, 2:1, each a t, Tp C*H*), 3.79 (2H, d, $J_{HH} = 2$ Hz, cyclopentene bound protons), 3.10 (2H, m, cyclopentene protons), 2.77 (2H, ddd, $J_{HH} = 14$, 8, 2 Hz, cyclopentene protons), 1.55 (2H, m, cyclopentene protons). ^{13}C NMR (CD$_2$Cl$_2$, δ): 202.2 (*C*O), 146.6, 142.6, 136.0, 135.1 (each a d, $^1J_{CH} = 185$ Hz, Tp *C*H), 106.8, 106.2 (each a d, $^1J_{CH} = 180$ Hz, Tp *C*H), 71.8 (d, $^1J_{CH} = 164$ Hz, bound *C* of cyclopentene), 34.8 (t, $^1J_{CH} = 129$ Hz, cyclopentene carbons), 21.4 (t, $^1J_{CH} = 131$ Hz, cyclopentene carbons). CV (DMA, TBAH, 100 mV/s): $E_{1/2} = 1.08$ V (NHE). Anal. Calcd for C$_{16}$H$_{18}$BN$_6$O$_2$Re: C, 36.72; H, 3.47; N, 16.06. Found: C, 36.21; H, 3.68; N, 16.14.

TpRe(CO)$_2$(η^1-thiophene) (5). A benzene solution of TpRe(CO)$_2$(THF) (**3**) (0.5569 g, 1.06 mmol) and thiophene (1.3 mL, 15.9 mmol) was purged with argon for 30 min. The solution was stirred for approximately 4 h, and then the solvent was removed under reduced pressure. The tan product was collected, washed with hexanes (75 mL), and dried under vacuum (0.4538 g, 79% yield). IR (CH$_2$Cl$_2$): $\nu_{CO} = 1927$, 1846 cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$, δ): 7.77, 7.71, 7.62, 7.59 (6H, 1:2:1:2, each a d, Tp C*H*), 7.42, 7.22 (4H, 2:2, each a m, thiophene protons), 6.21, 6.17 (3H, 2:1, each a t, Tp C*H*). ^{13}C NMR (CD$_2$Cl$_2$, δ): 201.3 (*C*O), 146.7, 143.9, 135.6 (each a d, $^1J_{CH} = 188$ Hz, 1:1:2, Tp *C*H), 136.9, 130.8 (each a d, $^1J_{CH} = 187$, 177 Hz, ring carbons of thiophene), 106.7, 106.3 (each a d, $^1J_{CH} = 179$ Hz,Tp *C*H). CV (CH$_2$Cl$_2$, TBAH, 100 mV/s): $E_{1/2} = 0.82$ V. Anal. Calcd for C$_{15}$H$_{14}$BN$_6$O$_2$ReS$\cdot^1/_6$C$_6$H$_6$ (note: in the ^{1}H NMR of the analysis sample, 1/6 molecule of benzene was found by integration vs proton signals of complex **5**): C, 34.79; H, 2.74; N, 15.21. Found: C, 34.76; H, 3.04; N, 15.55.

Tp(CO)$_2$Re(μ-2,3-η^2-4,5-η^2-furan)Re(CO)$_2$Tp (6). In a 250-mL flask, furan (0.58 mL, 8.04 mmol) was added to TpRe(CO)$_2$(THF) (**3**) (0.4241 g, 0.804 mmol). Dissolution in benzene (100 mL) was followed by purging with argon for 1 h. After 4 h a precipitate was observed. The pale yellow precipitate was collected by vacuum filtration and dried in vacuo (0.2283 g, 58% yield). IR (KBr): $\nu_{CO} = 1952$, 1852 cm^{-1}; (CH$_2$Cl$_2$) $\nu_{CO} = 1952$, 1872 cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$, δ): 8.24, 7.92, 7.77, 7.76, 7.72, 7.66 (12H, 2:2:2:2:2:2, each a d, Tp C*H*), 6.36, 6.28, 6.24 (6H, 2:2:2, each a t, Tp C*H*), 6.12 (2H, d, $^3J_{HH} = 3$ Hz, furan α-proton), 5.11 (2H, d, $^3J_{HH} = 3$ Hz, furan β-proton). ^{13}C NMR (CD$_2$Cl$_2$, δ): 203.0, 200.4 (*C*O), 146.5, 143.1, 142.3, 136.2, 135.8, 135.4 (each a d, $^1J_{CH} = 188$ Hz, Tp *C*H), 106.8, 106.6, 106.4 (each a d, $^1J_{CH} = 180$ Hz, Tp *C*H), 103.4 (d, $^1J_{CH} = 176$ Hz, furan α-carbon), 65.3 (d, $^1J_{CH} = 176$ Hz, furan β-carbon). CV (CH$_2$Cl$_2$, TBAH, 100 mV/s): E$_{1/2}$ = 0.98 V (quasi-reversible); $E_{p,a} = 1.25$ V. Anal. Calcd for C$_{26}$H$_{24}$B$_2$N$_{12}$O$_5$Re$_2$−C$_6$H$_6$: C, 36.37; H, 2.86; N, 15.91. Found: C, 37.06; H, 3.38; N, 15.88.

Tp(CO)$_2$Re(μ-2,3-η^2-4,5-η^2-*N*-methylpyrrole)Re(CO)$_2$Tp (7). In a representative reaction, a flask was charged with TpRe(CO)$_2$(THF) (**3**) (0.3817 g, 0.724 mmol), *N*-methylpyrrole (1.3 mL, 14.5 mmol), and approximately 75 mL of benzene. The solution was purged with argon throughout the course of the reaction. After 2 h of stirring, a yellow precipitate was noted. After 5 h (from the initial mixing of the reactants), the solution was vacuum filtered in order to collect the yellow precipitate. The pale yellow solid was washed with hexanes (2 × 15 mL) and dried under reduced pressure (35% yield). IR (CH$_2$Cl$_2$): $\nu_{CO} = 1931$, 1846 cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$, δ): 7.95, 7.80, 7.74, 7.72, 7.60, 7.58 (12H, 2:2:2:2:2:2, each a d, Tp C*H*), 6.85 (2H, d, $^3J_{HH} = 3$ Hz, α-proton on pyrrole), 6.27, 6.23, 6.17 (6H, 2:2:2, each a t, Tp C*H*),

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[48] For further information concerning the purification of solvents using activated alumina, see: Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.

[49] Trofimenko, S. *J. Am. Chem. Soc.* **1967**, *89*, 3170.

4.55 (2H, d, $^3J_{HH} = 3$ Hz, β-proton on pyrrole), 3.84 (3H, methyl group on nitrogen of pyrrole). ^{13}C NMR (CD_2Cl_2, δ): (note: *N*-methyl group not located) 205.9 (*C*O), 146.5, 143.3, 142.3, 136.0, 135.8, 135.2 (Tp *C*H), 106.7, 106.5, 106.2 (Tp *C*H), 100.7 (α-carbon of pyrrole), 67.8 (β-carbon of pyrrole). CV (DMA, TBAH, 100 mV/s): $E_{1/2} = 0.61$ V; $E_{p,a} = 0.89$ V. Anal. Calcd for $C_{27}H_{27}B_2N_{13}O_4Re_2{-}C_6H_6$: C, 37.05; H, 3.11; N, 17.02. Found: C, 37.70; H, 3.53; N, 16.99. (Note: this complex is >95% pure by NMR and IR spectroscopies and cyclic voltammetry.)

Tp(CO)$_2$Re(μ-1,2-η^2-3,4-η^2-naphthalene)Re(CO)$_2$Tp (8). Dissolution of TpRe(CO)$_2$(THF) (**3**) (0.4106 g, 0.779 mmol) and naphthalene (1.450 g, 11.7 mmol) in approximately 75 mL of benzene was followed by an argon purge (which was maintained during the course of the reaction). After 12 h, a yellow precipitate was collected by vacuum filtration. The solid was washed with hexanes (2 × 15 mL) and dried under vacuum (44% yield). IR (CH_2Cl_2): $\nu_{CO} = 1952, 1871$ cm^{-1}. ^{1}H NMR (CD_2Cl_2, δ): 7.82, 7.79, 7.77, 7.67, 7.60, 7.53 (12H, 2:2:2:2:2:2, each a d, Tp C*H*), 7.31, 7.24 (4H, 2:2, each a m, unbound naphthalene *H*'s), 6.31, 6.28, 6.12 (6H, 2:2:2, each a t, Tp C*H*), 5.47, 4.38 (4H, 2:2, each a d, $^3J_{HH} = 9$ Hz, bound naphthalene protons). ^{13}C NMR (CD_2Cl_2, δ): 202.4, 200.8 (*C*O), 146.6, 144.1, 142.5, 136.5, 136.3, 135.3 (Tp *C*H), 129.1, 128.7, 125.7 (unbound naphthalene carbons), 106.6, 106.5, 106.2 (Tp *C*H), 68.3, 64.8 (bound naphthalene carbons). CV (DMA, TBAH, 100 mV/s): $E_{1/2} = 0.91$ V (quasi-reversible); $E_{p,a} = 1.41$ V. Anal. Calcd for $C_{32}H_{28}B_2N_{12}O_4Re_2{-}C_6H_6$: C, 40.87; H, 3.07; N, 15.05. Found: C, 41.43; H, 3.49; N, 14.86.

Tp(CO)$_2$Re(μ-N$_2$)Re(CO)$_2$Tp (9). Under a dinitrogen atmosphere, a flask was charged with TpRe(CO)$_2$(THF) (**3**) (0.4283 g, 0.812 mmol) and benzene (75 mL). The pale yellow solution was stirred for 3 h, during which time a precipitate formed. The yellow precipitate was collected by vacuum filtration, washed with hexanes (30 mL), and dried under reduced pressure (0.2467 g, 65% yield). Recrystallization was performed by layering a CH_2Cl_2 solution of **9** with hexanes. IR (KBr): $\nu_{CO} = 1956, 1924, 1849$ (with high energy shoulder) cm^{-1} (CH_2Cl_2): $\nu_{CO} = 1957, 1931, 1848$ (br) cm^{-1}. ^{1}H NMR (CD_2Cl_2, δ): 7.69, 7.65, 7.64, 7.32 (6H, 1:2:1:2, each a d, Tp C*H*), 6.17, 6.07 (3H, 1:2, each a t, Tp C*H*). ^{13}C NMR (CD_2Cl_2, δ): 199.2 (*C*O), 146.3, 143.3, 136.2, 135.3 (Tp *C*H), 106.7, 106.6 (Tp *C*H). CV (DMA, TBAH, 100 mV/s): $E_{1/2} = 0.90$ V; $E_{p,a} = 1.55$ V. Anal. Calcd for $C_{22}H_{20}B_2N_{14}O_4Re_2{-}C_6H_6$: C, 33.08; H, 2.58; N, 19.29. Found: C, 34.36; H, 2.71; N, 18.81. (Note: Complex **9** was found to be > 95% pure by ^{1}H NMR, ^{13}C NMR, IR spectroscopy, and cyclic voltammetry.) Anal. Calcd for $C_{22}H_{20}B_2N_{14}O_4Re_2{-}CH_2Cl_2$ (from recrystallization): C, 26.99; H, 2.17; N, 19.16. Found: C, 27.22; H, 2.68; N, 19.38 (CH_2Cl_2 was observed in the crystal structure of complex **9**).

Crystal Structure of Tp(CO)$_2$Re(μ-N$_2$)Re(CO)$_2$Tp (9). A brown prism of dimensions 0.28 × 0.31 × 0.43 mm was grown by slow diffusion of hexanes into a methylene chloride solution of **9** at room temperature. The crystal was determined to be of monoclinic symmetry ($P2_1/c$ {No. 14}) with the following cell dimensions (λ (Mo) = 0.710 69 Å): $a = 7.675(2)$ Å; $b = 13.090(4)$ Å; $c = 16.567(6)$ Å; $\beta = 96.80(3)°$; $Z = 2$; $V = 1653(1)$ Å^3; fw = 1021.44 ($C_{23}H_{20}N_{14}O_4B_2Cl_2Re_2$); $D_{calc} = 2.05$ g cm^{-3}. Data were collected at −100 °C on a Rigaku AFC6S diffractometer as outlined in Table 1. Calculations were performed on a VAX station 3520 computer using the TEXSAN 5.0 software and on a Silicon Graphics Indigo 2 Extreme computer with the teXsan 1.7 package. Unit cell dimensions were determined by applying the setting angles of 25 high-angle reflections. Three standard reflections were monitored during the data collection showing no significant variance. The structure was solved by direct methods in SIR88. Full-matrix least-squares refinement with anisotropic displacement parameters for all atoms of the complex yielded the final *R* of 0.040 ($R_w = 0.054$). A difference Fourier map showed a few higher peaks that were ascribed to a dichloromethane solvent molecule. The molecule was found disordered around an inversion center in such a way that the chloride atoms of the two orientations overlap each other. The chloride and carbon atoms of the solvent were refined with isotropic thermal parameters. All hydrogen atoms of the complex were found in difference Fourier maps and included in calculations without further refinement. The final difference map showed a peak of 1.65 e/Å^3 close to the rhenium atom.

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Supporting Information Available: A labeled ORTEP diagram and tables of crystallographic data and collection parameters, atomic positional parameters, complete bond distances and angles, and anisotropic temperature factors for **9** (7 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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