5184 *Organometallics* **2006,** *25,* 5184−5187

# Development of Group 6 Dearomatization Agents

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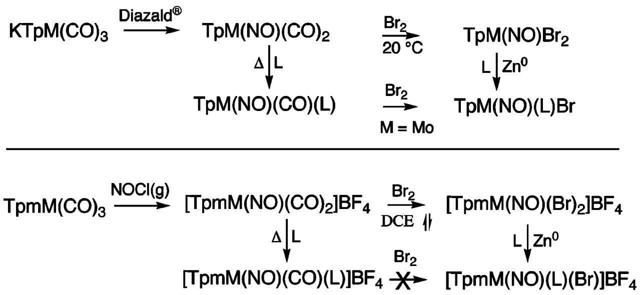
*Received July 3, 2006*

*Summary: A series of complexes having the general formulas [TpM(NO)(L)Br] and [TpmM(NO)(L)Br]BF$_4$ (M = Mo or W and L = a moderate $\sigma$-donor) have been prepared. Variations in L provide access to M(I) complexes having a broad range of electronic and steric properties. Reduction of a limited number of these complexes in the presence of aromatic molecules produces novel complexes with the general formula [TpM(NO)(L)($\eta^2$-aromatic)]$^{n+}$ (n = 0, 1).*

## Introduction

When a transition metal binds an aromatic molecule across two of its ring carbons, the uncoordinated portion of the ring is rendered dearomatized.[1] Consequently, pyrroles take on the character of enamines,[2,3] furans become vinyl ethers,[4,5] and arenes and pyridines are transformed into dienes and azadienes, respectively.[6,7] Such a methodology has been used to gain access to an array of previously unknown reaction types for aromatic molecules.[1,8] If the dearomatization agent contains a stereogenic center, the arene complex is often formed as a mixture of coordination diastereomers.[9] Provided that one diastereomer dominates, the use of an enantio-enriched complexing agent can result in enantio-enriched organic products.[7,10−12] Hence control of the diastereomer ratio is critical to the synthetic value of this approach. Several years ago, a family of rhenium-based dearomatization agents was developed for this purpose with the general form TpRe(CO)(L)(aromatic), where L = NH$_3$, MeIm, py, PMe$_3$, and *t*-BuNC.[13] The choice of L was shown to be critical in determining the coordination diastereomer ratio, air sensitivity, and the ability of the rhenium to bind to and to activate the organic molecule. The choice of L even can determine the relative position of reagent addition to the aromatic ring.[14]

**Scheme 1**



Recently, we reported the group 6 fragments TpW(NO)(PMe$_3$)[15] and TpMo(NO)(MeIm),[16] which were capable of binding a broad range of aromatic molecules in an $\eta^2$-fashion and activating them toward electrophilic and cycloaddition reactions. Compared to their rhenium predecessors, the group 6 dearomatization agents are more economical and may be prepared on larger scales (>10 g). The intention of this study was to determine the diversity of the coordination sphere for these systems, anticipating advantages similar to those gained for the rhenium analogues.

Earlier studies[15,17] demonstrated the successful strategy of using a combination of a single, strong $\pi$-acid and a scorpionate ligand.[18] Thus, the low oxidation state required for Re(I) or W(0) would be stabilized, but one d$\pi$-orbital would be orthogonal to the $\pi$-acid so that back-bonding with the aromatic would not be compromised. Thus, a two-pronged approach was undertaken to modify the ligand set of the TpMo(NO) and TpW(NO) systems. A series of TpM(NO)(L)Br complexes analogous to TpW(NO)(PMe$_3$)Br and TpMo(NO)(MeIm)Br were prepared as potential precursors to TpM(NO)(L)(arene) complexes, and their cationic analogues of the form [TpmM(NO)(L)Br]X (where Tpm = tris(pyrazolyl)methane) were also pursued.

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10.1021/om060597c CCC: $33.50

**Table 1. Electrochemical and Infrared Data for {M(NO)Br} Complexes**

| complex | $\nu_{NO}$ (cm $^{-1}$)[a] | $E_{1/2}$[b] | $E_{p,a}$ | yield (%) |
|---|---|---|---|---|
| Tp(MeIm)W(NO)Br (**5**) | 1563 | −1.55 | 0.14 | not isolated |
| Tp(DMAP)W(NO)Br (**6**) | 1567 | −1.36 | 0.16 | 1 |
| Tp(pyridine)W(NO)Br (**7**) | 1572 | −1.31 | 0.25 | 36 |
| Tp(nicotine)W(NO)Br (**8**) | 1576 | −1.35 | 0.21 | 10 |
| Tp($SMe_2$)W(NO)Br (**9**) | 1576 | −1.37 | 0.37 | 40 |
| Tp(*t*-BuMeS)W(NO)Br (**10**) | 1577 | −1.38 | 0.33 | 9 |
| Tp($PMe_3$)W(NO)Br (**11**) | 1578 | −1.38 | 0.35 | 67 |
| Tp($PEt_3$)W(NO)Br (**12**) | 1578 | −1.40 | 0.32 | 58 |
| Tp(THT)W(NO)Br (**13**)[f] | 1578 | −1.33 | 0.32 | 15 |
| Tp(DMN)W(NO)Br (**14**)[g] | 1578 | −1.20 | 0.28 | 19 |
| Tp($PH_2Cy$)W(NO)Br (**15**)[e] | 1587 | −1.24 | 0.39 | 58 |
| Tp($P(OMe)_3$)W(NO)Br (**16**) | 1597 | −1.04 | 0.51 | 78 |
| Tp(*t*-BuNC)W(NO)Br (**17**) | 1600 | −0.71 | 0.41 | 30 |
| [Tpm($P(OMe)_3$)W(NO)Br]$BF_4$ (**18**) | 1619 | −0.67 |  | 38 |
| Tp($NH_3$)Mo(NO)Br (**19**) | 1593 | −1.69 | 0.59 | 72 |
| Tp(Pic)Mo(NO)Br (**20**)[h] | 1605 | −1.42 | 0.50 | 89 |
| Tp(MeIm)Mo(NO)Br (**21**) | 1610 | −1.33 | 0.86 | 80 |
| Tp(DMAP)Mo(NO)Br (**22**)[c] | 1613 | −1.53 | 0.64 | 61 |
| Tp($PMe_3$)Mo(NO)Br (**23**) | 1617 | −1.19 |  | 76 |
| Tp(*t*-BuNC)Mo(NO)Br (**24**)[d] | 1618 | −1.23 | 0.76 | 45 |
| [Tpm(MeIm)Mo(NO)Br]$BF_4$ (**25**) | 1629 | −0.94 |  | 73 |
| [Tpm($PMe_3$)Mo(NO)Br]$BF_4$ (**26**) | 1640 | −0.85 |  | 66 |
| [Tpm($P(OMe)_3$)Mo(NO)Br]$BF_4$ (**27**) | 1651 | −0.53 |  | 53 |

[a] HATR glaze. [b] V, NHE. [c] DMAP = *N*,*N*-dimethyl-4-aminopyridine. [d] *t*-BuNC = *tert*-butylisonitrile. [e] Cy = cyclohexyl. [f] THT = tetrahydrothiophene. [g] DMN = *N*,*N*-dimethylnicotinamide. [h] Pic = 4-picoline.

**Table 2. Comparison of Tp and Tpm Complexes for Different Oxidation States**

| complex | NO stretch (cm$^{-1}$) | reduction (mV)[a] | oxidation (mV)[a] |
|---|---|---|---|
| $[TpmW(CO)_2(NO)]^+$ | 1664 | $E_{p,c} = -1611$ | $E_{p,a} = 1464$ |
| $TpW(CO)_2(NO)$ | 1632 | $E_{1/2} = -1870$ | $E_{p,a} = 1210$ |
| $[TpmW(NO)Br_2]^+$ | 1692 | $E_{1/2} = -234$ |  |
| $TpW(NO)Br_2$ | 1664 | $E_{1/2} = -200$ |  |
| $[TpmW(NO)(P(OMe)_3)Br]^+$ | 1619 | $E_{1/2} = -674$ |  |
| $TpW(NO)(P(OMe)_3)Br$ | 1597 | $E_{1/2} = -1040$ |  |

[a] Recorded at 100 mV/s in DMA solution with TBAH electrolyte.

## Results and Discussion

The pursuit of the desired W(I) complexes commenced with the preparation of $TpM(NO)(CO)_2$ and $[TpmM(NO)(CO)_2]BF_4$,[19] originally described by Trofimenko.[20] For the Tp system, Diazald was a sufficient $NO^+$ source, but for the Tpm system NOCl (g) was required, according to Scheme 1. Depending on the metal and scorpionate, the desired ligand L could be added to the metal either at the M(0) state or during the reduction from M(II) to M(I). While this substitution could not be achieved for $TpW(NO)(CO)_2$, in the case of $TpMo(NO)(CO)_2$, or the more electron-deficient $[TpmMo(NO)(CO)_2]BF_4$ or $[TpmW(NO)(CO)_2]BF_4$ complexes, substitution of a CO ligand by $PMe_3$, $PPh_3$, or $P(OMe)_3$ could be effected by heating (see Supporting Information).[21] However, attempted oxidation of these M(NO)(CO)(L) systems to their M(I) bromides by elemental bromine was unsuccessful (see Scheme 1), except for the TpMo(NO) system.[22]

Ultimately all four systems were oxidized with $Br_2$ to their M(II) dibromides ($TpMo(NO)(Br)_2$ (**1**),[23] $TpW(NO)(Br)_2$ (**2**),[24] $[TpmMo(NO)(Br)_2]BF_4$ (**3**), and $[TpmW(NO)(Br)_2]BF_4$ (**4**)). Whereas the $TpM(NO)(CO)_2$ complexes can be oxidized by $Br_2$ at 20 °C, the Tpm analogues needed to be refluxed in 1,2-dichloroethane (DCE, 83 °C) for several hours. Following the procedure used to prepare $TpW(NO)(PMe_3)Br$,[15] each of the dibromides was reduced with zinc powder in the presence of a $\sigma$-donor. Reactions were monitored and the paramagnetic products were characterized by the combination of electrochemistry and infrared absorption spectroscopy. Compounds that could be isolated in a purity of >90% (as assayed by IR and CV data) are reported in Table 1.[25] Representative combustion analyses were obtained for three of the examples of these 17*e* complexes (**18**, **26**, and **27**), which are somewhat less air-sensitive than the Tp analogues. While compounds **5**−**27** show NO stretches (1563−1651 cm$^{-1}$) and $d^5/d^6$ reduction potentials (−1.69 to −0.53 V) over a fairly broad range, a given compound can be readily evaluated in consideration of the benchmark W and Mo complexes (**11**, **19**, and **21**) that have been previously reported and the corresponding data for TpRe(CO)(L) systems.[13]

In Table 2, infrared data are collected comparing Tp and Tpm ligands for W in several different oxidation states. Consistent with the findings of Brown et al.,[26] experimental (vide supra), electrochemical, and spectroscopic observations indicate a significant increase of the electron density at the metal for Tp compared to Tpm, even though the negative formal charge in Tp is well removed from the metal. The nitrosyl stretch is 20−30 cm$^{-1}$ lower and reduction potentials ($E_{1/2}$) are 200−400 mV more negative for the Tp species.

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[19] Prepared using NOCl(g) followed by anion exchange with $NH_4BF_4$.

[20] Trofimenko, S. *J. Am. Chem. Soc.* **1970**, *92*, 5118−5126.

[21] Attempting this reaction with MeIm resulted in the complex $[(MeIm)_3M(CO)_2(NO)]BF_4$ for M = Mo or W.

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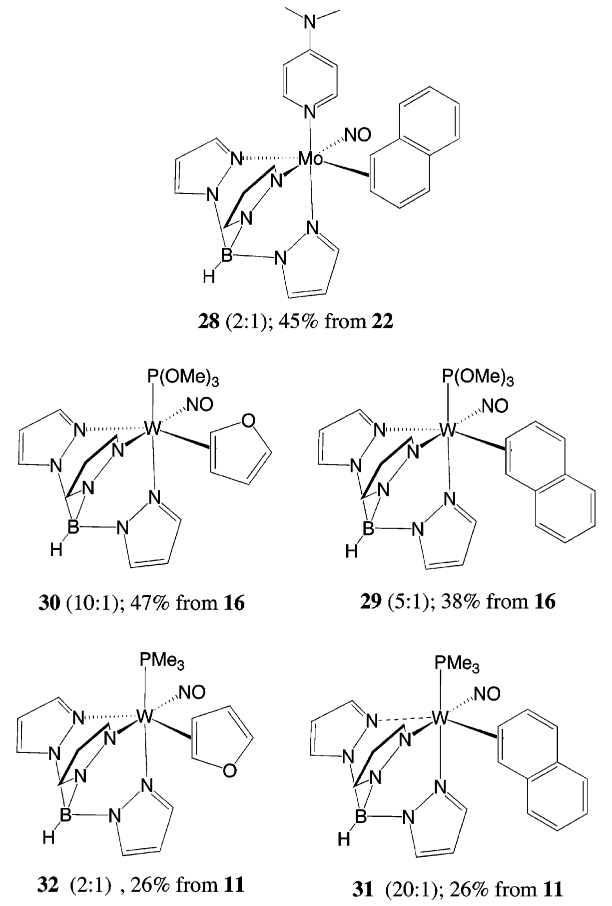
[25] The complex TpW(NO)(MeIm)Br was prepared in solution based on CV and IR data, but could not be isolated. These data are included in Table 1 for comparison.

[26] Seymore, S. B.; Brown, S. N. *Inorg. Chem.* **2000**, *39*, 325−332.


**28** (2:1); 45% from **22**

**30** (10:1); 47% from **16**

**29** (5:1); 38% from **16**

**32** (2:1) , 26% from **11**

**31** (20:1); 26% from **11**

**Figure 1.** $\eta^2$-Coordinated aromatic complexes (major coordination diastereomer shown). The O-down diastereomer of **32** is present as two rotamers.[28]

M(I) complexes **5**−**27** were each reduced with sodium metal in the presence of either benzene, naphthalene, or furan[27] according to the procedure used in the earlier reported preparations of TpW(NO)(PMe$_3$)($\eta^2$-furan)[28] and TpMo(NO)(MeIm)($\eta^2$-naphthalene).[16] Judging from CV and IR data of the reaction mixture, the majority of these reactions failed to yield stable $\eta^2$-aromatic complexes. However, in three cases reaction screening showed NO stretch and reduction potential values consistent with known $\eta^2$-aromatic complexes, and in these cases products were isolated and characterized. They include two naphthalene complexes, Tp(DMAP)Mo(NO)(3,4-$\eta^2$-naphthalene) (**28**) and Tp(P(OMe)$_3$)W(NO)(3,4-$\eta^2$-naphthalene) (**29**), and the heterocyclic species Tp(P(OMe)$_3$)W(NO)(3,4-$\eta^2$-furan) (**30**). The PMe$_3$ analogue of **29**, Tp(PMe$_3$)W(NO)(3,4-$\eta^2$-naphthalene) (**31**), was also prepared from **11** by the same method for purposes of comparison (vide infra). Notably, none of the Tpm complexes in Table 1 were successfully converted to $\eta^2$-aromatic complexes.

**Characterization of $\eta^2$-Arene Complexes.** Equilibrium diastereomer ratios for **28**−**31** are 2:1, 5:1, 10:1, and 1:>20, respectively, with the major coordination diastereomer shown in Figure 1. In each case, the minor diastereomer involves coordination of the opposite enatioface of the coordinated bond.[1] All four complexes exhibit characteristic upfield NMR shifts for bound carbons and their associated protons, and these signals along with COSY, NOESY, and $^{31}$P coupling data (**29**−**31**) can be used to unambiguously assign diastereomer configurations. For example, the major isomer of Tp(P(OMe)$_3$)W(NO)(3,4-$\eta^2$-naphthalene) (**29**) shows $^1$H NMR signals at 4.35 and 2.49 ppm for the protons of the two bound carbons. The former has a coupling constant of 23.5 Hz resulting from $^{31}$P coupling, which indicates that the corresponding proton is oriented toward the phosphite group. The latter signal is nearly 2 ppm upfield of the first, consistent with placement in the shielding region of the Tp pyrazolyl groups. Ultimately, the structure of the major diastereomer of **29** was confirmed by single-crystal X-ray diffraction (Figure 2). In Table 3, several representative examples are listed of $\eta^2$-naphthalene complexes with second- and third-row transition metals. As is typical, **29** shows elongation of the C3−C4 and C2−C3 bonds and a contracting C1−C2 bond length compared to the native hydrocarbon, indicating loss of aromatic character within the bound ring.

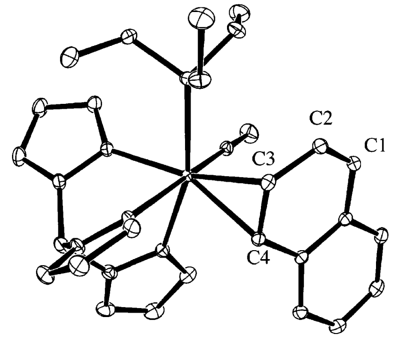


**Figure 2.** ORTEP diagram of $\eta^2$-naphthalene complex **29**.

**Table 3. Bond Lengths for the Bound Ring in Several $\eta^2$-Naphthalene Complexes**

| complexing agent | C3−C4 | C2−C3 | C1−C2 |
|---|---|---|---|
| {Os(NH$_3$)$_5$}$^{2+}$ [29] | 1.40(2) | 1.45(2) | 1.35(2) |
| {TpRe(CO)(py)}[13] | 1.44(1) | 1.43(4) | 1.35(1) |
| {TpMo(NO)MeIm)}[16] | 1.437(5) | 1.449(5) | 1.319(5) |
| {TpW(NO)(P(OR)$_3$} | 1.449(2) | 1.460(3) | 1.343(3) |
| {Cp*Ru(NO)}[30] | 1.418(8) | 1.426(8) | 1.346(8) |

Although these findings do not extend the range of aromatic molecules or the thermal stability of their complexes over the previously known TpW(NO), TpMo(NO), and TpRe(CO) systems, there are important differences in the diastereomer ratio of **29** or **30** and their {TpW(NO)(PMe$_3$)} counterparts (see Figure 1). Importantly, furan complex **30** is the first example of an $\eta^2$-furan complex in which an asymmetric complexing agent shows a high binding preference of only one enantioface of the furan (dr = 10:1). We note that this is in contrast to observed ratios ranging from 1:1 to 2.1:1 for other examples[9] of asymmetric $\eta^2$-furan complexes (e.g., **32** in Figure 1).[28] While we can safely assume from our past work[1] that this preference is thermodynamic in nature, its origin is not understood. Nonetheless, given the broad range of organic reactions demonstrated for $\eta^2$-furans that generate asymmetric ring carbons,[5,28,31,32] **30** shows promise as a chiral dearomatization agent for furans. The origin of the high coordination diastereomer ratio observed in the naphthalene complex **31** almost

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[27] All complexes reported in Table 1 were screened with benzene or naphthalene, and only in the case of a positive outcome with an arene was it tested for furan binding.

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[30] Tagge, C. D.; Bergman, R. G. *J. Am. Chem. Soc.* **1996**, *118*, 6908−6915.

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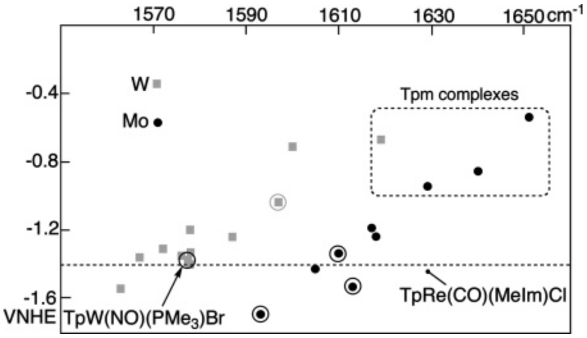

**Figure 3.** Plot of $E_{1/2}$ vs (NO) for the series of Mo(I) and W(I) nitrosyl bromides reported in Table 1 (circles indicate successful conversion to $\eta^2$-aromatic complex).

certainly is a result of a steric interaction in the purported minor diastereomer between the naphthalene and the $PMe_3$.[11]

Previous work has shown that the $d^5/d^6$ reduction potential is a particularly useful parameter in predicting the ability of a $d^6$-octahedral complex to support an $\eta^2$-coordinated aromatic ligand.[1,15−17,33] Specifically, the three known examples of $\eta^2$-benzene complexes that are substitution inert ($t_{1/2}$ > 1 h) at 20 °C ($\{Os(NH_3)_5\}^{2+}$, {TpRe(CO)(MeIm)}, and {TpW(NO)($PMe_3$)}) all have reduction potentials within 200 mV of 0.0V NHE.[34] While this is an important consideration in the design of future $d^6$ dearomatization agents, the arene complex must be in hand to measure its reduction potential. As an alternative, Table 1 lists data for purported *precursors to* M(0) complexes. In Figure 3, these IR and CV data are plotted and grouped according to metal. As expected for each group, an increase in formal reduction potential is accompanied by an increase in NO stretching frequency, which correlates to a more electron-deficient metal. In general, the tungsten complexes (squares) have nitrosyl stretching frequencies that are 20−30 $cm^{-1}$ lower than their molybdenum counterparts (dots) for a given reduction potential. For tungsten complexes **5**−**18**, a useful benchmark is TpRe(CO)(MeIm)Cl, the $d^5$ analogue to TpRe(CO)(MeIm)($\eta^2$-benzene), which shows a $d^5/d^6$ reduction potential of $E_{1/2} = -1.49$ V (Figure 3).[35] We note that the complex TpW(NO)($PMe_3$)Br (**11**) has a reduction potential that is practically identical to TpRe(CO)(MeIm)Cl. The other W(I) bromide that was successfully converted to a stable $\eta^2$-aromatic complex has a reduction potential that is more positive (circles in Figure 3), and none of these could be transformed into $\eta^2$-benzene complexes. However, other tungsten complexes that had potentials that were similar to **11** failed to be converted to any type of $\eta^2$-aromatic (e.g., where L = $PPh_3$. $PEt_3$). One reason for this failure is that steric attributes are not fully taken into account by either the infrared or electrochemical data reported in Table 1. The ligand sets of W(I) complexes that have reduction potentials even lower than **11** appear to be too electron-donating to support the W(0) oxidation state. Alternatively, as a reviewer of this work pointed out, the harshly reducing reaction conditions required for the M(I) → M(0) reduction may be to blame in some cases. With regard to the Mo complexes **19**−**27**, the more reducing reduction potentials do not result in a greater ability to bind arenes. Just as the back-bonding to the nitrosyl ligand is not as substantial with molybdenum compared to their heavy metal counterparts (see Figure 3), so the back-bonding with arenes must be less efficacious.

Finally, with regard to the Tpm analogues, the cationic charge in these complexes renders the four examples reported to be among the most electron-deficient examples tested (see Figure 3), and correspondingly, a purported M(0)−arene complex is apparently not sufficiently stabilized by $\pi$-back-bonding to be isolated. A complex such as $[TpmW(NO)(MeIm)]^+$ is expected to be in the correct range, but our attempts to generate this species from its dibromide precursor were unsuccessful.

## Concluding Remarks

Studies with TpRe(CO)(L)($\eta^2$-arene) complexes revealed that while naphthalene could form stable complexes with several different L ligands, obtaining the $\eta^2$-benzene analogue required a stringent ligand set (L = an imidazole).[13] The present study with tungsten and molybdenum nitrosyl complexes has a similar outcome: out of the 23 W(I) bromide complexes tested from Table 1, only one ({TpW(NO)($PMe_3$)}) yielded a stable $\eta^2$-benzene complex. However, the phosphite analogue {TpW(NO)($P(OMe)_3$)} does form stable complexes with naphthalene and furan, aromatic molecules that have a lower disruption in aromatic stabilization upon their coordination.[36] In the latter case, the coordination diastereomer ratio was the highest observed to date for this heterocycle, making **30** potentially useful as an asymmetric furan dearomatization agent.

**Acknowledgment** is made to the NSF (CHE-0111558, 9974875, and 0116492 (UR)), Korea Research Foundation Grant (KRF-2004-013-C00023), and Deutsche Forschungsgemeinschaft (#DI 1187/1-1) for financial support of this work.

**Supporting Information Available:** Crystallographic details for compound **30** and synthesis and characterization for all numbered complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

OM060597C

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[34] Reduction potentials are estimated values based on anodic peak current at 100 mV/s.

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