The Crystal Structures of the Dirhenium(III) Complexes $[Ph_4As][Re_2Cl_7L]$ ($L = PBu^n{}_3$, PPh_2Bu^n), and the Reduction Potentials of $[Re_2Cl_6(PPh_2Bu^n)_2]$ and $[Ph_4As][Re_2Cl_7PPh_2Bu^n]$

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Abstract

The crystal structures of the quadruply bonded complexes $[Re_2Cl_7L]^-$ ($L = PBu^n{}_3$ (**2a**) and PPh_2Bu (**2b**)) have been determined. The former contains a three fold disordered Re_2 unit while the latter is not disordered and shows only a slight deviation from eclipsed geometry of 4.7°. The electrochemical reduction of **2b** and $[Re_2Cl_6(PPh_2Bu^n)_2]$ (**3b**) have been investigated, and they show reduction potentials at -0.35 V which is considerably less negative and more reversible than values reported for $[Re_2Cl_8]^{2-}$.

Introduction

A recent kinetic study of the substitution of chloride by tertiary phosphine and arsine in $[Re_2Cl_8]^{2-}$ has shown that $[Re_2Cl_7L]^-$ monoanions are intermeidates in the formation of the well known neutral $Re_2Cl_6L_2$ complexes [1, 2]. The crystal structures of two of these intermediate systems have been determined and their redox properties examined in an attempt to further define the factors which influence the substitution reactions of quadruply bonded rhenium systems.

Experimental

Physical Measurements

UV–Vis spectra were recorded on either a Cary 17, a Phillips PU8740 or a Shimadzu UV-260 spectrometer. IR spectra were obtained on a Perkin-Elmer 983G spectrometer. Electrochemical measurements were carried out in dichloromethane solution using tetra-n-butylammonium tetrafluoroborate as supporting electrolyte. $E_{1/2}$ values, determined as $(E_{p,a} + E_{p,c})/2$ were referenced to a standard calomel electrode (SCE) at room temperature. Voltammetric experiments were performed with an Oxford Electrodes potentiostat, model PP2 connected to an Advance Bryans series 6000 X-Y recorder.

Complexes **2a** and **2b** were prepared as described previously and were recrystallized from CH_2Cl_2 in a CH_2Cl_2/hexane solvent gradient [1].

Crystallography

The experimental parameters for **2a** and **2b** are given in Table 1. All data were corrected for Lorentz and polarization effects and also for absorption by the method of Walker and Stuart [3]. The structures were solved by Patterson methods, SHELX86 [4], and refined by full matrix least-squares using SHELX76 [5]. Hydrogen atoms were included in calculated positions with fixed thermal parameters. The rhenium, chlorine, arsenic and phosphorus atoms of both structures were refined anisotropically. All non-hydrogen atoms of **2b** except the carbons of the cation and the butyl group were refined anisotropically. The thermal parameters were terms U_{ij} of

$$\exp(-2\Pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*))$$

The atomic scattering factors for non-hydrogen and hydrogen atoms and the anomalous dispersion correction factors for non-hydrogen atoms were taken from the literature [6–8]. All calculations were performed on a VAX 8700 computer. The ORTEP program was used to obtain the drawings [9].

Results and Discussion

The crystal structure of **2a**, anion only, is depicted in Figs. 1 and 2 and atomic coordinates and selected bond distances and angles are given in Tables 2 and 3. The Re_2 units are three fold disordered within the approximate cube defined by the chlorine and phosphorus atoms. The site occupancy factors refined very well to values of 0.565, 0.280 and 0.155. The average cube edge is 3.29(±0.12) Å, similar to

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TABLE 1. Experimental parameters for **2a** and **2b**

	2a	**2b**
Crystal size (mm)	0.21 × 0.30 × 0.18	0.30 × 0.35 × 0.15
Formula	$C_{36}H_{47}AsCl_7PRe_2$	$C_{40}H_{39}AsCl_7PRe_2$
Space group	$P2_1/n$	$P2_1/n$
a (Å)	10.638(1)	15.773(2)
b (Å)	20.480(2)	9.849(1)
c (Å)	20.107(2)	28.260(3)
α (°)	90	90
β (°)	95.86(1)	101.446(10)
γ (°)	90	90
U (Å^3)	4357.55	4303.03
μ (cm^{-1})	65.07	65.91
F(000)	2309.58	2383.58
Z	4	4
Radiation Mo Kα graphite monochromator	λ = 0.70930 Å	
Diffractometer	Enraf-Nonius CAD4	
Orienting reflections, range	25, 13 < θ < 28°	
Temperature (°C)	22	
Scan method	$\omega-2\theta$	
Data collection range	2 < 2θ < 48°	2 < 2θ < 56°
Unique data measured	9461	10144
Observed data	2144, $I > 2\sigma I$	4403, $I > 3\sigma I$
No. parameters fitted	280	320
Transmission factors, max./min.	1.0/0.79	1.0/0.56
R [a]	4.48%	3.72%
R_w [b]	2.79%	3.21%
Quality-of-fit indicator[c]	0.49	1.05
Largest shift/e.s.d., final cycle	<0.002	<0.001
Largest positive peak (e/Å^3)	0.30	0.68
Largest negative peak (e/Å^3)	−0.36	−0.57

[a] $R = [\Sigma|F_o - F_c|]/\Sigma|F_o|$. [b] $R_w = [[\Sigma w(|F_o - F_c|)^2]/[\Sigma w(|F_o|)^2]]^{1/2}$; $w = 1/[(\sigma F_o)^2]$. [c] Quality-of-fit = $[\Sigma w - (|F_o| - |F_c|)^2/(N_{obs} - N_{parameters})]^{1/2}$.

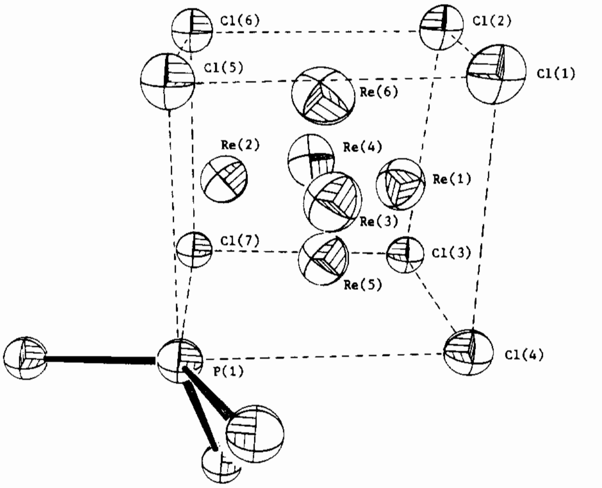

Fig. 1. An ORTEP drawing of $[Re_2Cl_7P^nBu_3]^-$ showing the rhenium disorder.

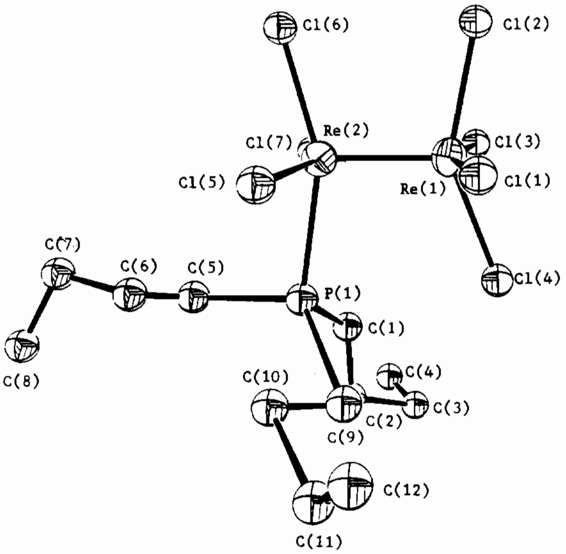

Fig. 2. An ORTEP drawing of $[Re_2Cl_7P^nBu_3]^-$ showing the major Re–Re location only.

TABLE 2. Fractional atomic coordinates for [AsPh$_4$]-[Re$_2$Cl$_7$PBu$^n{}_3$]

Atom	x	y	z	Site occupancy factor[a]
Re1	0.5642(3)	0.1750(2)	0.3100(1)	0.565
Re2	0.5827(2)	0.1713(2)	0.4208(1)	0.565
Re3	0.6819(5)	0.1769(4)	0.3584(2)	0.280
Re4	0.4755(5)	0.1725(4)	0.3640(2)	0.280
Re5	0.5619(13)	0.1205(6)	0.3518(6)	0.155
Re6	0.5821(16)	0.2264(5)	0.3643(7)	0.155
As1	0.7771(3)	0.4232(2)	0.5676(2)	
Cl1	0.7196(9)	0.2535(5)	0.2891(5)	
Cl2	0.4156(9)	0.2569(5)	0.2868(5)	
Cl3	0.4027(10)	0.0978(5)	0.2838(5)	
Cl4	0.6975(9)	0.0999(5)	0.2686(4)	
Cl5	0.7502(9)	0.2432(4)	0.4501(4)	
Cl6	0.4443(8)	0.2489(5)	0.4511(4)	
Cl7	0.4422(9)	0.0927(5)	0.4445(4)	
P1	0.7469(10)	0.0845(5)	0.4385(5)	
C1	0.6973(34)	−0.0037(17)	0.4093(16)	
C2	0.7933(42)	−0.0482(21)	0.4059(21)	
C3	0.7428(74)	−0.1107(37)	0.3473(37)	
C4	0.6743(67)	−0.1254(33)	0.3764(36)	
C5	0.7466(51)	0.0725(27)	0.5369(26)	
C6	0.7817(95)	0.1005(45)	0.5818(43)	
C7	0.7475(60)	0.0935(31)	0.6525(30)	
C8	0.8512(54)	0.0600(26)	0.6815(25)	
C9	0.9360(53)	0.1045(26)	0.3928(26)	
C10	0.9631(60)	0.1183(29)	0.4462(29)	
C11	1.1052(52)	0.1465(25)	0.4023(26)	
C12	1.1143(49)	0.1990(25)	0.3726(25)	
C13	0.8270(32)	0.5030(17)	0.6148(15)	
C14	0.7386(35)	0.5516(16)	0.6102(15)	
C15	0.7727(35)	0.6109(18)	0.6453(16)	
C16	0.8920(35)	0.6158(18)	0.6741(16)	
C17	0.9748(39)	0.5669(19)	0.6751(17)	
C18	0.9453(31)	0.5083(16)	0.6445(14)	
C19	0.9178(30)	0.3722(15)	0.5641(14)	
C20	0.9535(36)	0.3260(18)	0.6140(18)	
C21	1.0685(35)	0.2914(17)	0.6163(18)	
C22	1.1286(36)	0.2955(16)	0.5631(17)	
C23	1.0917(29)	0.3312(17)	0.5049(15)	
C24	0.9914(29)	0.3731(15)	0.5109(14)	
C25	0.7163(29)	0.4483(16)	0.4791(15)	
C26	0.7531(30)	0.5031(16)	0.4518(16)	
C27	0.7191(34)	0.5135(19)	0.3877(19)	
C28	0.6454(34)	0.4668(18)	0.3501(18)	
C29	0.6002(35)	0.4091(19)	0.3756(20)	
C30	0.6373(29)	0.3975(16)	0.4407(16)	
C31	0.6581(36)	0.3817(20)	0.6139(18)	
C32	0.6021(32)	0.4073(17)	0.6608(16)	
C33	0.5171(34)	0.3772(19)	0.6987(18)	
C34	0.4697(40)	0.3145(21)	0.6752(19)	
C35	0.5438(49)	0.2895(27)	0.6326(24)	
C36	0.6325(46)	0.3173(25)	0.5963(23)	

[a] Site occupancy factor is 1.0 unless stated otherwise.

TABLE 3. Selected bond lengths (Å) and angles (°) for [Re$_2$Cl$_7$PBu$^n{}_3$]$^-$

Re1–Re2	2.219(3)	Re3–Re4	2.211(7)
Re5–Re6	2.193(13)	Re1–Cl1	2.374(10)
Re1–Cl2	2.320(11)	Re1–Cl3	2.354(11)
Re1–Cl4	2.305(10)	Re2–Cl5	2.340(10)
Re2–Cl6	2.291(10)	Re2–Cl7	2.279(10)
Re2–P1	2.491(11)		
Cl1–Re1–Re2	102.1(3)	Cl2–Re1–Re2	102.4(3)
Cl2–Re1–Cl1	86.9(4)	Cl3–Re1–Re2	100.9(3)
Cl3–Re1–Cl1	157.0(3)	Cl3–Re1–Cl2	88.5(3)
Cl4–Re1–Re2	110.2(3)	Cl4–Re1–Cl1	85.6(3)
Cl4–Re1–Cl2	147.3(4)	Cl4–Re1–Cl3	86.1(4)
Cl5–Re2–Re1	102.6(3)	Cl6–Re2–Re1	104.5(3)
Cl6–Re2–Cl5	89.4(3)	Cl7–Re2–Re1	103.9(3)
Cl7–Re2–Cl5	153.0(3)	Cl7–Re2–Cl6	88.9(3)
P1–Re2–Re1	99.0(3)	P1–Re2–Cl5	84.8(3)
P1–Re2–Cl6	156.5(4)	P1–Re2–Cl7	86.1(4)

that reported for [Re$_2$Cl$_8$]$^{2-}$ [10]. The phosphorus atom was not disordered with the chlorines. While two fold disorder of the Re$_2$ unit is quite common, three fold disorder in structures of this type is rare. The first example observed was in a complex where [Re$_2$Cl$_8$]$^{2-}$ was present as a counterion with site occupancy factors of 0.57, 0.39 and 0.06 [2]. Recently Cotton *et al.* have reported the structure of [(n-Bu)$_4$N]$_2$[Re$_2$I$_8$] which had equal occupation of all three sites and in that case the increased disorder was ascribed to the loosely packed nature of the crystal [11]. The packing density of **2a** however is quite normal with a mean non-hydrogen atomic volume of 23.2 Å^3. The Re–Re distances observed for the three orientations in **2a** were the same within experimental error (Table 2) and the centres of the Re–Re bonds were almost coincident. The carbon atoms of the butyl groups did not refine well. The C–C bond distances deviated considerably from the expected values, however no effective disorder model was found and there were no significant peaks in the final difference map, the highest being only of 0.3 3/Å^3. In Fig. 2, only the dominant Re$_2$ unit is shown and in Table 3 only bond distances involving that Re$_2$ unit are given. Due to the disorder the Re–ligand bond lengths are averaged and expected differences are not observed. For example the Re(2)–Cl(6) bond *trans* to P does not show the expected *trans* influence.

The anion of **2b** is depicted in Fig. 3 and atomic coordinates and some bond lengths and angles are given in Tables 4 and 5. In this case no disorder was detected and the structure refined satisfactorily. The only bond length which deviated from the expected value was the terminal bond of the butyl group C(15)–C(16). However the terminal atom, C(16), had a large thermal parameter and its position may be less well defined than the rest of the structure. The slight reduction in M–M bond length of 2.220(1), relative to that of [Re$_2$Cl$_8$]$^{2-}$, 2.224(1), is probably due to the slight twist away from the eclipsed

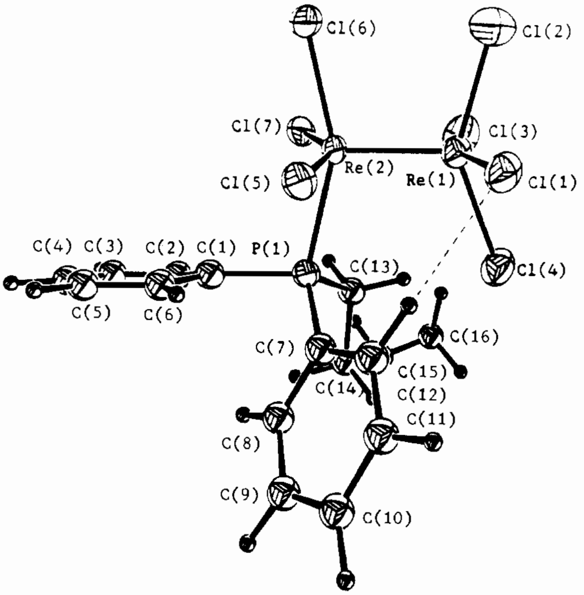

Fig. 3. An ORTEP drawing of $[Re_2Cl_7PPh_2{}^nBu]^-$.

TABLE 4. Fractional atomic coordinates for $[AsPh_4]$-$[Re_2Cl_7PPh_2Bu^n]$

Atom	*x*	*y*	*z*
Re1	0.41368(3)	0.07541(5)	0.17330(2)
Re2	0.42856(3)	0.20062(5)	0.11015(2)
As1	0.91461(8)	0.65703(13)	0.06264(4)
Cl1	0.5262(2)	−0.0771(3)	0.1768(1)
Cl2	0.3230(2)	−0.0960(3)	0.1392(1)
Cl3	0.2943(2)	0.1766(4)	0.1959(1)
Cl4	0.4935(2)	0.1625(4)	0.2450(1)
Cl5	0.5534(2)	0.1294(3)	0.0873(1)
Cl6	0.3523(2)	0.0818(3)	0.0435(1)
Cl7	0.3182(2)	0.3564(3)	0.0999(1)
P1	0.5112(2)	0.3955(3)	0.1512(1)
C1	0.5166(7)	0.5175(12)	0.1043(4)
C2	0.4692(9)	0.6392(14)	0.0985(4)
C3	0.4796(10)	0.7327(14)	0.0644(5)
C4	0.5316(11)	0.7089(18)	0.0336(5)
C5	0.5768(10)	0.5904(16)	0.0378(5)
C6	0.5704(8)	0.4988(13)	0.0719(4)
C7	0.6241(7)	0.3731(13)	0.1777(4)
C8	0.6794(8)	0.4902(13)	0.1832(4)
C9	0.7671(9)	0.4785(16)	0.2028(5)
C10	0.8021(8)	0.3544(16)	0.2171(4)
C11	0.7505(8)	0.2454(14)	0.2102(4)
C12	0.6629(8)	0.2519(12)	0.1914(4)
C13	0.4565(7)	0.4723(11)	0.1963(4)
C14	0.5050(8)	0.5800(13)	0.2277(4)
C15	0.4499(10)	0.6474(16)	0.2622(5)
C16	0.4282(14)	0.5616(21)	0.2914(7)
C17	0.9361(7)	0.7580(11)	0.0081(4)
C18	0.8682(8)	0.8025(12)	−0.0273(4)
C19	0.8854(9)	0.8775(13)	−0.0658(5)
C20	0.9677(8)	0.9039(13)	−0.0691(4)
C21	1.0342(8)	0.8607(12)	−0.0350(4)
C22	1.0209(7)	0.7868(11)	0.0042(4)
C23	1.0210(7)	0.6104(11)	0.1035(4)
C24	1.0459(8)	0.4748(13)	0.1096(4)
C25	1.1242(8)	0.4408(14)	0.1404(4)
C26	1.1736(9)	0.5388(13)	0.1651(5)
C27	1.1505(8)	0.6723(14)	0.1586(4)
C28	1.0736(7)	0.7078(13)	0.1278(4)
C29	0.8496(7)	0.7635(11)	0.0983(4)
C30	0.8741(8)	0.7798(12)	0.1478(4)
C31	0.8187(9)	0.8489(13)	0.1718(5)
C32	0.7447(9)	0.8978(13)	0.1502(5)
C33	0.7157(12)	0.8815(16)	0.1034(6)
C34	0.7695(10)	0.8112(16)	0.0768(6)
C35	0.8367(7)	0.5007(11)	0.0436(4)
C36	0.8218(7)	0.4679(13)	−0.0056(4)
C37	0.7673(8)	0.3534(14)	−0.0175(5)
C38	0.7411(8)	0.2786(14)	0.0176(5)
C39	0.7687(8)	0.3097(14)	0.0664(5)
C40	0.8200(7)	0.4226(12)	0.0787(4)

TABLE 5. Selected bond lengths (Å) and angles (°) for $[Re_2Cl_7PPh_2Bu^n]^-$

Re1–Re2	2.220(1)	Re1–Cl1	2.313(3)
Re1–Cl2	2.297(3)	Re1–Cl3	2.329(3)
Re1–Cl4	2.327(3)	Re2–Cl5	2.301(3)
Re2–Cl6	2.339(3)	Re2–Cl7	2.295(3)
Re2–P1	2.476(3)	P1–C1	1.805(12)
P1–C7	1.804(11)	P1–C13	1.838(10)
C1–C2	1.404(15)	C1–C6	1.378(14)
C2–C3	1.367(16)	C3–C4	1.329(18)
C4–C5	1.360(18)	C5–C6	1.339(15)
C7–C8	1.435(15)	C7–C12	1.362(14)
C8–C9	1.390(15)	C9–C10	1.368(17)
C10–C11	1.338(16)	C11–C12	1.379(14)
C13–C14	1.492(14)	C14–C15	1.576(16)
C15–C16	1.275(20)		
Cl1–Re1–Re2	101.1(1)	Cl2–Re1–Re2	103.2(1)
Cl2–Re1–Cl1	87.1(1)	Cl3–Re1–Re2	101.7(1)
Cl3–Re1–Cl1	157.2(1)	Cl3–Re1–Cl2	87.7(1)
Cl4–Re1–Re2	111.7(1)	Cl4–Re1–Cl1	85.6(1)
Cl4–Re1–Cl2	145.1(1)	Cl4–Re1–Cl3	86.0(1)
Cl5–Re2–Re1	106.8(1)	Cl6–Re2–Re1	104.5(1)
Cl6–Re2–Cl5	87.3(1)	Cl7–Re2–Re1	105.9(1)
Cl7–Re2–Cl5	147.0(1)	Cl7–Re2–Cl6	88.7(1)
P1–Re2–Re1	100.6(1)	P1–Re2–Cl5	88.1(1)
P1–Re2–Cl6	154.8(1)	P1–Re2–Cl7	81.7(1)
C1–P1–Re2	105.6(4)	C7–P1–Re2	118.9(4)
C7–P1–C1	101.5(5)	C13–P1–Re2	111.6(4)
C13–P1–C1	109.5(5)	C13–P1–C7	108.9(5)

geometry of 4.65°, Fig. 4 and Table 6. This structure is only the second example where a slight twist away from eclipsed geometry has been observed. The first

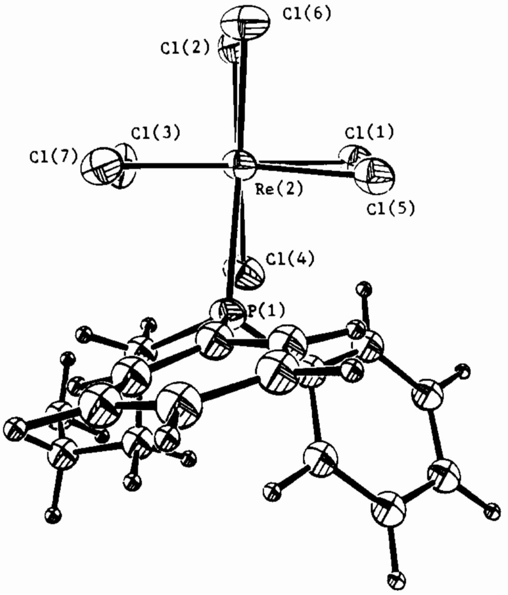

Fig. 4. View down the Re–Re bond of $[Re_2Cl_7PPh_2{}^nBu]^-$.

TABLE 6. Torsion angles (°) for **2b**

$Cl_3–Re_1–Re_2–Cl_7$	1.39
$Cl_2–Re_1–Re_2–Cl_6$	3.87
$Cl_1–Re_1–Re_2–Cl_5$	5.89
$Cl_4–Re_1–Re_2–P_1$	7.44
Average	4.65

example was the corresponding dibutylphenylphosphine complex which had a larger twist angle of 8.7° and a larger metal–metal bond length reduction [12]. The deviation from eclipsed geometry in **2b** could be due to an unbalanced interaction between the hydrogen on C(12) and Cl(1). The H...Cl(1) distance is 2.79 Å whereas the closest contact made by Cl(3) with the hydrogens on the alpha carbons of the butyl group is 3.13 Å (Fig. 3).

The redox chemistry of $[Re_2Cl_8]^{2-}$ has been investigated by Cotton and Pedersen [13]. A quasi-reversible reduction at $E_{1/2} = -0.84$ V in competition with the decomposition of $[Re_2Cl_8]^{3-}$ was observed. The reduction potentials of **2b** and $[Re_2Cl_6(PPh_2Bu^n)_2]$ (**3b**) were measured in dichloromethane solution. The $E_{1/2}$ values measured were -0.34 (±0.02) and -0.37 (±0.02) V respectively. The cyclic voltammogram for **2b** is shown in Fig. 5 and this is clearly an almost reversible process. The electron configuration of both **2b** and **3b** is $(\sigma)^2(\pi)^4(\delta)^2(\delta^*)^0$ and one electron reduction should give the configuration $(\sigma)^2(\pi)^4(\delta)^2(\delta^*)^1$. The δ–δ^* transition can be observed close to 700 nm. The substitution of phosphine for chloride leads to a shift to lower energy for this transition along the series $[Re_2Cl_8]^{2-}$, **2b**, **3b** of 685, 712, 722 nm.

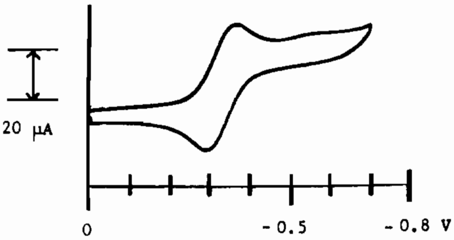

Fig. 5. Cyclic voltammogram for $[AsPh_4][Re_2Cl_7PPh_2{}^nBu]$.

The introduction of the first phosphine in **2b** produces a much greater effect, 27 nm, than does the second in **3b**, 10 nm. This effect is probably due to competition between Re–P backbonding and the Re–Re δ bond for d_{xy} electron density and provides some explanation for the similar and much less negative reduction potentials of **2b** and **3b**.

The kinetic study of the replacement by phosphines of two chlorines in $[Re_2Cl_8]^{2-}$ (**1**) showed that the reactions were reversible and that the mechanism was associative. The rate constants are in the order $k_2 \gg k_1$ and $k_{-2} \ggg k_{-1}$. There is clear evidence of a *trans* effect which could be operating across the M–M bond [1].

$$\underset{\mathbf{1}}{[Re_2Cl_8]^{2-}} \underset{\substack{-L\quad +Cl\\ k_{-1}}}{\overset{\substack{k_1\\ +L\quad -Cl}}{\rightleftharpoons}} \underset{\mathbf{2}}{[Re_2Cl_7L]^-} \underset{\substack{-L\quad +Cl\\ k_{-2}}}{\overset{\substack{k_2\\ +L\quad -Cl}}{\rightleftharpoons}} \underset{\mathbf{3}}{[Re_2Cl_6L_2]}$$

a, $L = PBu^n{}_3$
b, $L = PPh_2Bu^n$

The structure of **2b** was examined to try to further elucidate the importance of ground state factors in the reaction mechanism. There is clearly a *trans* influence by the phosphine ligand on the *trans* Re(2)–Cl(6) bond of 0.039(3) Å. A similar but smaller *trans* influence arises in $Re_2Cl_6(PMePh_2)_2$ with the Re–Cl (*trans* to P) lengthened by about 0.02 Å [14]. The four chlorines attached to Re(1) show no consistent variation in their Re–Cl bond lengths. However Cl(4) which is *cis* to P on Re(2) exhibits the largest Re–Re–Cl angle of 112°. Thus on the basis of this structure the chlorines in **2b** most likely to be replaced are Cl(4) and Cl(6). To give the known *trans* geometry for **3b** initial substitution of Cl(4) giving *cis* **3b** would require rotation about the M–M bond to the *trans* isomer while replacement of Cl(6) would require a flip of the Re_2 unit within the ligand cube followed by rotation to the *trans* form. The latter would be an example of the internal flip mechanism proposed by Cotton *et al.* for the transformation of $Mo_2Cl_4(P\text{-}P)_2$ from the α to the β form [15, 16].

These results can be compared with those of the recently reported phosphine bridged systems, $[Bu^n_4N]_2[(Re_2Cl_7)_2(\mu$-(L-L)] where L-L was $Ph_2PC\equiv CPPh_2$ and *trans*-$Ph_2PCH{=}CHPPh_2$ [17]. These complexes are almost totally insoluble and were difficult to characterize. Their reduction potentials however are close to those reported here for **2b**. Insoluble complexes which were difficult to characterize have also been observed for other chelating phosphines [2].

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