Crystal and Molecular Structure of the Complex [1,2-Bis(diphenylphosphino)ethane](diethylphenylphosphine)tri-isothiocyanatorhenium(III) and the Electrochemistry of Isothiocyanato-derivatives of Rhenium(III) and Rhenium(IV)

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Crystals of the title complex are triclinic, space group $P\bar{1}$, with unit-cell dimensions $a = 9.680(3)$, $b = 12.519(4)$, $c = 19.072(8)$ Å, $\alpha = 68.86(3)$, $\beta = 71.82(3)$, $\gamma = 75.40(2)^\circ$, and $Z = 2$. The intensities of 4 025 reflections above background have been collected and the structure refined by least-squares techniques to R' 0.046. The complex exists as discrete pseudo-octahedral monomers. The rhenium atom in a given molecule is co-ordinated by three phosphorus and three nitrogen atoms in a *mer* configuration. Cyclic-voltametric studies on dichloromethane solutions of $[Re(NCS)_3(PEt_2Ph)L']$ [L' = 1,2-bis(diphenylphosphino)ethane, 2,2'-bipyridyl, or 1,10-phenanthroline] show that these complexes exhibit three electrochemically reversible one-electron waves attributable to $[Re]^{1+} \longleftarrow [Re]^{0} \longrightarrow [Re]^{1-} \longrightarrow [Re]^{2-}$, thereby demonstrating the existence of an extensive redox chemistry for these species. The results of these electrochemical studies are compared with the related behaviour of $[NBu_4]_2[Re_2(NCS)_8]$ and $[NBu_4]_2[Re(NCS)_6]$.

THE reactions of $[NBu_4]_2[Re_2(NCS)_8]$ with uni- and bidentate tertiary phosphines produce complexes of the type $[NBu_4]_2[Re_2(NCS)_8L_2]$ which are believed to contain dimeric thiocyanate-bridged anions with magnetically dilute rhenium(III) centres.[1] Further reactions of $[NBu_4]_2[Re_2(NCS)_8(PEt_2Ph)_2]$ with L' = 1,2-bis(diphenylphosphino)ethane (dppe), 2,2'-bipyridyl (bipy), and 1,10-phenanthroline (phen) lead to disruption of the thiocyanate bridges and the formation of the six-co-ordinate monomers $[Re(NCS)_3(PEt_2Ph)L']$.[1] This is the first extensive series of complexes which has been prepared directly from anions of the type $[Re_2X_8]^{2-}$ (X = Cl, Br, or NCS) where cleavage of the Re–Re

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[1] T. Nimry and R. A. Walton, *Inorg. Chem.*, 1977, **16**, 2829.

quadruple bond [2] is the rule rather than the exception. To support these structural conclusions we have carried out a single-crystal *X*-ray structure analysis of the complex $[Re(NCS)_3(PEt_2Ph)(dppe)]$ in order to confirm the monomeric nature of this species and to identify the mode of thiocyanate bonding (*N*- or *S*-). This study also proved to be of relevance to our investigations of the electrochemical properties of complexes which either contain strong multiple metal–metal bonds or are derived from such species,[3] since it provided the necessary structural information for a monomer of the type $[Re(NCS)_3L_3]$ whose redox properties we wished to compare with that of the metal–metal-bonded dimer $[Re_2(NCS)_8]^{2-}$. Full details of these structural and electrochemical studies are now reported.

EXPERIMENTAL

Crystallography.—Red crystals of $[Re(NCS)_3(PEt_2Ph)(dppe)]$ were formed on heating 1,2-bis(diphenylphosphino)ethane (dppe) under reflux in acidified methanol with the thiocyanate-bridged dimer $[NBu_4]_2[Re_2(NCS)_8(PEt_2Ph)_2]$, the latter species being the product of the reaction of $[NBu_4]_2[Re_2(NCS)_8]$ with PEt_2Ph.

Crystal data. $C_{39}H_{39}N_3P_3ReS_3$, $M = 925.1$, $a = 9.680(3)$, $b = 12.519(4)$, $c = 19.072(8)$ Å, $\alpha = 68.86(3)$, $\beta = 71.82(3)$, $\gamma = 75.40(2)°$; $U = 2\,022$ Å^3, $D_m = 1.519(5)$, $Z = 2$, $D_c = 1.519$ g cm^{-3}, Mo-K_α radiation, $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 51.2 cm^{-1}, space group $P\bar{1}$ (no. 2).

Data collection. Weissenberg and precession photographs showed the space group to be triclinic. On the basis of two molecules per unit cell a centre of symmetry was assumed giving space group $P\bar{1}$ (no. 2). Subsequent refinement confirmed this assumption. An equidimensional crystal of length 0.15 mm was mounted along a non-principal crystallographic direction on an Enraf–Nonius CAD-4 *X*-ray diffractometer. Unit-cell parameters were determined from least-squares refinement of the 2θ values of 62 reflections measured at positive and negative 2θ ($34 < 2\theta < 48°$) by use of graphite-monochromated Mo-K_α radiation. All the 5 462 reflections from a hemisphere of reciprocal space with $2\theta < 48°$ were collected using the techniques described in ref. 4. The data were corrected for Lorentz and polarization effects but not for absorption, then equivalent reflections were averaged giving 4 025 independent reflections having $I \geqslant \sigma(I)$.

Structure analysis. The position of the unique rhenium atom was determined from a Patterson function. The remaining non-hydrogen atoms were located from two subsequent difference-syntheses. The structure was refined by minimizations of $\Sigma w(F_o - F_c)^2$ by a modified block-diagonal technique owing to storage limitations of the computer. Sequential refinement of the scale factor and positional and thermal parameters of the rhenium and thiocyanates together with those of the PEt_2Ph or one or the other half of the dppe ligand reduced R to 0.040 and R' to 0.046. Weights were taken as $w = 1/\sigma^2(F_o) = 4F_o^2/\sigma^2(F_o^2)$. Atomic scattering factors with real and imaginary anomalous scattering corrections for Re, S, and P were taken from ref. 5. The final estimated standard deviation of an observation of unit weight was 1.24. Final positional parameters are listed in Table 1 and molecular dimensions in Table 2. Observed and calculated structure factors, thermal parameters, individual phenyl C–C distances, and C–C–C bond angles are listed in Supplementary Publication No. SUP 22289 (31 pp.).*

TABLE 1

Positional parameters ($\times 10^4$) *

Atom	x	y	z
Re	4 963.1(5)	2 846.5(4)	2 378.5(2)
S(1)	9 135(4)	3 564(4)	256(2)
S(2)	2 822(4)	6 847(3)	1 489(2)
S(3)	666(4)	2 288(4)	4 482(2)
P(1)	4 021(3)	2 350(2)	1 490(2)
P(2)	5 984(3)	923(2)	3 101(2)
P(3)	5 834(3)	3 427(2)	3 245(1)
N(1)	6 798(10)	3 117(7)	1 540(4)
N(2)	3 995(9)	4 528(7)	1 928(4)
N(3)	3 104(9)	2 586(7)	3 220(5)
C(1)	7 788(13)	3 330(10)	998(7)
C(2)	3 481(11)	5 504(9)	1 735(6)
C(3)	2 058(13)	2 482(9)	3 743(6)
C(23)	6 032(12)	1 079(9)	4 031(6)
C(32)	6 862(12)	2 119(8)	3 816(6)
C(121)	2 136(14)	1 957(10)	1 892(7)
C(122)	961(17)	3 016(12)	2 001(8)
C(131)	3 940(12)	3 607(9)	598(6)
C(132)	3 360(14)	3 360(10)	1(7)
C(111)	5 121(11)	1 166(8)	1 116(6)
C(112)	6 395(14)	1 397(10)	538(7)
C(113)	7 325(16)	489(12)	231(8)
C(114)	6 875(17)	9 402(12)	508(8)
C(115)	5 599(16)	9 189(11)	1 066(8)
C(116)	4 676(14)	78(10)	1 393(7)
C(211)	7 863(12)	281(9)	2 730(6)
C(212)	8 372(16)	518(11)	1 943(8)
C(213)	9 875(21)	9 933(15)	1 645(10)
C(214)	676(19)	9 278(14)	2 144(10)
C(215)	10 209(23)	8 953(16)	2 896(12)
C(216)	8 685(20)	9 500(14)	3 269(10)
C(221)	4 940(12)	9 704(9)	3 427(6)
C(222)	5 550(15)	8 790(11)	3 105(7)
C(223)	4 638(19)	7 876(13)	3 338(9)
C(224)	3 336(18)	7 987(12)	3 851(9)
C(225)	2 721(16)	8 847(12)	4 166(8)
C(226)	3 572(14)	9 771(10)	3 962(7)
C(311)	7 079(11)	4 500(8)	2 830(5)
C(312)	6 998(13)	5 305(10)	2 106(6)
C(313)	7 954(15)	6 170(11)	1 782(8)
C(314)	8 954(15)	6 167(11)	2 165(7)
C(315)	9 055(15)	5 332(11)	2 881(8)
C(316)	8 096(14)	4 479(10)	3 219(7)
C(321)	4 348(11)	3 987(8)	3 953(5)
C(322)	3 278(12)	4 848(9)	3 698(6)
C(323)	2 089(13)	5 306(9)	4 208(6)
C(324)	1 984(15)	4 881(11)	4 995(8)
C(325)	3 025(18)	3 969(13)	5 273(9)
C(326)	4 258(16)	3 482(12)	4 753(8)

* Numbers in parentheses are the estimated standard deviations of the least significant digit.

Electrochemistry.—Electrochemical measurements were made in dichloromethane solutions containing 0.2 mol dm^{-3} tetra-n-butylammonium hexafluorophosphate as the supporting electrolyte *versus* the saturated sodium chloride calomel electrode (s.s.c.e.) at 22 ± 2 °C, and are uncorrected for junction potentials. All the potentials reported are reduction potentials *versus* the s.s.c.e. Cyclic-voltammetry experiments were carried out using a BioAnalytical Systems model CV-1A instrument in conjunction with a Hewlett–Packard model 7035B *xy* recorder. A Bioanalytical

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1977, Index issue.

[2] F. A. Cotton, *Chem. Soc. Rev.*, 1975, 27.

[3] D. J. Salmon and R. A. Walton, *J. Amer. Chem. Soc.*, 1978, **100**, 991.

[4] J. A. Jaecker, W. R. Robinson, and R. A. Walton, *J.C.S. Dalton*, 1975, 698.

[5] 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1968, vol. 3.

potentiostat was used for potential control for exhaustive electrolysis experiments. Values of n, where n is the total number of equivalents of electrons transferred, were calculated after measuring the total area under curves of current against time for the complete reaction. Reactions were judged to be complete when the current had decreased to <1% of its initial value. All the voltammetric measurements were carried out at platinum electrodes in solutions deaerated with nitrogen.

TABLE 2

Bond distances (Å) and angles (°)

(*a*) Distances			
Re–P(1)	2.470(3)	P(1)–C(111)	1.825(10)
Re–P(2)	2.435(3)	P(1)–C(121)	1.862(13)
Re–P(3)	2.452(3)	P(1)–C(131)	1.862(10)
Re–N(1)	1.992(8)	P(2)–C(23)	1.868(10)
Re–N(2)	2.062(8)	P(2)–C(211)	1.823(11)
Re–N(3)	2.009(8)	P(2)–C(221)	1.855(11)
N(1)–C(1)	1.170(12)	P(3)–C(32)	1.851(10)
N(2)–C(2)	1.166(11)	P(3)–C(311)	1.827(10)
N(3)–C(3)	1.175(12)	P(3)–C(321)	1.830(9)
C(1)–S(1)	1.591(12)	C(23)–C(32)	1.564(10)
C(2)–S(2)	1.591(11)	C(121)–C(122)	1.544(17)
C(3)–S(3)	1.611(12)	C(131)–C(132)	1.565(15)
(*b*) Angles			
N(1)–Re–N(2)	90.6(3)	Re–P(1)–C(111)	116.9(3)
N(1)–Re–N(3)	179.5(4)	Re–P(1)–C(121)	115.0(4)
N(1)–Re–P(1)	87.8(2)	Re–P(1)–C(131)	110.0(4)
N(1)–Re–P(2)	95.1(2)	Re–P(2)–C(23)	104.8(3)
N(1)–Re–P(3)	92.6(2)	Re–P(2)–C(211)	120.2(4)
N(2)–Re–N(3)	89.0(3)	Re–P(2)–C(221)	119.5(4)
N(2)–Re–P(1)	86.5(2)	Re–P(3)–C(32)	107.9(3)
N(2)–Re–P(2)	171.2(2)	Re–P(3)–C(311)	119.3(3)
N(2)–Re–P(3)	91.0(2)	Re–P(3)–C(321)	113.6(3)
N(3)–Re–P(1)	92.2(2)	C(111)–P(1)–C(121)	104.2(5)
N(3)–Re–P(2)	85.4(2)	C(111)–P(1)–C(131)	103.5(4)
N(3)–Re–P(3)	87.4(2)	C(121)–P(1)–C(131)	106.1(5)
P(1)–Re–P(2)	100.5(1)	C(23)–P(2)–C(211)	103.9(5)
P(1)–Re–P(3)	177.4(1)	C(23)–P(2)–C(221)	103.2(5)
P(2)–Re–P(3)	82.0(1)	C(211)–P(2)–C(221)	103.0(5)
Re–N(1)–C(1)	173.4(9)	C(32)–P(3)–C(311)	104.8(5)
Re–N(2)–C(2)	172.7(8)	C(32)–P(3)–C(321)	105.9(4)
Re–N(3)–C(3)	174.3(9)	C(311)–P(3)–C(321)	104.2(4)
N(1)–C(1)–S(1)	177.4(11)	P(1)–C(121)–C(122)	111.5(9)
N(2)–C(2)–S(2)	177.6(11)	P(1)–C(131)–C(132)	113.2(7)
N(3)–C(3)–S(3)	177.4(10)		

The following complexes, which were prepared by standard literature procedures,[1,6] were investigated using these electrochemical techniques: $[NBu_4]_2[Re_2(NCS)_8]$, $[NBu_4]_2$-$[Re(NCS)_6]$, and $[Re(NCS)_3(PEt_2Ph)L']$ (L′ = dppe, bipy, or phen).

RESULTS AND DISCUSSION

As shown in Figure 1, $[Re(NCS)_3(PEt_2Ph)(dppe)]$ exists as discrete pseudo-octahedral molecules with no metal–metal bonding. The rhenium atom in a given molecule is co-ordinated by three phosphorus and three nitrogen atoms with the *mer* configuration. There is a significant distortion from regular octahedral geometry due to the presence of the bidentate dppe ligand, and a distinct *trans* effect is also apparent in the molecule.

Rhenium–nitrogen distances within the *trans* N(1)–Re–N(3) system average 2.000(8) Å, while Re–N(2), *trans* to a P ligand, is 2.062(8) Å (Figure 2). The Re–P distances in the *trans* P(1)–Re–P(3) system are 2.470(1) and 2.452(3) Å, respectively, while Re–P(2) is 2.435(3) Å. Other distances (Table 2) within the molecule are consistent with those observed in other systems of this type[4,7–12] with P–C(phenyl) averaging 1.832, P–C(alkyl) 1.861, C–N 1.170, C–S 1.598, C(alkyl)–C(alkyl) 1.558, and C(phenyl)–C(phenyl) 1.405 Å, with a range from 1.301 to 1.529 Å and a root-mean-square (r.m.s.) deviation of 0.039 Å from the average.

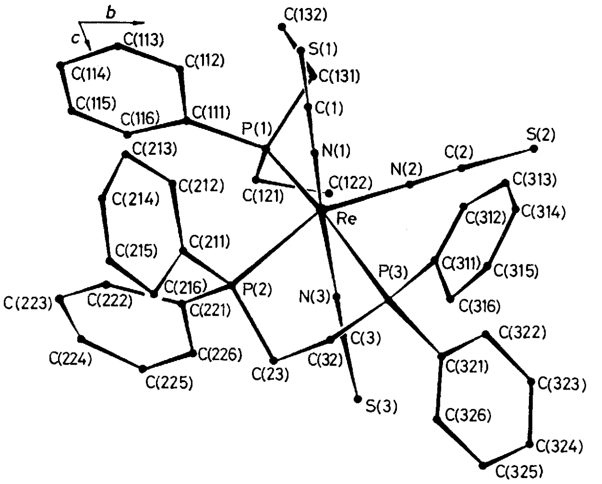

FIGURE 1 Molecular structure of $[Re(NCS)_3(PEt_2Ph)(dppe)]$ and the numbering scheme for the atoms

The largest deviation from 90° octahedral angles is found with the P(2)–Re–P(3) angle of 82.0(1)°, the bite angle of the dppe ligand, and with its supplement, the P(1)–Re–P(3) angle of 100.5(1)°. These angles reflect the restraining effect of the C_2H_4 bridge in dppe, a structural feature common to other dppe complexes[4,7–12] of rhenium and of iridium and rhodium. Other variations in the octahedral angles range from 0.6 to 5° (Table 2). The Re–N–C angles deviate from linearity by 7.5° while the thiocyanate ligands are linear.

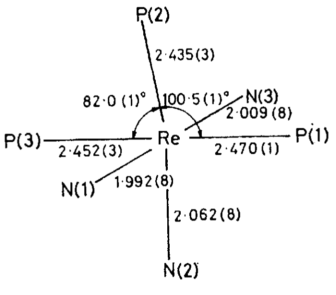

FIGURE 2 Rhenium co-ordination polyhedron with distances (Å)

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[7] V. G. Albano and P. L. Bellon, *J. Organometallic Chem.*, 1972, **37**, 151.

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The Re–P–C angles exhibit the usual tendency for the Re–P–C(phenyl) angles to be larger than the Re–P–C(alkyl) by 5—10°. Other angles may be found in Table 2 except for C–C–C angles which have been deposited. The C–C–C angles range from 114 to 128° [mean 120(3)°].

A comparison of chloride-containing structures similar to that of [Re(NCS)$_3$(PEt$_2$Ph)(dppe)] is instructive. The Re–N distance *trans* to a phosphine is 3% longer than that *trans* to a NCS ligand. In the corresponding chloride systems the difference between the Re–Cl distance *trans* to a phosphine relative to the Re–Cl distance *trans* to a chloride ranged from 4 to 8%.[4,13] The differences in the Re–P distances exhibit analogous behaviour. The Re–P distance *trans* to a NCS differs from those *trans* to phosphine ligands by 1% while the corresponding comparison in the chloride system shows that the Re–P distances *trans* to chloride are *ca.* 2.3% shorter than Re–P distances *trans* to phosphine ligands.[4,13] Apparently the *trans* structural effect of *N*-thiocyanate ligands in the *mer*-[Re(PR$_3$)$_3$X$_3$] system is larger than that of chloride ligands.

The electrochemical properties of [Re(NCS)$_3$(PEt$_2$Ph)(dppe)] and its bipy and phen analogues, together with related data for [NBu$_4$]$_2$[Re$_2$(NCS)$_8$] and [NBu$_4$]$_2$[Re(NCS)$_6$], are summarized in Table 3. All the five complexes exhibit three-wave electrochemical behaviour, comprising one oxidation step and two one-electron reductions. In the case of [Re(NCS)$_3$(PEt$_2$Ph)L′] (L′ = dppe, bipy, or phen), the three waves [Figure 3(*a*)] are electrochemically reversible (*i.e.* $\Delta E_p \simeq 60$ mV and $i_{p,c}/i_{p,a} \simeq 1$),[14] thereby demonstrating the existence of an extensive redox chemistry for these complexes. This behaviour indicates that the complexes remain intact throughout the sequence $[\mathrm{Re}]^{1+} \longleftarrow [\mathrm{Re}]^0 \longrightarrow [\mathrm{Re}]^{1-} \longrightarrow [\mathrm{Re}]^{2-}$. Exhaustive electrolysis of a dichloromethane solution of the red complex [Re(NCS)$_3$(PEt$_2$Ph)(dppe)] at 1.2, −0.8, and −1.6V produces solutions of the 1+ (purple), 1− (orange), and 2− (yellow) ions, respectively. All these conversions are reversible and, within experimental error, quantitative (*i.e.* *n* values vary between 0.99 and 0.92). This extensive redox behaviour is quite different from that exhibited by rhenium(III) chloride monomers of the type [ReCl$_3$(PR$_3$)$_3$] for which a reversible oxidation and an irreversible one-electron reduction have been observed.[15,16]

TABLE 3

$E_{\frac{1}{2}}$ values for isothiocyanato-complexes of rhenium(III) and rhenium(IV) in dichloromethane [a]

	$E_{\frac{1}{2}}$ [b]/V *versus* s.s.c.e.		
Complex	(ox)	(red) (1)	(red) (2)
[Re(NCS)$_3$(PEt$_2$Ph)(dppe)]	0.84 (0.98)	−0.34 (0.98)	−1.35 (0.94)
[Re(NCS)$_3$(PEt$_2$Ph)(bipy)]	0.68 (0.97)	−0.38 (0.97)	−1.50 (0.92)
[Re(NCS)$_3$(PEt$_2$Ph)(phen)]	0.68 (0.96)	−0.38 (0.98)	−1.48 (0.93)
[NBu$_4$]$_2$[Re(NCS)$_6$]	1.03 [c]	−0.28 (0.95)	−1.63 [d]
[NBu$_4$]$_2$[Re$_2$(NCS)$_8$]	1.03 [c]	−0.10 (0.94)	−0.82 [d]

[a] With 0.2 mol dm^{-3} [NBu$^n_4$][PF$_6$] as supporting electrolyte. [b] With a platinum-bead working electrode; *n* values are given in parentheses. [c] *n* Not obtained for this reversible oxidation wave due to its proximity to the solvent limit. [d] Quasi-reversible ($\Delta E_p > 100$ mV).

The two other rhenium isothiocyanate complexes studied, [NBu$_4$]$_2$[Re$_2$(NCS)$_8$] and [NBu$_4$]$_2$[Re(NCS)$_6$], also exhibit three-wave electrochemical behaviour [Figure 3(*b*) and (*c*)]. However, not all the waves in these cyclic voltammograms are reversible. Both complexes have a reversible one-electron (by coulometry) reduction, but the second reduction is irreversible, a situation similar to that found for [Re$_2$X$_8$]$^{2-}$ (X = Cl, Br, or I) where two reductions have been observed, the first being at least quasi-reversible and

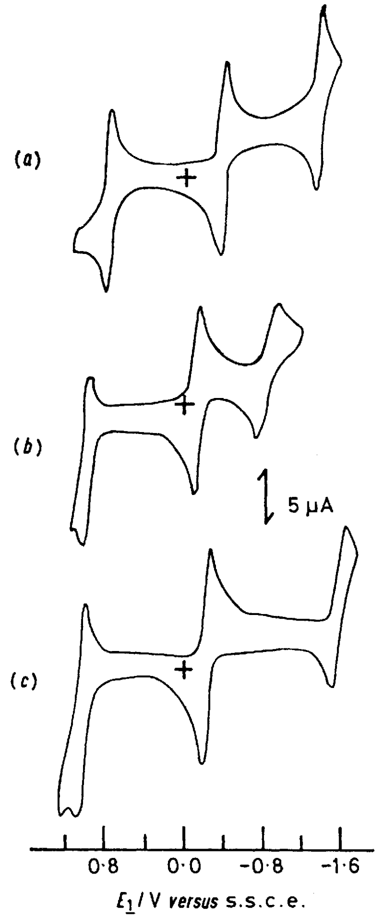

FIGURE 3 Cyclic voltammograms in 0.2 mol dm^{-3} [NBu$^n_4$]-[PF$_6$]–dichloromethane of: (*a*) [Re(NCS)$_3$(PEt$_2$Ph)(dppe)], (*b*) [NBu$_4$]$_2$[Re$_2$(NCS)$_8$], and (*c*) [NBu$_4$]$_2$[Re(NCS)$_6$] (scan rate 200 mV s^{-1} at a platinum-bead electrode *versus* s.s.c.e. at 22 ± 2 °C)

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associated with the configuration change $(\sigma)^2(\pi)^4(\delta)^2 \longrightarrow (\sigma)^2(\pi)^4(\delta)^2(\delta^*)^1$ while the second is irreversible.[17,18] These latter complexes also exhibit an oxidation which is reversible on the cyclic-voltammetry time scale, but attempts to produce the oxidized product failed because of proximity to the solvent limit (*ca.* 1.2V).

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