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PAPER

# Anodic electrochemistry of Mn and Re tricarbonyl complexes of tris(oxazoliny)phenyl borate ligands: comparison to tris(pyrazolyl) borate complexes†‡

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$M(CO)_3$  ( $M = Mn, Re$ ) complexes of two tris(oxazoliny)phenylborate ligands ( $To^M$  and  $To^P$ ) have been prepared and characterized by spectroscopic, electrochemical and crystallographic methods. The steric bulk imparted by the  $sp^3$ -hybridized carbons in the oxazoline ring gives the tris(oxazoliny)borate ligands significant structural protection against dimerization while leaving the  $M(CO)_3$  face open for possible reactivity. The anodic electrochemistry of these systems in relatively benign media showed that their one-electron oxidation products were stable and persistent in the case of Re, but of limited stability in the case of Mn. The anodic oxidation of Mn and Re complexes of four tris(pyrazolyl)borate (Tp and Tp\*) ligands was also investigated, once again showing that the radical cations of the Re complexes were longer lived than their Mn congeners in  $CH_2Cl_2/[NBu_4][B(C_6F_5)_4]$ . The  $E_{1/2}$  data were used to classify the electron-donating properties of the different scorpionate ligands in comparison with their cyclopentadienyl counterparts as  $Tp^* > Cp^* > To^P, Tp, To^M > Cp$ . Comparison of the  $\nu_{CO}$  IR frequencies of these complexes gave a slightly different sequence of donor strength,  $Cp^*, To^M, To^P > Tp^* > Tp > Cp$ . The electronic effects of the tris(oxazoliny)phenyl borate ligands are that they convey “Tp\*-like” character in terms of the chemical reactivity of their complexes, and “Tp-like” character in terms of the redox potentials of these complexes.

## Introduction

There has been a steady interest in developing mimics of the cyclopentadienyl (Cp) ligand as a monoanionic formal six-electron donor. Among the most broadly investigated analogues are the hydridotris(pyrazolyl)borate (Tp) ligands, which differ from the Cp ligand in terms of steric constraints and metal–ligand bonding.<sup>1</sup> A number of papers have compared the stoichiometric and catalytic reactivities of metal complexes derived from these two classes of ligands.<sup>2</sup> Quite recently, one of our groups introduced a new type of scorpionate ligand, tris(oxazoliny)phenyl borate, which contains

three oxazoline donor groups in place of the pyrazolyl groups of the Tp ligand class.<sup>3</sup> The oxazoline moiety provides access to chiral structures, and the substitution of B–C for B–N linkages limits the Lewis acid-mediated ligand epimerizations that complicate the chemistry of metal–Tp complexes.<sup>4</sup>

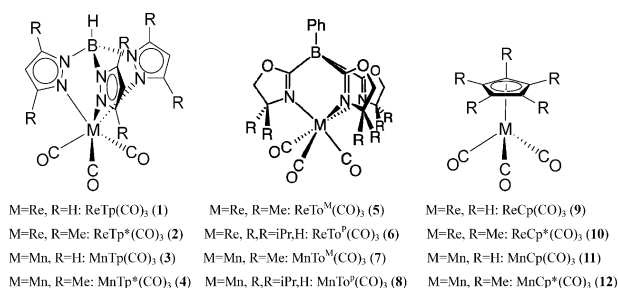
Owing to the fact that ligand electronic properties are important in determining the reactivity of metal complexes, effort has been made to characterize the relative donor properties of Cp- vs. scorpionate-type ligands. The most comprehensive of these studies is the compilation by Tellers *et al.* of the donor-related physical parameters published prior to 2000.<sup>5</sup> Based largely on IR and electrochemical data, these authors discouraged generalizations about the relative donating abilities of the two types of ligands. We took an interest in whether such a comparison could be delineated for one particular group of complexes, namely those containing group VII  $M(CO)_3$  moieties ( $M = Mn, Re$ ). Definitive electrochemical  $E_{1/2}$  data on this set of complexes were not available previously, owing in part to poor chemical reversibility and sensitivity to medium effects in the oxidation of  $MCp(CO)_3$  complexes. The milder conditions possible when using weakly-coordinating electrolyte anions<sup>6</sup> have since allowed characterization of the simple one-electron oxidative reactions of the

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† Dedicated to Prof. Didier Astruc in recognition of his outstanding contributions to organometallic electron-transfer chemistry.

‡ Electronic supplementary information (ESI) available: Two figures showing cyclic voltammograms referred to in the manuscript [(a) complex **2** before bulk electrolysis, (b) complex **7** before and after bulk anodic electrolysis] and four sets of crystallographic data (cif) of compounds **5–8**. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1nj20222g



Scheme 1

MCp(CO)<sub>3</sub> complexes, and reliable anodic  $E_{1/2}$  values are now available.<sup>7</sup> In the interest of comparing the electron-donating abilities of cyclopentadienyl, hydridotris(pyrazolyl)borate, and tris(oxazolinyl)phenyl borate ligands, the appropriate M(CO)<sub>3</sub> complexes were prepared and their anodic  $E_{1/2}$  potentials and IR data were measured under identical conditions. Previous studies on the donor ability of oxazolines have focused on photoelectron spectroscopy and *ab initio* calculation of uncoordinated groups, and few comparisons to ligands such as cyclopentadienyl are available.<sup>8,9</sup>

While in the process of determining the oxidation potentials of the Tp, Tp\* [Tp\* = hydrotis(3,5-dimethylpyrazolyl)borate], and oxazoline complexes, we also studied the longevity of their one-electron oxidation products and characterized, where possible, their IR spectra.

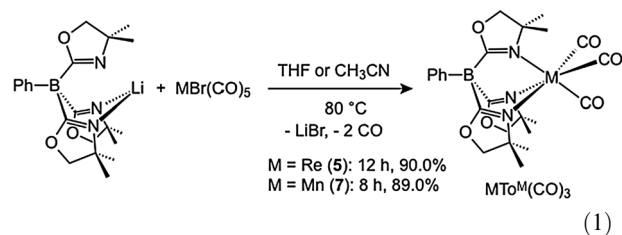
The structures and numerical ordering of the compounds described in this paper are shown in Scheme 1. The acronym To<sup>M</sup> is used for the tris(4,4-dimethyl-2-oxazolinyl)phenyl borate ligand and To<sup>P</sup> is employed for the tris(4*S*-isopropyl-2-oxazolinyl)phenyl borate ligand.

## Results and discussion

### Synthesis and characterization of tris(oxazolinyl)borate compounds

Group 7 tris(oxazolinyl)borate compounds MTo<sup>M</sup>(CO)<sub>3</sub> [M = Re (5), Mn (7)] were prepared by adaptation of the salt metathesis route that provides MTp(CO)<sub>3</sub> (M = Mn, Re). Thus, Li[To<sup>M</sup>] and MBr(CO)<sub>5</sub> (M = Mn, Re) were reacted in THF or acetonitrile at 80 °C to afford MTo<sup>M</sup>(CO)<sub>3</sub> in good yield (eqn (1)).

These compounds were fully characterized by spectroscopic (Table 1), analytical, and single crystal X-ray diffraction methods. The <sup>1</sup>H NMR spectrum of ReTo<sup>M</sup>(CO)<sub>3</sub> (5) in benzene-*d*<sub>6</sub> contained singlet resonances for the methyl and



methylene groups of the oxazoline moiety and three downfield multiplets corresponding to the phenyl group. The equivalence of the oxazoline rings indicates a  $\kappa^3$ -N,N,N-coordination of the To<sup>M</sup> ligand, consistent with a C<sub>3v</sub>-symmetric structure. Likewise, the <sup>13</sup>C spectrum of 5 contained a single set of oxazoline resonances and a single carbonyl resonance at 197.90 ppm. Crosspeaks between the oxazoline nitrogen and the ring methyl and methylene groups in a <sup>1</sup>H-<sup>15</sup>N HMBC experiment (performed at natural <sup>15</sup>N abundance) provided a characteristic <sup>15</sup>N NMR chemical shift of -176.8 ppm for 5. This chemical shift is in the range of late transition-metal complexes containing the To<sup>M</sup> ligand and downfield from 2H-dimethyl-2-oxazoline (-127.9 ppm).

One  $\nu_{\text{CN}}$  band at 1582 cm<sup>-1</sup> was observed in the solid-state infrared spectrum (KBr) of ReTo<sup>M</sup>(CO)<sub>3</sub>, which further supports the  $\kappa^3$ -coordination. The solid state IR spectrum of ReTo<sup>M</sup>(CO)<sub>3</sub> also contains one sharp band and one broad absorption (2012 and 1892 cm<sup>-1</sup>), corresponding to the symmetric and anti-symmetric carbonyl modes. These bands shift to slightly higher energy in the solution-phase spectrum acquired in THF (2013 and 1894 cm<sup>-1</sup>) or dichloromethane (2019 and 1898 cm<sup>-1</sup>).

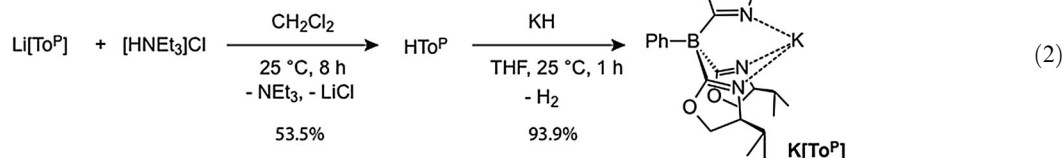
X-Ray quality single crystals of 5 and 7 were obtained from a concentrated toluene solution cooled to -30 °C. The solution to the single crystal X-ray diffraction study confirms the identity of ReTo<sup>M</sup>(CO)<sub>3</sub> and reveals the tridentate *fac*-N,N,N-To<sup>M</sup> coordination (Fig. 1). The relatively large rhenium(i) center and the steric and chelating properties of the To<sup>M</sup> ligand result in small N-Re-N angles (80.6(3)° to 85.4(3)°). The carbonyl ligands are also slightly compressed, with C-Re-C angles less than 90° (from 86.1(5)° to 87.2(5)°), away from the bulky To<sup>M</sup> ligand. Compounds 5 and 7 form a fine isomorphous pair.

Reaction of optically active Li[To<sup>P</sup>] [To<sup>P</sup> = tris(4*S*-isopropyl-2-oxazolinyl)phenyl borate] and MBr(CO)<sub>5</sub> (M = Re, Mn) in THF at 80 °C gave MTo<sup>P</sup>(CO)<sub>3</sub> contaminated with unidentified impurities that were not removed by recrystallization from toluene. We had previously found that the potassium salt K[To<sup>M</sup>] reacts under milder conditions than Li[To<sup>M</sup>] as an

**Table 1** Summary of the characteristic data for tris(oxazolinyl)phenylboratorhenium and manganese tricarbonyl complexes

Compound	$\nu_{\text{CO}}$ (KBr, cm <sup>-1</sup> )	$\nu_{\text{CO}}$ (solvent, cm <sup>-1</sup> )	$\nu_{\text{CN}}$ (KBr, cm <sup>-1</sup> )	<sup>15</sup> N NMR/ppm
ReTo <sup>M</sup> (CO) <sub>3</sub> , 5	2012, 1892	2013, 1894 (THF) 2019, 1898 (CH <sub>2</sub> Cl <sub>2</sub> )	1582	-176.8
ReTo <sup>P</sup> (CO) <sub>3</sub> , 6	2010, 1892	2012, 1896 (THF) 2014, 1897 (CH <sub>2</sub> Cl <sub>2</sub> )	1589	-195.6
MnTo <sup>M</sup> (CO) <sub>3</sub> , 7	2018, 1899	2017, 1902 (THF) 2020, 1912 (CH <sub>2</sub> Cl <sub>2</sub> )	1592	-172.1
MnTo <sup>P</sup> (CO) <sub>3</sub> , 8	2016, 1961	2017, 1908 (THF)	1601	Not detected
H[To <sup>P</sup> ]	n.a.	n.a.	1601 (broad)	-195.6
K[To <sup>P</sup> ]	n.a.	n.a.	1601	-149.1

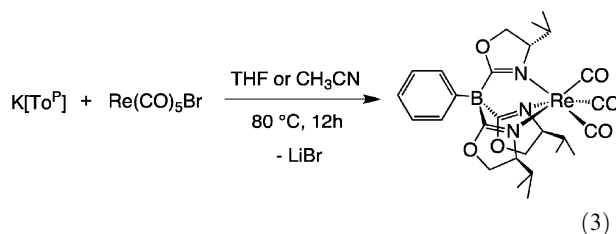
effective  $[\text{To}^{\text{M}}]$ -transfer agent. Therefore,  $\text{K}[\text{To}^{\text{P}}]$  was synthesized from  $\text{Li}[\text{To}^{\text{P}}]$  via  $\text{HTo}^{\text{P}}$  according to eqn (2). A reaction between  $\text{Li}[\text{To}^{\text{P}}]$  and  $[\text{HEt}_3\text{N}]\text{Cl}$  in methylene chloride, followed by a filtration through a plug of neutral alumina, provided anhydrous  $\text{HTo}^{\text{P}}$  in 54% yield as a light yellow gel.



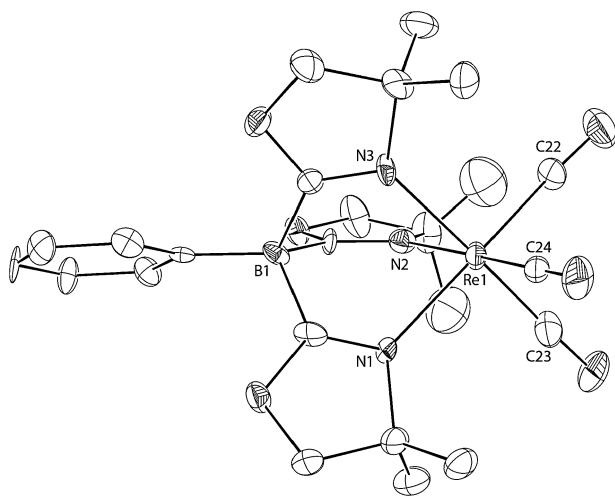
$\text{HTo}^{\text{P}}$  was characterized by  $^1\text{H}$ ,  $^{11}\text{B}$ ,  $^{13}\text{C}\{^1\text{H}\}$ , and  $^{15}\text{N}$  NMR spectroscopy, IR, and high-resolution mass spectrometry. In particular, the  $^1\text{H}$  NMR spectrum of  $\text{HTo}^{\text{P}}$  in benzene- $d_6$  shows the presence of a single diastereomer as the  $S,S,S$  enantiomer and a high-resolution mass spectrum producing the parent ion peak at 426.3.  $\text{HTo}^{\text{P}}$  reacts upon treatment with  $\text{KH}$  in THF at  $25\text{ }^\circ\text{C}$  to provide  $\text{K}[\text{To}^{\text{P}}]$  as a light yellow solid along with hydrogen gas evolution.

Although we were unable to grow X-ray quality single crystals for  $\text{K}[\text{To}^{\text{P}}]$ , the other solid as well as solution phase spectroscopic data ( $^1\text{H}$ ,  $^{11}\text{B}$ ,  $^{13}\text{C}$ ,  $^{15}\text{N}$  NMR and IR) were indicative of the presence of an optically active  $\text{To}^{\text{P}}$  proligand. In particular, the diastereotopic methyl resonances from the isopropyl group indicate the presence of a stereocenter, and the solution NMR data ( $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{11}\text{B}$ ,  $^1\text{H}$ - $^{15}\text{N}$  HMBC) indicated a pseudo- $\text{C}_3$ -symmetric geometry of the  $\text{To}^{\text{P}}$ -ligand, thus making all the three oxazoline rings equivalent. Thus, only one diastereomer (containing three identical stereocenters) is present. In the solid-state IR spectrum a sharp single band for the oxazoline  $\text{C}=\text{N}$  stretching at  $1601\text{ cm}^{-1}$  indicates that  $\text{KTo}^{\text{P}}$  has similar geometry as the  $\text{LiTo}^{\text{P}}$ . As mentioned earlier, individual salt metathesis reactions of

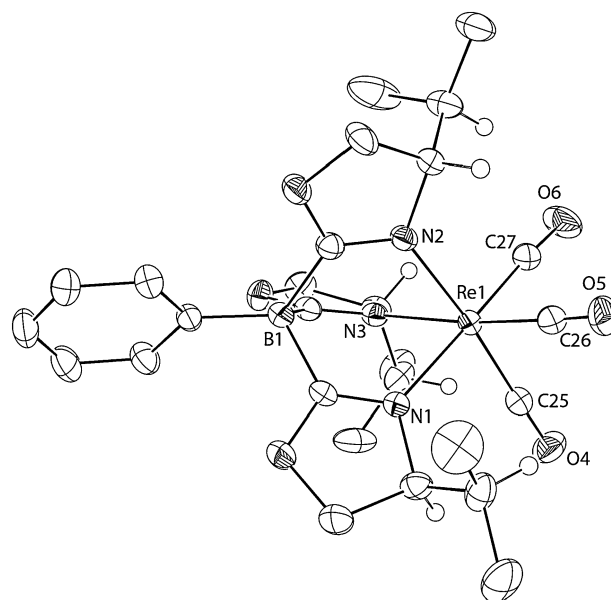
$\text{K}[\text{To}^{\text{P}}]$  with  $\text{Re}(\text{CO})_5\text{Br}$  and  $\text{Mn}(\text{CO})_5\text{Br}$  in THF at  $80\text{ }^\circ\text{C}$  afforded  $\text{ReTo}^{\text{P}}(\text{CO})_3$  (**6**) and  $\text{MnTo}^{\text{P}}(\text{CO})_3$  (**8**), respectively, in 85% and 87% isolated yields (eqn (3)). As discussed for  $\text{ReTo}^{\text{M}}(\text{CO})_3$ , both **6** and **8** were characterized by crystallography and spectroscopy (Table 1).



X-Ray quality crystals were obtained for compounds **6** and **8**, and their structures reported here are the first containing the chiral  $\text{To}^{\text{P}}$  ligand. The X-ray crystal structures for these two compounds are isomorphous. The value of the Flack parameter, **6** = 0.010(6) and **8** = 0.005(9), establishes the absolute configuration of the structure as  $S$ , and this configuration is expected from our use of  $L$ -valine to prepare  $4S$ -isopropyl-2-oxazoline. These structural studies provide valuable information about the steric properties of the chiral  $\text{To}^{\text{P}}$  ligand as well as the conformation favored in the solid state. The two



**Fig. 1** ORTEP diagram of **5**. Ellipsoids are drawn at 50% probability, and hydrogen and a disordered toluene (about an inversion center) are omitted for clarity. Compound **7** is isomorphous with **5**.



**Fig. 2** ORTEP diagram of  $\text{ReTo}^{\text{P}}(\text{CO})_3$  (**6**). Hydrogen atoms on the methine carbons are shown to illustrate the  $S$  absolute configuration and isopropyl conformation for the oxazolines; all other hydrogen atoms and two co-crystallized toluene molecules are not included in the plot. A similar structure was observed for **8**.

MT<sup>o</sup>(CO)<sub>3</sub> complexes have very similar structures, and the ORTEP diagram of **6** is shown in Fig. 2 (see ESI† for the X-ray structure of **8**). Significantly, in both **6** and **8**, the isopropyl groups are oriented so that the methine CH, rather than a methyl group, on each oxazoline is directed toward the Re(CO)<sub>3</sub> moiety. This conformation appears to minimize unfavorable inter-ligand interactions.

### Comparison of steric properties of To<sup>M</sup>, To<sup>P</sup>, Tp, Tp\*, Cp and Cp\* ligands in Re(CO)<sub>3</sub> complexes

A qualitative comparison of the steric properties of tris(oxazolanyl)borate and tris(pyrazolyl)borate ligands was obtained from Newman projections of the structures along their C<sub>3</sub> axis (Fig. 3). The steric bulk of the planar pyrazole groups in the Tp\* ligand is projected in the plane of the aromatic ring, leaving three large wedges of open space between the donor groups. In contrast, the non-planar oxazoline groups in To<sup>M</sup> and To<sup>P</sup> give a significantly different shape. The 4,4-dimethyl groups on To<sup>M</sup> create a bowl-like hemisphere of steric bulk around the –Re(CO)<sub>3</sub> moiety. In To<sup>P</sup>, the steric bulk creates a windmill-like shape that blocks only one side of each carbonyl ligand.

Solid angles provide a quantitative assessment of steric properties of a ligand,<sup>10</sup> and may be calculated conveniently using coordinates from crystal structures or molecular models with the program Solid-G.<sup>11</sup> A solid angle is defined as the surface area of a projection of a ligand on a sphere surrounding a complex, and this approach for quantifying steric properties accounts for a ligand's shape.

Crystal structures have been reported for ReCp(CO)<sub>3</sub>,<sup>12</sup> ReCp\*(CO)<sub>3</sub>,<sup>13</sup> ReTp(CO)<sub>3</sub>, and ReTp\*(CO)<sub>3</sub>,<sup>14</sup> as well as the corresponding manganese complexes. Those structures provided the coordinates to calculate solid angles for Cp, Cp\*, Tp, and Tp\* ligands (Table 2) in steradians. The crystal structures of To<sup>M</sup> and To<sup>P</sup> compounds reported here also were used to calculate solid angles. The second parameter given is the percent of a sphere's surface area that is taken up by the ligand's two dimensional projection (maximized at 100% for a ligand that entirely surrounds a metal center).

Comparison of the solid angles calculated for rhenium compounds provides the trend in steric bulk for the ancillary ligands: Cp < Cp\* < Tp < Tp\* < To<sup>P</sup> < To<sup>M</sup>, and the same trend is obtained for the manganese complexes. Notably, the tris(oxazolanyl)borate ligands occupy greater than a hemisphere around the rhenium center, and thus limit possible dimerization or ligand redistribution processes.

**Table 2** Solid angles for tris(oxazolanyl)phenyl borates, tris(pyrazolyl)borates, and cyclopentadienyls in rhenium tricarbonyl complexes

Compound	Solid angle/ steradians	Percent of sphere occupied
ReTo <sup>M</sup> (CO) <sub>3</sub> , <b>5</b>	6.88	54.7
ReTo <sup>P</sup> (CO) <sub>3</sub> , <b>6</b>	6.61	52.6
ReTp*(CO) <sub>3</sub> , <b>2</b>	6.49	51.6
ReTp(CO) <sub>3</sub> , <b>1</b>	5.26	41.8
ReCp*(CO) <sub>3</sub> , <b>10</b>	4.72	37.6
ReCp(CO) <sub>3</sub> , <b>9</b>	4.20	33.4

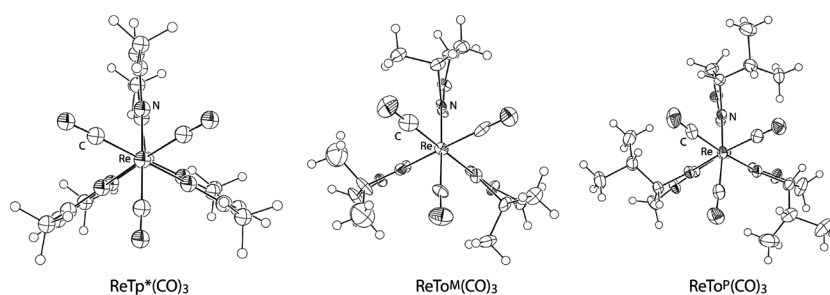
### Electrochemistry of rhenium complexes

Electrochemical experiments used dried dichloromethane containing 0.05 M [NBu<sub>4</sub>][TFAB] (TFAB = [B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>−</sup>) as the supporting electrolyte, and potentials are given *versus* the ferrocene/ferrocenium couple. Details are given in the Experimental section. An overview of our findings is that all four rhenium complexes showed quasi-Nernstian one-electron oxidations giving cation radicals that were persistent, whereas one-electron oxidation of the three manganese complexes gave electrochemically observable, but less stable, cations.

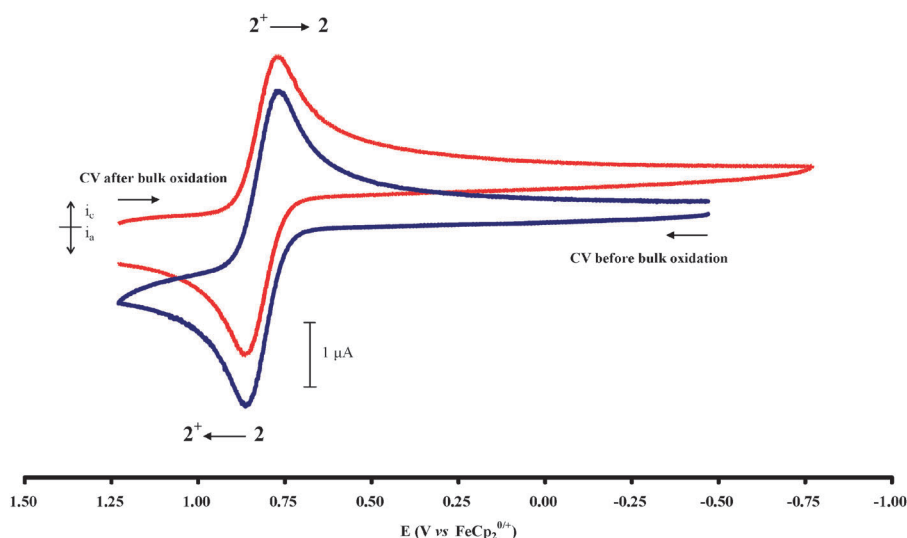
### Anodic electrochemical and spectroelectrochemical investigation of Re complexes

A single feature was observed in the cyclic voltammetry (CV) scans of the four Re complexes **1**, **2**, **5**, and **6**, of which the blue line of Fig. 4 is representative. At room temperature, these curves fit the standard criteria for diffusion controlled, chemically reversible, one-electron oxidation processes. The *E*<sub>1/2</sub> values, collected in Table 3, are all negative of the literature potential<sup>15</sup> (1.16 V) for the oxidation of the Cp analogue **9**. It is important to note that even at relatively high concentrations (up to 2 mM), none of the rhenium complexes showed evidence that the radical cation reacted to form the type of metal–metal bonded dimer dication that has been documented in the case of radical **9**<sup>+</sup>.<sup>15</sup> The steric hindrance of the scorpionate ligand is apparently sufficient to mitigate against formation of the rhenium–rhenium based dimer.

That the cation radicals of the rhenium complexes are long-lived was demonstrated by bulk anodic electrolysis tracked by IR spectroelectrochemistry. Bulk electrolyses of **1**, **2**, **5** and **6** were performed at room temperature employing a platinum gauze electrode at an applied potential which was at least 200 mV positive of the compound's *E*<sub>1/2</sub> value. Both **1** and **2** released *ca.* 1.0 F after complete oxidation as the solutions



**Fig. 3** ORTEP diagrams of ReTp\*(CO)<sub>3</sub>,<sup>14</sup> ReTo<sup>M</sup>(CO)<sub>3</sub>, and ReTo<sup>P</sup>(CO)<sub>3</sub> molecules viewed along the C<sub>3</sub>-axis.



**Fig. 4** Blue line is CV scan of 0.95 mM **2** in  $\text{CH}_2\text{Cl}_2/0.05 \text{ M } [\text{NBu}_4][\text{TFAB}]$  prior to bulk electrolysis. After bulk anodic electrolysis at  $E_{\text{appl}} = 1.25 \text{ V}$ , an identical scan initiated at 1.25 V produced the CV having the red line owing to formation of  $2^+$ . Conditions: 298 K, 1 mm GCE,  $200 \text{ mV s}^{-1}$ . A CV of the neutral complex alone is available in ESI† as Fig. S1.

**Table 3** Summary of  $E_{1/2}$  and IR data for compounds in  $\text{CH}_2\text{Cl}_2$  at room temperature, except for  $5^+$  and  $6^+$ , which were obtained at 253 K.  $0.05 \text{ M } [\text{NBu}_4][\text{B}(\text{C}_6\text{F}_5)_4]$  was present in measurements of cationic species

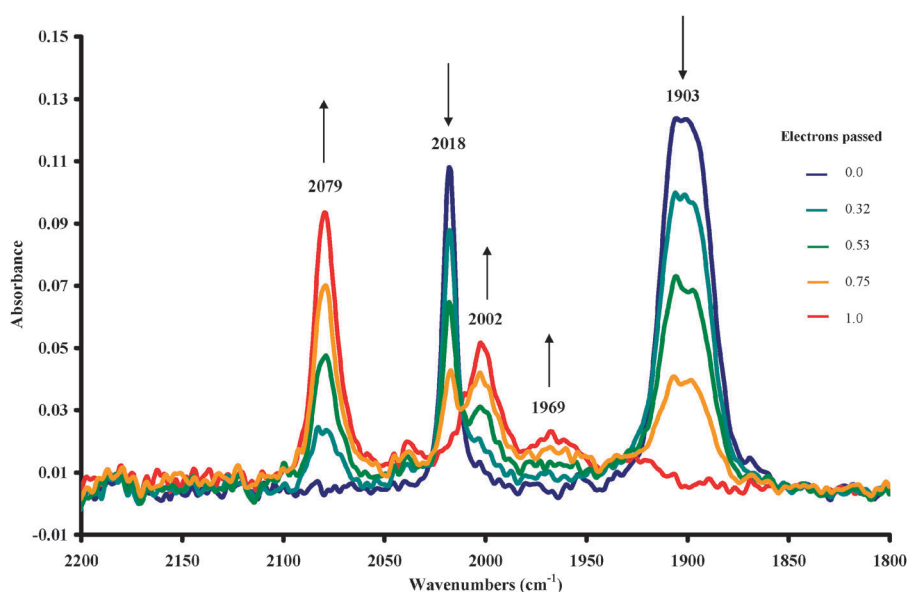
Cmpd	$E_{1/2} \text{ (V vs. FeCp}_2^{0/+})$	$\nu_{\text{sym}}/\text{cm}^{-1}$	$\nu_{\text{asym}}/\text{cm}^{-1}$	Avg $\nu_{\text{co}} \text{ (cm}^{-1}\text{)} = (\nu_{\text{sym}} + 2\nu_{\text{asym}})/3$
$\text{ReTp}(\text{CO})_3$ , <b>1</b>	0.98	2026	1912	1950
$1^+$		2097	2021, 1986	2035
$\text{ReTp}^*(\text{CO})_3$ , <b>2</b>	0.82	2018	1903	1941
$2^+$		2079	2002, 1969	2017
$\text{MnTp}(\text{CO})_3$ , <b>3</b>	0.74	2035	1932	1966
$\text{MnTp}^*(\text{CO})_3$ , <b>4</b>	0.59	2027	1922	1957
$\text{ReTo}^{\text{M}}(\text{CO})_3$ , <b>5</b>	1.00	2019	1898	1938
$5^+$		2086	2005, 1962	2018
$\text{ReTo}^{\text{P}}(\text{CO})_3$ , <b>6</b>	0.97	2014	1897	1936
$6^+$		2085	2004, 1964	2018
$\text{MnTo}^{\text{M}}(\text{CO})_3$ , <b>7</b>	0.72	2020	1912	1948
$\text{ReCp}(\text{CO})_3$ , <b>9</b>	1.16	2024	1926	1959
$9_2^{2+}$		2105	2031	2056
$\text{ReCp}^*(\text{CO})_3$ , <b>10</b>	0.91	2005	1906	1939
$10_2^{2+}$		2062	2015	2031
$\text{MnCp}(\text{CO})_3$ , <b>11</b>	0.92	2022	1934	1963
$11^+$		2116	2061, 2050	2078
$\text{MnCp}^*(\text{CO})_3$ , <b>12</b>	0.64	2004	1917	1946
$12^+$		2093	2033	2053

turned deep purple. CV scans on the electrolyzed solutions showed only one product wave (see Fig. 4), a reversible reduction attributed to  $2^+$  (or  $1^+$ ). Electrolyses of **5** and **6** at 298 K (1.2 F passed) produced deep green solutions of the monocations  $5^+$  and  $6^+$ . Subsequent voltammetry and back-electrolysis showed that some decomposition of the cations had occurred. However, when the electrolyses were carried out at 253 K,  $5^+$  and  $6^+$  were more stable and back-electrolysis at  $E_{\text{appl}} = 0.40 \text{ V}$  regenerated about 90% of the starting material (based on CV and linear scan voltammetry data). Thus, the oxidation of all four rhenium scorpionates follows the simple one-electron reaction of eqn (4). In none of



these cases were side-product waves observed giving evidence of the formation of hydrogen or chlorine atom-transfer products,  $[\text{Re}(\text{CO})_3(\text{scorpionate})\text{X}]^+$  ( $\text{X} = \text{H}$  or  $\text{Cl}$ ), such as were found for the Cp analogue.<sup>15</sup> This may be due to the milder oxidizing strength of the metal scorpionate cations.

The Re complexes were also investigated by fiber-optic spectroelectrochemical experiments recorded in the metal carbonyl IR region. The example of compound **2** at room temperature is given in Fig. 5. As the electrolysis proceeded, the bands at 1918 and about 1903  $\text{cm}^{-1}$  for neutral **2** were replaced by the three new bands of  $2^+$  at 2079, 2002, and 1969  $\text{cm}^{-1}$ . Similar results were obtained for the other rhenium complexes, with the electrolyses being carried out at 253 K for compounds **5** and **6** to accommodate the shorter lifetimes of the cation radicals derived from the  $\text{To}^{\text{M}}$  and  $\text{To}^{\text{P}}$  complexes.



**Fig. 5** Representative fiber-optic IR spectra of 1.5 mM **2** in  $\text{CH}_2\text{Cl}_2/0.05 \text{ M } [\text{NBu}_4][\text{TfAB}]$  as the bulk oxidation proceeded at 298 K with  $E_{\text{appl}} = 1.0 \text{ V}$  (vs.  $\text{FeCp}_2^{0/+}$ ). Spectra of **5** and **6** (neither shown here) were obtained at 253 K.

The IR data are collected in Table 3. It is worth noting that all three carbonyl bands are resolved in the spectra of the radical cations. Whether the implied reduction in  $C_{3v}$  symmetry arises from structural changes or from medium effects is not known.

Shifts in the carbonyl IR frequencies were evaluated as a weighted average of the three  $\nu_{\text{CO}}$  absorptions expressed in  $\text{cm}^{-1}$ . This takes into account that two or three CO bands may be observed, depending on whether or not the formally degenerate pair of asymmetric bands is resolved. Thus, the average value of  $\nu_{\text{CO}}$  is the simple average if all three bands are resolved, but takes on the value  $[\nu_{\text{CO}(\text{sym})} + 2\nu_{\text{CO}(\text{asym})}]/3$  if the asymmetric bands are not resolved. The average increase in CO frequencies is between  $76 \text{ cm}^{-1}$  and  $85 \text{ cm}^{-1}$  in going from the neutral complexes to the radical cations. These shifts are a bit small compared to those reported for a number of other piano-stool metal carbonyl oxidation processes, which tend to be greater than  $100 \text{ cm}^{-1}$ .<sup>7,16</sup>

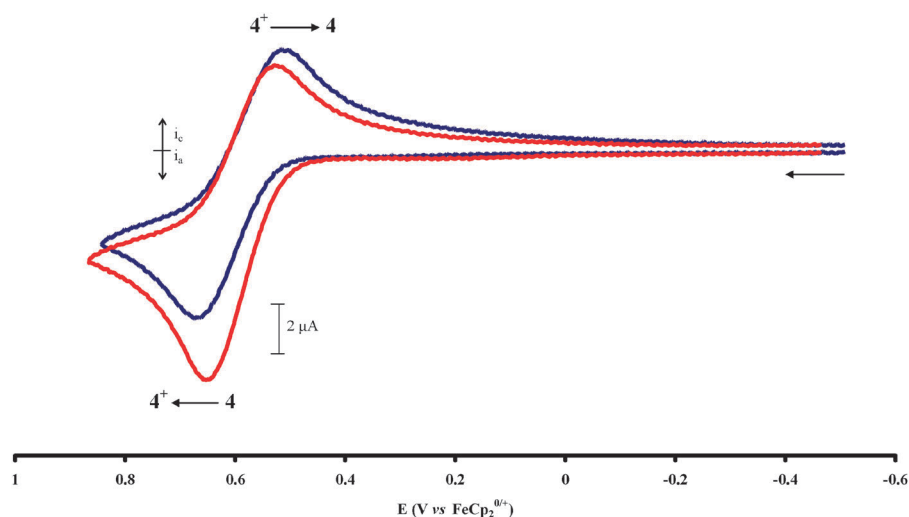
However, a direct comparison with the  $\text{ReCp}$  complex **9** is not available owing to the dominant dimerization reaction of its radical cation. The CO weighted-average for the metal–metal bonded dimer dication  $[\text{Re}_2\text{Cp}_2(\text{CO})_6]^{2+}$  is  $97 \text{ cm}^{-1}$  and that of its  $\text{Cp}^*$  analogue is  $92 \text{ cm}^{-1}$ .<sup>15</sup> It is safe to conclude that oxidation of the  $\text{Re}(\text{CO})_3(\text{scorpionate})$  complexes involves a predominantly metal-based orbital, but it would not be surprising if calculations were to show that the degree of metal character in the SOMO of the radical cation was somewhat less than that seen for many other 17-electron half-sandwich complexes.<sup>17</sup>

Attempts were made to record ESR spectra of the cation radicals. Solutions containing them were taken from electrolysis solutions, transferred to an ESR sample tube, and frozen to 77 K before removing the samples from the drybox. Each of the radical cations was ESR-silent at 77 K, owing undoubtedly to fast electronic relaxation effects, in concert with the behavior of a large number of  $d^5$  sandwich or half-sandwich radicals possessing pseudo- $C_{3v}$  or higher symmetry.<sup>7,18</sup> These solutions were also, as expected, ESR-silent at room

temperature. Our results suggest that the radical cations would be NMR-active in room temperature solutions, but experiments of this type were not attempted.

### Electrochemistry of manganese complexes

The manganese complexes **3**, **4** and **7** all gave one-electron oxidations at somewhat milder potentials than the corresponding Re complexes, consistent with the behavior of their Cp analogues.<sup>7,15</sup> The corresponding radical cations were less stable, however, than their Re counterparts. Thus, a CV scan rate of  $0.2 \text{ V s}^{-1}$  showed some degree of anodic chemical irreversibility for each of the complexes, and the oxidation of complex **7** was fully irreversible at room temperature. At lower temperatures, greater chemical reversibility was observed in each case (see Fig. 6). From the reverse-to-forward current ratios at different CV scan rates, we estimate the half-lives of the Mn-based radicals at room temperature to decrease in the order  $4^+ (2.2 \text{ s}) > 3^+ (0.8 \text{ s}) > 7^+ (< 0.4 \text{ s})$ .<sup>19</sup> Similarly, the half-life of  $7^+$  was determined to be 8 s at 253 K. Bulk anodic electrolysis of each of these complexes at 253 K confirmed the one-electron process, as 1.0 F was passed in each case, with only 10% to 30% yields of the radical cations. No other electroactive products were detected. Attempts at determining IR spectra of the radical cations gave uncertain results. Rationalization of the shorter lifetimes of the Mn cations compared to their Re counterparts must be somewhat speculative, owing to the fact that the follow-up reaction products of the former have not been determined. Since bulk electrolyses of these complexes did not yield electroactive follow-up products, gross decomposition may be occurring. In that case, weaker metal-to-scorpionate bonding for Mn compared to Re may be responsible for the difference in radical longevity. It is important to emphasize that the  $E_{1/2}$  potentials measured for both the Re and Mn complexes are thermodynamically significant.



**Fig. 6** Representative CVs of 1.3 mM **4** in  $\text{CH}_2\text{Cl}_2/0.05 \text{ M } [\text{NBu}_4][\text{TFAB}]$  at 298 K (red) and 253 K (blue),  $200 \text{ mV s}^{-1}$ , 1.5 mm GCE. The anodic peak current becomes smaller at lower temperature due to the smaller diffusion coefficient.

## Analysis and conclusions

Combining the present results with literature values allows comparison of the spectroscopic IR and electrochemical  $E_{1/2}$  data for a dozen scorpionate and cyclopentadienyl complexes of  $\text{M}(\text{CO})_3$ ,  $\text{M} = \text{Mn}$  or  $\text{Re}$ . In terms of the IR data, ligand (L) donor properties have traditionally been ranked by the  $\nu_{\text{CO}}$  frequencies of  $\text{ML}(\text{CO})$  complexes, with decreasing stretching frequencies being interpreted as increasing L donor strength.<sup>4,20</sup> Based on the weighted average of the three  $\nu_{\text{CO}}$  frequencies listed in Table 3, the scorpionate and cyclopentadienyl donor properties fall in the sequence  $\text{Cp}^*, \text{To}^{\text{M}}, \text{To}^{\text{P}} > \text{Tp}^* > \text{Tp}, \text{Cp}$  for the Mn complexes (Table 4). In this, we make no distinction in rank unless the difference in averaged frequencies is greater than the resolution of the IR measurement ( $4 \text{ cm}^{-1}$ ). For the Re complexes, the sequence is little changed:  $\text{Cp}^*, \text{To}^{\text{M}}, \text{To}^{\text{P}} > \text{Tp}^* > \text{Tp} > \text{Cp}$ . This analysis follows almost exactly the earlier trends summarized by Tellers *et al.*<sup>5</sup> for Tp- and Cp-type complexes and suggests that the tris(oxazolinyl)phenylborate ligands have an increased donor strength compared to  $\text{Tp}^*$ .

A second commonly-used measure of ligand donor strength is the shift in  $E_{1/2}$  for the one-electron oxidation of metal complexes ( $\text{ML}/\text{L}$ ) in which only L is changed. This approach has been employed and discussed in a number of different contexts,<sup>21–24</sup> the underlying assumption being that increasing ligand donor strength is manifested in decreasing  $E_{1/2}$  values. In this analysis, the donor strength for the six ligands under examination decreases in the sequence  $\text{Tp}^* > \text{Cp}^* > \text{To}^{\text{P}}, \text{Tp}, \text{To}^{\text{M}} > \text{Cp}$  (Table 4) for both Mn and Re complexes.<sup>25</sup>

Although the  $E_{1/2}$  values were measured with an accuracy of better than 10 mV, differences of more than 30 mV were judged to be necessary to place a ligand in a different rank.

The most commonly employed quantitative measure of ligand  $E_{1/2}$  shifts is the “ligand electronic factor”  $E_{\text{L}}$  popularized by Lever.<sup>24</sup> The  $E_{\text{L}}$  values of the scorpionate ligands can be easily obtained through the  $E_{1/2}$  shifts (in volt) of their complexes from those of the corresponding  $\text{MCp}(\text{CO})_3$  complexes, since the  $E_{\text{L}}$  value of the Cp ligand (0.33) is known.<sup>24</sup> The  $E_{\text{L}}$  values for the six relevant ligands are collected in Table 5. By this measure, the donor strengths of the tris(oxazolinyl)phenylborate ligands are essentially the same as the Tp ligand but, in contrast to the conclusions based on IR data, less than the  $\text{Tp}^*$  ligand (see Table 4).

The apparent dichotomy between the IR and electrochemical-based conclusions may arise from an inherent difference between the two analytical approaches: the IR absorption energies are determined by the atomic motions of the molecule in one redox state, whereas the  $E_{1/2}$  value is determined by the

**Table 5** Literature  $E_{\text{L}}$  values in this paper are taken from: <sup>a</sup>ref. 24, <sup>b</sup>ref. 26, <sup>c</sup>ref. 7 or <sup>d</sup>ref. 15(b)

Ligand	$E_{\text{L}}$ (literature)	$E_{\text{L}}$ (this work) of Mn, Re cmpds	$E_{\text{L}}$ (avg, this work)
Cp	0.33 <sup>a</sup>	0.33 <sup>a</sup>	0.33 <sup>a</sup>
$\text{To}^{\text{M}}$	Not reported	0.17, 0.13	0.15
Tp	0.42 <sup>b</sup> (see the text)	0.15, 0.15	0.15
$\text{To}^{\text{P}}$	Not reported	0.14 (Re)	0.14
$\text{Cp}^*$	0.06 <sup>a</sup>	0.08, <sup>c</sup> 0.05 <sup>d</sup>	0.065 <sup>c,d</sup>
$\text{Tp}^*$	Not reported	0.00, −0.01	−0.005

**Table 4** Rankings of ligand donor properties based on data reported in this paper. The average IR frequency is the weighted average of the three CO stretching frequencies in dichloromethane, taken from data in Table 3

Experimental basis	Rankings of ligand donor property
Avg $\nu_{\text{CO}}$ of Mn complexes <b>3, 4, 7, 11, 12</b>	$\text{Cp}^*, \text{To}^{\text{M}}, \text{To}^{\text{P}} > \text{Tp}^* > \text{Tp}, \text{Cp}$
Avg $\nu_{\text{CO}}$ of Re complexes <b>1, 2, 5, 6, 9, 10</b>	$\text{Cp}^*, \text{To}^{\text{M}}, \text{To}^{\text{P}} > \text{Tp}^* > \text{Tp} > \text{Cp}$
Anodic $E_{1/2}$ of Mn complexes <b>3, 4, 7, 11, 12</b>	$\text{Tp}^* > \text{Cp}^* > \text{To}^{\text{P}}, \text{Tp}, \text{To}^{\text{M}} > \text{Cp}$
Anodic $E_{1/2}$ of Re complexes <b>1, 2, 5, 6, 9, 10</b>	$\text{Tp}^* > \text{Cp}^* > \text{To}^{\text{P}}, \text{Tp}, \text{To}^{\text{M}} > \text{Cp}$

difference in free energy for the molecule in two redox states. The  $E_{1/2}$ -based analysis assumes that the energetics of any changes in medium effects and molecular structure are constant within the compounds being compared. The rigidity of the pseudo-octahedral complexes under investigation would seem to eliminate concerns about significant structural rearrangements. In terms of the possibility of significant differences in medium effects for redox reactions involving the six types of ligands, the  $E_{1/2}$  values were measured under relatively benign conditions in which changes in both solvation and ion-pairing effects would be minimized.<sup>27</sup> However, we cannot rule out differences in medium effects that could influence the  $E_{1/2}$  values. A reasonable working model for the electronic effects of the tris(oxazolinyl)phenyl borate ligands is that they convey “Tp\*-like” character in terms of the chemical reactivity of their complexes, and “Tp-like” character in terms of the redox potentials of their complexes.

We also point out that the  $E_L$  value determined hereby for the Tp ligand (0.14) is considerably less than the value of 0.42 previously reported based on electrochemical measurements on RuTpCIL<sub>2</sub> complexes, where L is a strongly donating phosphine.<sup>26</sup> The source of this discrepancy may arise from the dramatic difference in the properties of the ancillary ligands in the M(CO)<sub>3</sub> and RuCIL<sub>2</sub> systems.

Finally, the persistence (*i.e.*, thermal stability) of the Re and Mn-based cation radicals [ML(CO)<sub>3</sub>]<sup>+</sup> under the present electrolyte conditions is ranked in the sequences (for ReL): ReTp, ReTp\* > ReTo<sup>M</sup>, ReTo<sup>P</sup> > ReCp, ReCp\*<sup>28</sup> and (for MnL): MnCp, MnCp\* >> MnTp\* > MnTp > MnTo<sup>M</sup>.

## Experimental

All reactions were performed under a dry argon atmosphere using standard Schlenk techniques or under a nitrogen atmosphere in a glovebox, unless otherwise indicated. Water and oxygen were removed from benzene, toluene, pentane, acetonitrile, diethyl ether, and tetrahydrofuran solvents using an IT PureSolv system at Iowa State or using previously described methods<sup>29</sup> at Vermont. Benzene-*d*<sub>6</sub> and tetrahydrofuran-*d*<sub>8</sub> were heated to reflux over Na/K alloy and vacuum-transferred. Re(CO)<sub>5</sub>Br and Mn(CO)<sub>5</sub>Br were prepared according to the literature procedure,<sup>30</sup> starting from Re<sub>2</sub>(CO)<sub>10</sub> and Mn<sub>2</sub>(CO)<sub>10</sub> respectively. Re(CO)<sub>5</sub>Br was further purified by sublimation. Mn(CO)<sub>5</sub>Br was used without further sublimation. Li[To<sup>M</sup>]<sup>3(a)</sup> and Li[To<sup>P</sup>]<sup>3(c)</sup> were prepared by literature procedures. <sup>15</sup>N chemical shifts were determined by <sup>1</sup>H-<sup>15</sup>N HMBC experiments on a Bruker Avance II 700 spectrometer with a Bruker Z-gradient inverse TXI <sup>1</sup>H/<sup>13</sup>C/<sup>15</sup>N 5 mm cryoprobe; <sup>15</sup>N chemical shifts were originally referenced to liquid NH<sub>3</sub> and recalculated to the CH<sub>3</sub>NO<sub>2</sub> chemical shift scale by adding −381.9 ppm. <sup>11</sup>B NMR spectra were referenced to an external sample of BF<sub>3</sub>·Et<sub>2</sub>O. Elemental analyses were performed using a Perkin-Elmer 2400 Series II CHN/S by the Iowa State Chemical Instrumentation Facility or at the Robertson laboratory for samples prepared in Vermont. X-Ray diffraction data were collected on a Bruker-AXS SMART or APEX II as described in crystallographic files (cif) as part of the ESI.† The Tp and Tp\* complexes of Mn and Re were prepared by the literature methods.<sup>31,32</sup> The supporting electrolyte, [NBu<sub>4</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>], was

prepared by metathesis of [NBu<sub>4</sub>]Br with K[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] in MeOH,<sup>33</sup> recrystallized three times from CH<sub>2</sub>Cl<sub>2</sub>/OEt<sub>2</sub>, and dried at 90 °C overnight.

### ReTo<sup>M</sup>(CO)<sub>3</sub> (5)

A solution of LiTo<sup>M</sup> (0.419 g, 1.08 mmol) in THF (20 mL) was added to Re(CO)<sub>5</sub>Br (0.439 g, 1.08 mmol) suspended in THF (5 mL). The solution mixture was degassed with freeze–pump–thaw cycles (3×) and then heated to 80 °C for 8 h in a sealed flask. The volatile materials were removed under reduced pressure giving a yellowish solid, which was then extracted with benzene (12 mL). The benzene was evaporated to dryness providing an off-white solid that was washed with pentane (3 × 5 mL) and further dried under vacuum yielding 0.635 g of ReTo<sup>M</sup>(CO)<sub>3</sub> (0.973 mmol, 90.0%) as a white powder. X-Ray quality single crystals were grown from a concentrated toluene solution of ReTo<sup>M</sup>(CO)<sub>3</sub> at −30 °C. <sup>1</sup>H NMR (400 MHz, methylene chloride-*d*<sub>2</sub>): δ 1.08 (s, 18H, CNCMe<sub>2</sub>CH<sub>2</sub>O), 3.36 (s, 6H, CNCMe<sub>2</sub>CH<sub>2</sub>O), 7.36 (t, <sup>3</sup>J<sub>HH</sub> = 6.6 Hz, 1H, *para*-C<sub>6</sub>H<sub>5</sub>), 7.54 (t, <sup>3</sup>J<sub>HH</sub> = 7.6 Hz, 2H, *meta*-C<sub>6</sub>H<sub>5</sub>), 8.28 (d, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz, 2H, *ortho*-C<sub>6</sub>H<sub>5</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (175 HMz, methylene chloride-*d*<sub>2</sub>): δ 28.18 (CNCMe<sub>2</sub>CH<sub>2</sub>O), 70.47 (CNCMe<sub>2</sub>CH<sub>2</sub>O), 81.15 (CNCMe<sub>2</sub>CH<sub>2</sub>O), 126.16 (*para*-C<sub>6</sub>H<sub>5</sub>), 126.95 (*meta*-C<sub>6</sub>H<sub>5</sub>), 135.77 (*ortho*-C<sub>6</sub>H<sub>5</sub>), 145.71 (br, *ipso*-C<sub>6</sub>H<sub>5</sub>), 188.43 (br, CNCMe<sub>2</sub>CH<sub>2</sub>O), 197.90 (Re(CO)<sub>3</sub>). <sup>11</sup>B NMR (128 MHz, methylene chloride-*d*<sub>2</sub>): δ −17.4. <sup>15</sup>N{<sup>1</sup>H} NMR (71 MHz, methylene chloride-*d*<sub>2</sub>): δ −176.8. IR (KBr, cm<sup>−1</sup>): 2973 (w), 2934 (w), 2012 (s, CO), 1892 (s, CO), 1582 (s, CN), 1462 (m), 1390 (w), 1373 (w), 1354 (w), 1289 (m), 1254 (w), 1203 (m), 1179 (w), 1161 (w), 963 (w). Anal. calcd. for C<sub>24</sub>H<sub>29</sub>BN<sub>3</sub>O<sub>6</sub>Re: C, 44.18; H, 4.48; N, 6.44. Found: C, 44.13; H, 4.61; N, 6.07. Mp: 236 °C (decomp.).

### MnTo<sup>M</sup>(CO)<sub>3</sub> (7)

The preparation of MnTo<sup>M</sup>(CO)<sub>3</sub> follows the method used for ReTo<sup>M</sup>(CO)<sub>3</sub> given above. LiTo<sup>M</sup> (0.380 g, 0.976 mmol) and Mn(CO)<sub>5</sub>Br (0.269 g, 0.979 mmol) afforded 0.454 g of MnTo<sup>M</sup>(CO)<sub>3</sub> (0.871 mmol, 89.0%) as a crystalline yellow solid following that procedure. X-Ray quality single crystals were grown from a concentrated toluene solution of MnTo<sup>M</sup>(CO)<sub>3</sub> at −30 °C. <sup>1</sup>H NMR (400 MHz, benzene-*d*<sub>6</sub>): δ 1.16 (s, 18H, CNCMe<sub>2</sub>CH<sub>2</sub>O), 3.40 (s, 6H, CNCMe<sub>2</sub>CH<sub>2</sub>O), 7.35 (br m, 1H, *para*-C<sub>6</sub>H<sub>5</sub>), 7.53 (br m, 2H, *meta*-C<sub>6</sub>H<sub>5</sub>), 8.30 (br m, 2H, *ortho*-C<sub>6</sub>H<sub>5</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (175 HMz, benzene-*d*<sub>6</sub>): δ 27.53 (CNCMe<sub>2</sub>CH<sub>2</sub>O), 69.54 (CNCMe<sub>2</sub>CH<sub>2</sub>O), 80.96 (CNCMe<sub>2</sub>CH<sub>2</sub>O), 126.30 (*para*-C<sub>6</sub>H<sub>5</sub>), 127.29 (*meta*-C<sub>6</sub>H<sub>5</sub>), 136.32 (*ortho*-C<sub>6</sub>H<sub>5</sub>), 142.80 (br, *ipso*-C<sub>6</sub>H<sub>5</sub>), 189.59 (br, CNCMe<sub>2</sub>CH<sub>2</sub>O), 222.74 (Mn(CO)<sub>3</sub>). <sup>11</sup>B NMR (128 MHz, benzene-*d*<sub>6</sub>): δ −17.1. <sup>15</sup>N{<sup>1</sup>H} NMR (71 MHz, benzene-*d*<sub>6</sub>): δ −172.1. IR (KBr, cm<sup>−1</sup>): 2969 (w), 2930 (w), 2879 (w), 2018 (s, CO), 1899 (s, CO), 1592 (s, CN), 1463 (m), 1390 (w), 1372 (w), 1352 (w), 1285 (m), 1200 (m), 1181 (w), 1158 (w), 993 (w), 969 (w). Anal. calcd. for C<sub>24</sub>H<sub>29</sub>BN<sub>3</sub>O<sub>6</sub>Mn: C, 55.30; H, 5.61; N, 8.06. Found: C, 55.10; H, 5.75; N, 8.05. Mp: 210–212 °C.

### HTo<sup>P</sup>

LiTo<sup>P</sup> (6.150 g, 14.26 mmol) and [HNEt<sub>3</sub>]Cl (2.159 g, 15.68 mmol) were dissolved in methylene chloride and were stirred for 8 h at

room temperature. The solution was filtered through a plug of neutral alumina. The methylene chloride was evaporated under reduced pressure giving a yellow solid, which was extracted with benzene. The filtrate was evaporated to dryness, providing 3.245 g of  $\text{HTo}^{\text{P}}$  (7.63 mmol, 53.5%) as a yellow gel.  $^1\text{H}$  NMR (benzene- $d_6$ , 400 MHz):  $\delta$  0.68 (d, 9H,  $^3J_{\text{HH}} = 6.8$  Hz,  $\text{CNC}(\text{CHMe}_2)\text{HCH}_2\text{O}$ ), 0.87 (d, 9H,  $^3J_{\text{HH}} = 6.4$  Hz,  $\text{CNC}(\text{CHMe}_2)\text{HCH}_2\text{O}$ ), 1.43 (m, 3H,  $\text{CNC}(\text{CHMe}_2)\text{HCH}_2\text{O}$ ), 3.44 (m, 3H,  $\text{CNC}(\text{CHMe}_2)\text{HCH}_2\text{O}$ ), 3.61 (t, 3H,  $^3J_{\text{HH}} = 8.4$  Hz,  $\text{CNC}(\text{CHMe}_2)\text{HCH}_2\text{O}$ ), 3.85 (m, 3H,  $\text{CNC}(\text{CHMe}_2)\text{HCH}_2\text{O}$ ), 7.26 (t, 1H,  $^3J_{\text{HH}} = 7.2$  Hz, *para*- $\text{C}_6\text{H}_5$ ), 7.46 (t, 2H,  $^3J_{\text{HH}} = 7.2$  Hz, *meta*- $\text{C}_6\text{H}_5$ ), 8.11 (br, 2H, *ortho*- $\text{C}_6\text{H}_5$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (benzene- $d_6$ , 100 MHz):  $\delta$  19.00 ( $\text{CNC}(\text{CHMe}_2)\text{HCH}_2\text{O}$ ), 19.01 ( $\text{CNC}(\text{CHMe}_2)\text{HCH}_2\text{O}$ ), 33.20 ( $\text{CNC}(\text{CHMe}_2)\text{HCH}_2\text{O}$ ), 69.56 ( $\text{CNC}(\text{CHMe}_2)\text{HCH}_2\text{O}$ ), 71.06 ( $\text{CNC}(\text{CHMe}_2)\text{HCH}_2\text{O}$ ), 126.40 (*para*- $\text{C}_6\text{H}_5$ ), 127.87 (*meta*- $\text{C}_6\text{H}_5$ ), 134.90 (*ortho*- $\text{C}_6\text{H}_5$ ), 146.20 (br, *ipso*- $\text{C}_6\text{H}_5$ ), 188.10 (br,  $\text{CNCMe}_2\text{CH}_2\text{O}$ ).  $^{11}\text{B}$  NMR (benzene- $d_6$ , 128.4 MHz):  $\delta$  -16.6.  $^{15}\text{N}$  NMR (benzene- $d_6$ , 71 MHz):  $\delta$  -195.6. IR (KBr,  $\text{cm}^{-1}$ ): 2961 (w, br), 1601 (s, CN), 1468 (m), 1424 (w), 1385 (w), 1313 (w), 1262 (m), 1169 (w), 1105 (w), 1026 (w), 968 (m). MS (TOF EI) Exact mass calc. for  $\text{C}_{24}\text{H}_{36}\text{BN}_3\text{O}_3$ ;  $m/e$  425.2850 ( $[\text{M}]^+$ ), found 425.2866.

### $\text{KTo}^{\text{P}}$

Solid KH was slowly added in small portions to a solution of  $\text{HTo}^{\text{P}}$  (0.602 g, 1.415 mmol) in THF (15 mL) until gas evolution was no longer observed. The suspension was stirred at room temperature for 1 h and filtered. THF was evaporated affording a pale yellow gel, which was then triturated with pentane providing 0.616 g of  $\text{KTo}^{\text{P}}$  (1.33 mmol, 93.9%) as an off-white solid.  $^1\text{H}$  NMR (acetonitrile- $d_3$ , 400 MHz):  $\delta$  0.79 (d, 9H,  $^3J_{\text{HH}} = 6.8$  Hz,  $\text{CNC}(\text{CHMe}_2)\text{HCH}_2\text{O}$ ), 0.90 (d, 9H,  $^3J_{\text{HH}} = 6.8$  Hz,  $\text{CNC}(\text{CHMe}_2)\text{HCH}_2\text{O}$ ), 1.58 (m, 3H,  $\text{CNC}(\text{CHMe}_2)\text{HCH}_2\text{O}$ ), 3.54 (t, 3H,  $^3J_{\text{HH}} = 7.6$  Hz,  $\text{CNC}(\text{CHMe}_2)\text{HCH}_2\text{O}$ ), 3.69 (m, 3H,  $\text{CNC}(\text{CHMe}_2)\text{HCH}_2\text{O}$ ), 3.79 (m, 3H,  $\text{CNC}(\text{CHMe}_2)\text{HCH}_2\text{O}$ ), 6.94 (t, 1H,  $^3J_{\text{HH}} = 6.8$  Hz, *para*- $\text{C}_6\text{H}_5$ ), 7.02 (t, 2H,  $^3J_{\text{HH}} = 7.2$  Hz, *meta*- $\text{C}_6\text{H}_5$ ), 7.56 (d, 2H,  $^3J_{\text{HH}} = 6.4$  Hz, *ortho*- $\text{C}_6\text{H}_5$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (acetonitrile- $d_3$ , 100 MHz):  $\delta$  18.35 ( $\text{CNC}(\text{CHMe}_2)\text{HCH}_2\text{O}$ ), 19.88 ( $\text{CNC}(\text{CHMe}_2)\text{HCH}_2\text{O}$ ), 33.67 ( $\text{CNC}(\text{CHMe}_2)\text{HCH}_2\text{O}$ ), 67.29 ( $\text{CNC}(\text{CHMe}_2)\text{HCH}_2\text{O}$ ), 73.72 ( $\text{CNC}(\text{CHMe}_2)\text{HCH}_2\text{O}$ ), 124.80 (*para*- $\text{C}_6\text{H}_5$ ), 126.90 (*meta*- $\text{C}_6\text{H}_5$ ), 135.90 (*ortho*- $\text{C}_6\text{H}_5$ ), 152.74 (br, *ipso*- $\text{C}_6\text{H}_5$ ), 183.65 (br,  $\text{CNCMe}_2\text{CH}_2\text{O}$ ).  $^{11}\text{B}$  NMR (benzene- $d_6$ , 128.4 MHz):  $\delta$  -16.7.  $^{15}\text{N}$  NMR (benzene- $d_6$ , 71 MHz):  $\delta$  -149.1. IR (KBr,  $\text{cm}^{-1}$ ): 2956 (w, br), 2882 (w), 1601 (s, CN), 1480 (m), 1467 (m), 1430 (m), 1385 (m), 1367 (m), 1263 (m), 1105 (w, br), 967 (m, br), 899 (m), 855 (m), 739 (w), 705 (m). Exact mass calc. for  $\text{C}_{48}\text{H}_{70}\text{B}_2\text{KN}_6\text{O}_6$ ;  $m/e$  887.5180 ( $[\text{2M-K}]^+$ ), found 887.5279. Mp: 95–97 °C.

### $\text{ReTo}^{\text{P}}(\text{CO})_3$ (6)

The preparation of  $\text{ReTo}^{\text{P}}(\text{CO})_3$  follows the method used for  $\text{ReTo}^{\text{M}}(\text{CO})_3$  given above.  $\text{KTo}^{\text{P}}$  (0.314 g, 0.677 mmol) and  $\text{Re}(\text{CO})_5\text{Br}$  (0.276 g, 0.677 mmol) afforded 0.400 g of  $\text{ReTo}^{\text{P}}(\text{CO})_3$  (0.576 mmol, 85.1%) as a pale yellow solid. X-Ray quality colorless single crystals were grown from a concentrated toluene solution of  $\text{ReTo}^{\text{P}}(\text{CO})_3$  at -30 °C.  $^1\text{H}$  NMR

(acetonitrile- $d_3$ , 400 MHz):  $\delta$  0.64 (d, 9H,  $^3J_{\text{HH}} = 4.0$  Hz,  $\text{CNC}(\text{CHMe}_2)\text{HCH}_2\text{O}$ ), 0.94 (d, 9H,  $^3J_{\text{HH}} = 4.0$  Hz,  $\text{CNC}(\text{CHMe}_2)\text{HCH}_2\text{O}$ ), 2.46 (m, 3H,  $\text{CNC}(\text{CHMe}_2)\text{HCH}_2\text{O}$ ), 4.1 (m, 3H,  $\text{CNC}(\text{CHMe}_2)\text{HCH}_2\text{O}$ ), 4.26 (m, 6H,  $\text{CNC}(\text{CHMe}_2)\text{HCH}_2\text{O}$ ), 7.13 (t, 1H,  $^3J_{\text{HH}} = 4.2$  Hz, *para*- $\text{C}_6\text{H}_5$ ), 7.19 (t, 2H,  $^3J_{\text{HH}} = 4.4$  Hz, *meta*- $\text{C}_6\text{H}_5$ ), 7.63 (d, 2H,  $^3J_{\text{HH}} = 4.0$  Hz, *ortho*- $\text{C}_6\text{H}_5$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (acetonitrile- $d_3$ , 100 MHz):  $\delta$  13.89 ( $\text{CNC}(\text{CHMe}_2)\text{HCH}_2\text{O}$ ), 18.90 ( $\text{CNC}(\text{CHMe}_2)\text{HCH}_2\text{O}$ ), 30.19 ( $\text{CNC}(\text{CHMe}_2)\text{HCH}_2\text{O}$ ), 70.63 ( $\text{CNC}(\text{CHMe}_2)\text{HCH}_2\text{O}$ ), 73.83 ( $\text{CNC}(\text{CHMe}_2)\text{HCH}_2\text{O}$ ), 126.54 (*para*- $\text{C}_6\text{H}_5$ ), 127.43 (*meta*- $\text{C}_6\text{H}_5$ ), 136.16 (*ortho*- $\text{C}_6\text{H}_5$ ), 142.62 (br, *ipso*- $\text{C}_6\text{H}_5$ ), 189.35 (br,  $\text{CNCMe}_2\text{CH}_2\text{O}$ ), 198.31 ( $\text{Re}(\text{CO})_3$ ).  $^{11}\text{B}$  NMR (acetonitrile- $d_3$ , 128.4 MHz):  $\delta$  -18.1.  $^{15}\text{N}$  NMR (acetonitrile- $d_3$ , 71 MHz):  $\delta$  -195.6. IR (KBr,  $\text{cm}^{-1}$ ): 3045 (w), 2964 (m), 2873 (w), 2010 (s, CO), 1892 (s, br, CO), 1589 (s, CN), 1480 (m), 1463 (m), 1391 (m), 1373 (m), 1363 (m), 1352 (m), 1324 (w), 1277 (w), 1219 (s), 1143 (w), 1115 (m), 1046 (w), 1016 (w), 971 (m), 956 (m), 874 (m), 795 (w), 739 (w), 702 (m). Anal. calcd. for  $\text{C}_{24}\text{H}_{35}\text{BN}_3\text{O}_6\text{Re}$ : C, 46.69; H, 5.08; N, 6.05. Found: C, 45.94; H, 4.93; N, 5.82. Mp: 205–207 °C (decomp.).

### $\text{MnTo}^{\text{P}}(\text{CO})_3$ (8)

The preparation of  $\text{MnTo}^{\text{P}}(\text{CO})_3$  follows the method used for  $\text{To}^{\text{M}}\text{Re}(\text{CO})_3$  given above.  $\text{KTo}^{\text{P}}$  (0.213 g, 0.460 mmol) and  $\text{Mn}(\text{CO})_5\text{Br}$  (0.127 g, 0.462 mmol) yielded 0.227 g of  $\text{MnTo}^{\text{P}}(\text{CO})_3$  (0.402 mmol, 87%) as a yellow solid. X-Ray quality single crystals were grown from a concentrated solution of  $\text{MnTo}^{\text{P}}(\text{CO})_3$  in a benzene–pentane mixture at ambient temperature.  $^1\text{H}$  NMR (acetonitrile- $d_3$ , 400 MHz):  $\delta$  0.64 (d, 9H,  $^3J_{\text{HH}} = 4.0$  Hz,  $\text{CNC}(\text{CHMe}_2)\text{HCH}_2\text{O}$ ), 0.94 (d, 9H,  $^3J_{\text{HH}} = 4.0$  Hz,  $\text{CNC}(\text{CHMe}_2)\text{HCH}_2\text{O}$ ), 2.46 (m, 3H,  $\text{CNC}(\text{CHMe}_2)\text{HCH}_2\text{O}$ ), 4.1 (m, 3H,  $\text{CNC}(\text{CHMe}_2)\text{HCH}_2\text{O}$ ), 4.26 (m, 6H,  $\text{CNC}(\text{CHMe}_2)\text{HCH}_2\text{O}$ ), 7.13 (t, 1H,  $^3J_{\text{HH}} = 4.2$  Hz, *para*- $\text{C}_6\text{H}_5$ ), 7.19 (t, 2H,  $^3J_{\text{HH}} = 4.4$  Hz, *meta*- $\text{C}_6\text{H}_5$ ), 7.63 (d, 2H,  $^3J_{\text{HH}} = 4.0$  Hz, *ortho*- $\text{C}_6\text{H}_5$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (benzene- $d_6$ , 100 MHz):  $\delta$  13.96 ( $\text{CNC}(\text{CHMe}_2)\text{HCH}_2\text{O}$ ), 19.17 ( $\text{CNC}(\text{CHMe}_2)\text{HCH}_2\text{O}$ ), 29.90 ( $\text{CNC}(\text{CHMe}_2)\text{HCH}_2\text{O}$ ), 69.90 ( $\text{CNC}(\text{CHMe}_2)\text{HCH}_2\text{O}$ ), 72.95 ( $\text{CNC}(\text{CHMe}_2)\text{HCH}_2\text{O}$ ), 126.17 (*para*- $\text{C}_6\text{H}_5$ ), 127.22 (*meta*- $\text{C}_6\text{H}_5$ ), 136.03 (*ortho*- $\text{C}_6\text{H}_5$ ), 142.80 (br, *ipso*- $\text{C}_6\text{H}_5$ ), 189.43 (br,  $\text{CNCMe}_2\text{CH}_2\text{O}$ ), 222.85 ( $\text{Mn}(\text{CO})_3$ ).  $^{11}\text{B}$  NMR (benzene- $d_6$ , 128.4 MHz):  $\delta$  -18.1. IR (KBr,  $\text{cm}^{-1}$ ): 3045 (w), 2963 (m), 2873 (w), 2016 (s, CO), 1961 (s, br, CO), 1601 (s, CN), 1496 (w), 1481 (m), 1464 (m), 1432 (w), 1391 (m), 1372 (m), 1364 (m), 1350 (m), 1325 (w), 1278 (w), 1226 (s), 1116 (m), 1044 (m), 972 (m), 873 (m), 798 (m), 738 (w), 702 (m). Anal. calcd. for  $\text{C}_{27}\text{H}_{35}\text{BN}_3\text{O}_6\text{Mn}$ : C, 57.57; H, 6.26; N, 7.46. Found: C, 57.20; H, 6.53; N, 7.36. Mp: 194–196 °C.

### Electrochemistry

Except for IR spectroelectrochemistry which was conducted under Schlenk-type conditions, all electrochemistry was carried out in a Vacuum Atmospheres drybox under nitrogen, using a Princeton Applied Research (PAR) Model 273A potentiostat interfaced to a personal computer. Voltammetry scans were recorded using a glassy carbon working electrode disk of either 1 or 3 mm diameter (Bioanalytical Systems).

The disks were pretreated using a standard sequence of polishing with diamond paste (Buehler) of decreasing sizes (3 to 0.25  $\mu\text{m}$ ) interspersed by washings with nanopure water and finally vacuum drying. Bulk electrolyses were carried out in a three-compartment "H-type" cell having reference, counter and working compartments separated by two fine glass frits and the working electrode was a basket shaped Pt gauze. The reference electrode in all cases was a Ag/AgCl wire, but all potentials have been recorded *versus* the  $\text{FeCp}_2^{0/+}$  redox couple obtained by using  $\text{FeCp}_2$  as an internal standard.<sup>34</sup> IR spectra at Vermont were obtained with an ATI-Mattson Infinity Series FTIR interfaced to a personal computer employing Winfirst software at a resolution of 4  $\text{cm}^{-1}$ . *In situ* spectroelectrochemistry was performed using a mid-IR fiber-optic "dip" probe (Remspec, Inc) in conjunction with the Mattson FTIR,<sup>35</sup> and a standard H-type electrolysis cell under argon.  $^1\text{H}$  NMR spectra were obtained with a Bruker ARX 500 MHz spectrometer, and ESR spectra were recorded using a Bruker ESP 300E spectrometer.

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