Electrochemical Synthesis of Zinc(II), Cadmium(II), and Nickel(II) Complexes of Tetradentate Schiff-base Ligands derived from Aminothioether Imidazoles†

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The electrochemical synthesis and physicochemical properties of neutral zinc(II), cadmium(II), and nickel(II) complexes of Schiff bases derived from aminothioether imidazoles and substituted salicylaldehydes are reported.

Cationic copper(II) complexes of tetradentate Schiff bases derived from aminothioether imidazoles and salicylaldehydes (**1**) and (**2**) (R′ = H, 3-Br, 3-NO_2, 5-NO_2, 3-Cl, or 3,5-Cl_2) have been synthesized by reaction of the appropriate ligand with $Cu(ClO_4)_2 \cdot 6H_2O$ and NaOH in methanol.[1] The corresponding neutral copper(II) complexes (**3a**) and (**4**) may be generated either by reaction of the cationic complex with a molar excess of NaOH, or by reaction of copper(II) acetate with the ligand in acetonitrile.[1] Attempts to form neutral copper(II) complexes from the Schiff bases derived from *o*-hydroxyacetophenones and 4(5)-[(2-aminoethyl)thiomethyl]imidazole (**3c**; M = Cu) following the procedure were unsuccessful and so an electrochemical synthetic technique was employed in which the complexes were synthesized at a sacrificial copper anode using acetonitrile as a solvent.[2]

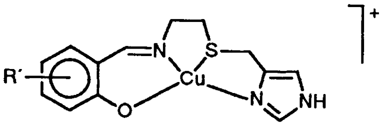
We report here an extension of the electrochemical procedure to facilitate the synthesis of neutral complexes of copper, zinc, cadmium, and nickel involving Schiff-base ligands derived from aminothioether imidazoles and salicylaldehydes (**3a**)—(**3c**) and (**4**) [R′ = H, 3-OEt, 5-OMe, 5-Br, 4,6-$(OMe)_2$, 3,5-Br_2, or 5-Me].

Results and Discussion

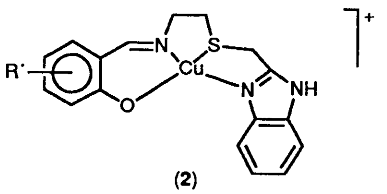
Benzimidazole-derived Complexes (**4**).—The Schiff-base ligands were prepared by the reaction of 2-[(2′-aminoethyl)-thiomethyl]benzimidazole with the salicylaldehyde and characterized by i.r. and ^1H n.m.r. spectroscopy. The i.r. spectra of the ligands showed a broad background superimposed on bands ascribable to aromatic and aliphatic ν(C–H) vibrations, and often extending down to 2 500 cm^{-1}. This is indicative of strong hydrogen bonding of both the O–H and N–H groups in the ligands. All the ligands gave a strong absorption at *ca.* 1 630 cm^{-1} attributable to the imine group. The ^1H n.m.r. spectra of the ligands, run in $(CD_3)_2SO$ (Table 1), show peaks at *ca.* δ 12.4 and *ca.* 14.0 assignable to the OH and NH groups, with the peaks for the azomethine hydrogens at *ca.* δ 8.4.

The neutral nickel(II), zinc(II), and cadmium(II) complexes were then prepared by the electrochemical route using the appropriate metal as the sacrificial anode. Acetonitrile was employed as the solvent and the experimental conditions are given in Table 2. The reaction involved in the preparation of the complexes can be represented by equation (1). The electrochemical efficiency, defined as the quantity of metal dissolved per Faraday of charge, is close to 0.5 mol F^{-1}, indicating that the synthesis of the complexes involves the processes (2) and (3).

$$M + H_2L \longrightarrow ML + H_2 \qquad (1)$$



(1)



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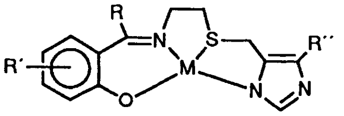
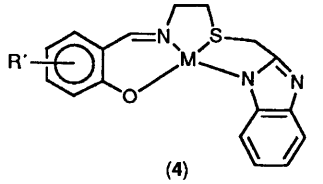


(**3a**) R = H, R″ = H
(**3b**) R = H, R″ = Me
(**3c**) R = Me, R″ = H



(4)

$$\text{Cathode: } H_2L + 2e^- \longrightarrow H_2 + L^{2-} \qquad (2)$$

$$\text{Anode: } L^{2-} + M \longrightarrow ML + 2e^- \qquad (3)$$

In all cases, the complexes obtained were recovered as powders, and they were characterized by elemental analysis (Table 2), i.r., mass, and visible spectroscopy. The major difference between the i.r. spectra of the ligands and those of the complexes is the absence of bands corresponding to phenolic hydroxyl and benzimidazole NH stretches, and the band ascribed to the imine stretch has been shifted to lower frequency for the complexes. Throughout this work it was found that for those complexes where a water molecule was present a corresponding broad band was found in the i.r. at *ca.* 3 400

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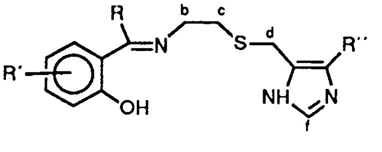
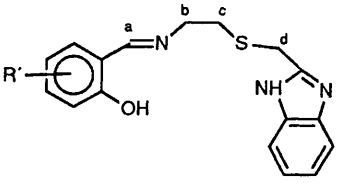
† *Non-S.I. unit employed:* B.M. ≈ 9.27×10^{-24} J T^{-1}.

Table 1. Proton n.m.r. data for the ligands in $(CD_3)_2SO$ with $SiMe_4$ as internal reference



R′	a	b	c	d	e	f	R′	Aromatic
(*b*) R = H^a, R″ = CH^e_3								
H	8.50 (s)	3.70 (t)	2.76 (t)	3.63 (s)	2.09 (s)	7.39 (s)		7.37 (m), 6.90 (m)
3-OEt*	8.30 (s)	3.75 (t)	2.77 (t)	2.71 (s)	2.20 (s)	7.46 (s)	4.11 (q) OCH_2 1.47 (t) CH_3	6.94—6.74 (m)
5-OMe*	8.29 (s)	3.76 (t)	2.79 (t)	3.71 (s)	2.21 (s)	7.47 (s)	3.78 (s) OCH_3	7.47 (m), 6.91 (m), 6.77 (m)
5-Br*	8.23 (s)	3.74 (t)	2.80 (t)	3.70 (s)	2.21 (s)	7.39 (s)		7.48 (m), 6.86 (m), 6.82 (m)
4,6-$(OMe)_2$*	8.30 (s)	3.60 (t)	2.71(t)	3.70 (s)	2.19 (s)	7.47 (s)	3.76 (s) OCH_3 3.77 (s) OCH_3	5.85, 5.58 (AB)
3,5-Br_2	8.49 (s)	3.78 (t)	2.79 (t)	3.67 (s)	2.10 (s)	7.46 (s)		7.79, 7.56 (AB)
(*c*) R = CH^a_3, R″ = H^e								
H	2.34 (s)	3.73 (t)	2.82 (t)	3.67 (s)	6.99 (s)	7.55 (s)		7.64 (m), 7.54 (m), 6.76 (m)
5-Me	2.31 (s)	3.70 (t)	2.79 (t)	3.68 (s)	6.95 (s)	7.54 (s)	2.23 (s)	7.44 (m), 7.06 (m), 6.67 (m)
(*a*) R = H^a, R″ = H^e								
H	8.53 (s)	3.74 (t)	2.78 (t)	3.65 (s)	6.99 (s)	7.55 (s)		7.43 (m), 7.31 (m), 6.87 (m)



R′	a	b	c	d	R′	Aromatic
H	8.47 (s)	3.78 (t)	2.90 (t)	3.97 (s)		7.51 (m), 7.35 (m), 7.16 (m), 6.89 (m)
3-OEt	8.45 (s)	3.78 (t)	2.89 (t)	3.96 (s)	4.02 (q) OCH_2 1.32 (t) CH_3	7.50 (m), 7.16 (m), 6.98 (m), 6.77 (m)
5-OMe	8.40 (s)	3.76 (t)	2.89 (t)	3.95 (s)	3.70 (s) OCH_3	7.51 (m), 7.14 (m), 6.93 (m), 6.81 (m)
5-Br	8.43 (s)	3.79 (t)	2.91 (t)	3.96 (s)		7.56 (m), 7.46 (m), 7.16 (m), 6.85 (m)
4,6-$(OMe)_2$	8.42 (s)	3.72 (t)	2.84 (t)	3.97 (s)	3.72 (s) OCH_3 3.76 (s) OCH_3	7.51 (m), 7.15 (m), 5.79, 5.72 (AB)

* In $CDCl_3$.

cm^{-1}. The sparing solubility of the complexes restricted studies in solution, but ^1H n.m.r. determinations in $(CD_3)_2SO$ were possible for the zinc and cadmium complexes. In the ^1H n.m.r. spectra of the complexes the ligand peaks at *ca.* δ 12.4 and *ca.* 14.0, assignable to the OH and NH groups, are absent showing that both hydrogen atoms are lost during the electrochemical synthesis and that the ligands behave as dianionic ligands. The peak for the azomethine hydrogen at *ca.* δ 8.4 undergoes a slight shift towards high field for the cadmium complexes; however for the zinc complexes the shift is to low field. Also the spectra show changes in the proton signals of the aromatic ring, for example, for the free ligand in [**4**; R′ = 4,6-$(OMe)_2$] the protons of the phenolic ring form an AB system, but in the spectra of the complexes these signals appear as two singlets (δ 5.84 and 5.66, M = Zn; 5.76 and 5.55, M = Cd). These results indicate that the ligands behave in a tetradentate manner, bonding to the metals through the phenolic oxygen, the sulphur atom, and the azomethine and pyrrolic nitrogens.

A molecular-ion peak is observed at $[M + 1]$ in the fast atom bombardment mass spectra of the metal complexes [*e.g.* (**4**; R′ = H), M = Cu, *m/z* 373; Cd, 422; Zn, 374; and Ni, 368]; the spectra of nickel complexes also show a higher molecular ion peak corresponding to the molecular weight of a dimeric species [*e.g.* (**4**; R′ = H), *m/z* 375]. In the spectra of all sets of complexes, breakdown peaks were found attributable, *e.g.*, to the co-ordination of M^{II} to the fragments produced by cleavage of the ligand on either side of the ethylene link. The diffuse reflectance spectra for the nickel(II) complexes (Table 3) show spectral bands at *ca.* 1 000 and *ca.* 600 nm. These values are well within the range of typical octahedral nickel complexes, so the

Table 2. Experimental conditions for the electrochemical synthesis of benzimidazole-derived complexes (**4**)·nH$_2$O and analytical data

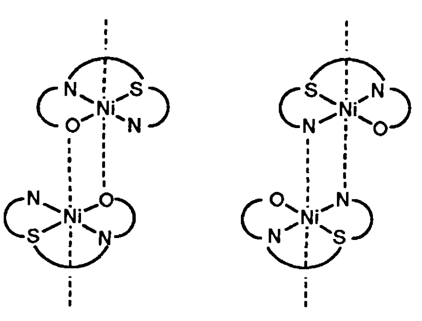
M	R′	n	Amount of ligand (g)[a]	Initial potential (V)[b]	Time (h)	Metal used (mg)	E_f (mol F^{-1})	Analysis[c] C	N	H
Zn	H	1	0.24	11.7	2.42	30.1	0.52	51.90 (52.00)	10.75 (10.70)	4.35 (4.35)
	3-OEt	1	0.27	18.0	2.50	33.1	0.49	52.95 (52.25)	9.25 (9.60)	5.15 (4.80)
	5-OMe	3	0.21	32.0	2.83	35.3	0.51	47.70 (47.10)	9.30 (9.15)	5.40 (5.00)
	4,6-(OMe)$_2$	1	0.27	27.6	1.58	29.0	0.62	51.70 (50.40)	8.80 (9.30)	4.15 (4.65)
	5-Br	1	0.21	15.0	1.67	20.3	0.50	42.45 (43.30)	9.25 (8.90)	3.25 (3.40)
Ni	H	2	0.14	15.0	1.50	16.0	0.49	49.20 (50.55)	10.65 (10.40)	4.05 (4.70)
	3-OEt	0	0.16	13.6	1.50	16.0	0.51	55.35 (55.40)	10.20 (10.20)	4.60 (4.60)
	5-OMe	1	0.21	13.6	2.00	21.7	0.49	51.50 (51.95)	10.25 (10.10)	4.55 (4.55)
	4,6-(OMe)$_2$	0	0.24	14.7	2.50	26.7	0.49	53.15 (53.30)	9.50 (9.80)	4.15 (4.60)
	5-Br	3	0.23	12.6	2.67	29.5	0.50	41.50 (40.75)	7.90 (8.40)	3.50 (4.00)
Cd	H	1.5	0.23	14.0	2.17	51.9	0.57	45.10 (45.50)	9.40 (9.35)	4.25 (4.00)
	3-OEt	1	0.19	13.0	2.33	48.7	0.50	47.60 (47.15)	7.60 (8.70)	4.70 (4.35)
	5-OMe	1	0.22	10.0	2.00	47.0	0.56	45.25 (46.00)	9.05 (8.95)	4.05 (4.05)
	4,6-(OMe)$_2$	1	0.25	10.0	2.17	54.4	0.60	45.70 (45.65)	8.55 (8.40)	4.45 (4.20)
	5-Br	1	0.23	10.0	2.33	55.0	0.56	39.60 (39.35)	8.45 (8.10)	3.15 (3.10)

[a] Plus NMe$_4$ClO$_4$ (*ca.* 10 mg). [b] Voltage to produce a current of 10 mA. [c] Calculated values in parentheses.

Table 3. Ligand-field maxima for the nickel(II) and copper(II) complexes (**3**) and (**4**) (n H$_2$O)

Complex	M	R′	n	$\lambda_{max.}$*/nm
(**4**)	Ni	H	2	1 000, 581
(**4**)	Ni	3-OEt	0	1 000, 602
(**4**)	Ni	5-OMe	1	1 163, 568
(**4**)	Ni	4,6-(OMe)$_2$	0	1 000
(**4**)	Ni	5-Br	3	1 042, 555
(**3c**)	Ni	H	3	1 064, 581
(**3c**)	Ni	5-Me	1	1 041, 578
(**3b**)	Ni	H	0	1 064, 555
(**3b**)	Ni	5-OMe	1	1 052, 555
(**3b**)	Ni	5-Br	2	1 064, 526
(**3b**)	Ni	4,6-(OMe)$_2$	2	1 064, 555
(**3b**)	Ni	3,5-Br$_2$	1	1 064, 526
(**3c**)	Cu	H	1	602 (br), 463 (sh)
(**3c**)	Cu	5-Me	0.5	584 (br)
(**3b**)	Cu	H	0.75	625, 461 (sh)
(**3b**)	Cu	5-OMe	3	625, 461 (sh)
(**3b**)	Cu	5-Br	3	625, 454 (sh)
(**3b**)	Cu	3,5-Br$_2$	2	667 (sh), 500 (sh)

* Diffuse reflectance spectra; sh = shoulder, br = broad.



(*a*) (*b*)

bands can be assigned to $^3A_{2g} \longrightarrow {}^3T_{2g}$ and $^3A_{2g} \longrightarrow {}^3T_{2g}(F)$ transitions.[3–5] These results suggest that the nickel complexes are, at least, dimeric, either through the phenolic oxygen (*a*) or the imidazole nitrogen (*b*), with an octahedral geometry around the metal.[6]

For the zinc and cadmium complexes, we propose a monomeric distorted tetrahedral structure.

Imidazole-derived Complexes (**3a**)—(**3c**).—The electrochemical method, as described above, was also used to prepare nickel(II), zinc(II), and cadmium(II) complexes of Schiff bases derived from aminothioether imidazoles (Table 4). The complexes were characterized by elemental analysis (Table 4), i.r., mass, and visible spectroscopy. The insolubility of the complexes precluded any solution studies and ^{1}H n.m.r. spectra were not possible for the zinc and cadmium complexes. The diffuse reflectance spectra (Table 3) gave bands at *ca.* 1 000 and *ca.* 550 nm. The magnetic moment was determined for (**3b**; R′ = H) as 3.5 B.M.; this value is inside the range 2.9—4.2 B.M. predicted by theoretical considerations for high-spin octahedral nickel(II) complexes.[3] The fast atom bombardment mass spectra again showed molecular ion peaks at $[M + 1]$ for the metal complexes and for the nickel complexes it was also possible to detect peaks corresponding to higher oligomers, *e.g.* (**3b**; R′ = 5-Br), m/z 823 (dimer) and [**3b**; R′ = 4,6-(OMe)$_2$], m/z 785 (dimer), with both of these complexes showing breakdown fragments from the trimers at m/z 1 178 and 1 137 respectively. This together with similarities in the i.r. and visible spectra suggest a structural similarity between these compounds and the complexes derived from aminothioether benzimidazoles.

As it had proved difficult to synthesize neutral copper(II) complexes of the corresponding Schiff bases derived from acetophenones or from methylaminothioether imidazoles, the electrochemical method was used to facilitate their production using the experimental conditions given in Table 4. The analytical data reported in Table 4 show that the procedure can be satisfactorily used for the synthesis of these compounds. The complexes obtained are recovered as powders, and the electrochemical efficiency was close to 1 mol F^{-1} indicating that the synthesis involves the processes (4) and (5), followed by the oxidation reaction (6).

$$\text{Cathode: } H_2L + e^- \longrightarrow HL^- + \tfrac{1}{2}H_2 \qquad (4)$$

$$\text{Anode: } HL^- + Cu \longrightarrow Cu(HL) + e^- \qquad (5)$$

$$Cu(HL) \longrightarrow CuL + \tfrac{1}{2}H_2 \qquad (6)$$

The i.r. spectra show that the ligands behave in a bianionic tetradentate manner and the mass spectra show an ion peak assignable to the monomer. The diffuse reflectance spectra (Table 3) show a broad *d–d* band at *ca.* 625 nm with a shoulder at *ca.* 460 nm. The similarity in spectra between the imidazole

Table 4. Experimental conditions for the electrochemical synthesis of imidazole-derived complexes (**3**)·nH$_2$O and analytical data

M	R	R′	R″	n	Amount of ligand (g)[a]	Initial potential (V)[b]	Time (h)	Metal used (mg)	E_f (mol f^{-1})	Analysis[c]		
										C	N	H
Cu	H	H	H	0.5	0.22	25.0	1.16	24.0	0.87	46.95 (47.05)	12.70 (12.65)	3.95 (4.20)
	Me	H	H	1	0.20	20.0	2.00	45.0	0.95	47.40 (47.40)	11.95 (11.85)	4.45 (4.80)
	Me	5-Me	H	0.5	0.22	20.0	2.00	48.0	1.00	50.15 (50.05)	12.05 (11.70)	4.95 (5.00)
	H	H	Me	0.75	0.33	15.0	2.00	32.2	1.10	48.15 (48.00)	11.65 (12.00)	4.45 (4.70)
	H	5-OMe	Me	3	0.17	19.0	2.00	47.3	1.00	42.65 (42.80)	10.05 (10.00)	4.95 (5.45)
	H	4,6-(OMe)$_2$	Me	0.5	0.92	15.0	4.00	71.1	0.75	47.25 (47.35)	10.55 (10.35)	5.20 (4.95)
	H	5-Br	Me	3	0.22	15.0	2.50	59.7	1.00	35.05 (35.80)	8.70 (8.95)	3.85 (4.25)
	H	3,5-Br$_2$	Me	2	0.14	16.5	2.00	18.9	0.80	31.85 (31.65)	7.35 (7.90)	2.70 (3.20)
Zn	H	H	H	0.5	0.22	30.0	3.00	51.4	0.46	47.00 (46.80)	12.90 (12.60)	4.15 (4.20)
	Me	H	H	0	0.31	16.3	3.00	32.9	0.45	50.90 (49.65)	12.25 (12.40)	5.00 (4.45)
	Me	5-Me	H	0	0.23	20.0	3.30	36.2	0.45	51.40 (51.10)	12.30 (11.90)	5.10 (4.80)
	H	H	Me	0	0.27	20.0	4.50	26.6	0.54	49.55 (49.65)	11.90 (12.40)	4.45 (4.45)
	H	5-OMe	Me	0.5[d]	0.29	20.0	7.00	42.8	0.50	48.90 (49.35)	12.50 (12.60)	5.30 (4.75)
	H	4,6-(OMe)$_2$	Me	2.5	0.15	10.0	2.00	21.5	0.44	43.90 (43.30)	9.55 (9.45)	4.80 (5.40)
	H	5-Br	Me	1	0.17	20.0	2.50	29.2	0.48	38.25 (38.60)	9.65 (9.65)	3.85 (3.65)
	H	3,5-Br$_2$	Me	1	0.19	13.0	2.40	27.8	0.48	32.30 (32.60)	8.00 (8.15)	2.90 (3.10)
Ni	H	H	H	0.5	0.21	12.0	2.00	10.5	0.48	47.85 (47.75)	12.65 (12.85)	4.35 (4.30)
	Me	H	H	3	0.20	19.2	2.50	37.0	0.45	43.30 (43.50)	10.75 (10.90)	4.85 (5.45)
	Me	5-Me	H	1	0.16	10.0	4.00	21.8	0.50	48.55 (49.50)	11.85 (11.55)	5.00 (5.20)
	H	H	Me	0	0.41	18.7	6.00	21.2	0.40	50.60 (50.65)	12.25 (12.65)	5.05 (4.50)
	H	5-OMe	Me	1	0.29	12.0	6.50	37.4	0.52	47.85 (47.40)	10.90 (11.05)	4.80 (5.00)
	H	4,6-(OMe)$_2$	Me	3	0.16	13.5	2.69	29.1	0.49	42.55 (43.10)	9.40 (9.40)	5.40 (5.60)
	H	5-Br	Me	2	0.24	20.0	3.75	36.5	0.49	37.15 (37.60)	9.55 (9.40)	3.55 (4.05)
	H	3,5-Br$_2$	Me	1	0.15	18.0	2.00	21.7	0.49	32.95 (33.15)	8.25 (8.25)	3.35 (2.95)
Cd	H	H	H	0.25[d]	0.21	20.0	2.16	19.2	0.42	43.20 (42.45)	11.90 (11.90)	3.85 (3.60)
	Me	H	H	0.5[d]	0.19	20.0	2.50	52.4	0.50	44.35 (44.35)	11.65 (12.05)	4.60 (4.05)
	Me	5-Me	H	0	0.10	25.0	2.00	39.4	0.47	45.20 (45.05)	10.80 (10.50)	4.55 (4.25)
	H	H	Me	0	0.30	10.9	4.00	51.7	0.62	44.90 (43.60)	10.80 (10.90)	4.20 (3.90)
	H	5-OMe	Me	0.25	0.30	20.0	6.00	84.6	0.67	42.20 (42.65)	9.45 (9.95)	3.90 (4.15)
	H	4,6-(OMe)$_2$	Me	1.5	0.21	17.0	3.11	71.0	0.54	40.45 (40.65)	8.90 (8.90)	4.55 (4.65)
	H	5-Br	Me	3	0.18	15.0	2.58	59.2	0.54	32.50 (32.30)	8.20 (8.05)	3.20 (3.45)
	H	3,5-Br$_2$	Me	0	0.14	22.7	2.33	23.9	0.49	32.35 (30.90)	7.75 (7.75)	2.80 (2.40)

[a] Plus NMe$_4$ClO$_4$ (*ca.* 10 mg). [b] Voltage to produce a current of 10 mA. [c] Calculated values in parentheses. [d] MeCN.

complexes reported here and the imidazole and benzimidazole complexes previously reported[1] suggest that there is an overall similarity in their structure. The latter complexes have been proposed as being closely similar to the precursor cationic complexes the crystal structure of one of which shows a distortion from a square-planar environment towards a tetrahedral one caused by a large out-of-plane displacement of the sulphur atom.

Experimental

Microanalyses were determined using a Perkin-Elmer 240B microanalyser. I.r. spectra were recorded as Nujol mulls or liquid films using a Perkin-Elmer 180 spectrometer, diffuse reflectance spectra of solids using a Philips Scientific SP 700 spectrophotometer, proton n.m.r. using a Bruker WM 250 FT spectrometer, and fast atom bombardment mass spectra on a Kratos MS50TC spectrometer.

The Schiff bases were prepared by the method described in ref. 1. The electrochemical method used in the syntheses of the metal complexes is similar to that described by Habeeb *et al.*[7] The cell was a tall-form beaker (100 cm^3) fitted with a rubber bung through which the electrochemical leads entered into the cell. The anode, in foil form, was suspended from a platinum wire and the cathode was a platinum wire. The ligand was dissolved in acetonitrile and tetramethylammonium perchlorate (10 mg) was added to the solution as the supporting electrolyte; the acetonitrile was used as supplied. The cell used can be summarized as Pt|CH$_3$CN + H$_2$L|M. The experimental conditions for the reactions are detailed in Tables 2 and 4. At the completion of the reaction the compounds were collected, washed with acetonitrile, and dried in vacuum.

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