A Kinetic Study of the Transmission of Ligand Effects Across the Quadruple Bond in $[Re_2Cl_8]^{2-}$

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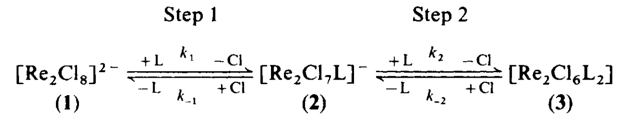
The kinetics of the stepwise replacement of two chlorides by tertiary phosphines and arsines (L) in $[Re_2Cl_8]^{2-}$ to yield $[Re_2Cl_6L_2]$ has been measured in dichloromethane solution. Only one associative reaction step is observed. Isolation of the intermediate $[Re_2Cl_7L]^-$ complexes allows direct measurement of a second reaction step. The kinetics of the reverse reactions has also been measured and two associative reaction steps are observed. Large ligand-labilising effects are transmitted across the quadruple bond when chloride is substituted by tertiary phosphines and arsines.

Despite considerable interest in the synthesis and structure of metal–metal quadruply bonded systems there are a small number of reports of kinetic studies of their simple ligand-substitution reactions.[1–5] There has been only one previous report of an attempt to study the kinetics of octahalogenodirhenate substitution reactions.[1] That attempt was made using hydroxylic solvents in which, in the absence of large chloride-ion concentrations, $[Re_2Cl_8]^{2-}$ is unstable.[1] However, solutions of $[Re_2Cl_8]^{2-}$ in dichloromethane are stable for extended periods and replacement of chloride by phosphine ligands can be more conveniently studied in this medium.

Results

Reaction of $[Re_2Cl_8]^{2-}$ *with Phosphines and Arsines.*—Tri-n-butylphosphine reacts in dichloromethane solution under pseudo-first-order conditions (phosphine in excess) with $[Re_2Cl_8]^{2-}$ (**1**) to give the disubstituted complex $[Re_2Cl_6(PBu^n{}_3)_2]$ (**3a**), Scheme. The reaction was followed by monitoring an absorption at 400 nm which went from zero to finite as the concentration of (**3a**) increased. During the course of the reaction the peak assigned to the δ–δ* transition at 685 nm is replaced by a peak at 720 nm with good isosbestic behaviour, Figure 1. The reaction follows a second-order rate law and a plot of $k_{obs.}$ *vs.* phosphine concentration gives a good straight line with zero intercept. Observed rate constants are given in Table 1 and second-order rate constants in Table 6. These results are typical of a single step associative process and the quadruple bond is clearly retained. Di-n-butylphenylphosphine reacts with complex (**1**) in a similar manner to to give $[Re_2Cl_6(PBu^n{}_2Ph)_2]$ (**3b**).



$$\underset{(1)}{[Re_2Cl_8]^{2-}} \underset{-L\;\; k_{-1}\;\; +Cl}{\overset{+L\;\; k_1\;\; -Cl}{\rightleftharpoons}} \underset{(2)}{[Re_2Cl_7L]^-} \underset{-L\;\; k_{-2}\;\; +Cl}{\overset{+L\;\; k_2\;\; -Cl}{\rightleftharpoons}} \underset{(3)}{[Re_2Cl_6L_2]}$$

Scheme. L = $PBu^n{}_3$ (**a**), $PBu^n{}_2Ph$ (**b**), PBu^nPh_2 (**c**), PEt_2Ph (**d**), $AsEt_2Ph$ (**e**), $AsBu_3$ (**f**), $AsBu_2Ph$ (**g**), and $AsBuPh_2$ (**h**)

n-Butyldiphenylphosphine reacts with complex (**1**) in dichloromethane solution. In this case the δ–δ* transition expected for $[Re_2Cl_6(PBu^nPh_2)_2]$ (**3c**) at 720 nm is not observed, the final $\lambda_{max.}$ being located at 710 nm. Since the red shift is associated with the replacement of chloride by phosphine, it is reasonable that this reaction involves replacement of only one chloride ligand to yield $[Re_2Cl_7(PBu^nPh_2)]^-$ (**2c**). There is also a large absorption change from zero to a finite value at 400 nm, which is ideal for monitoring the reaction. The kinetics of this reaction was measured in dichloromethane solution with the ligand, PBu^nPh_2, in excess. The reaction follows a second-order rate law. Attempts to drive the reaction to give a disubstituted product led only to decomposition and concomitant loss of good isosbestic behaviour.

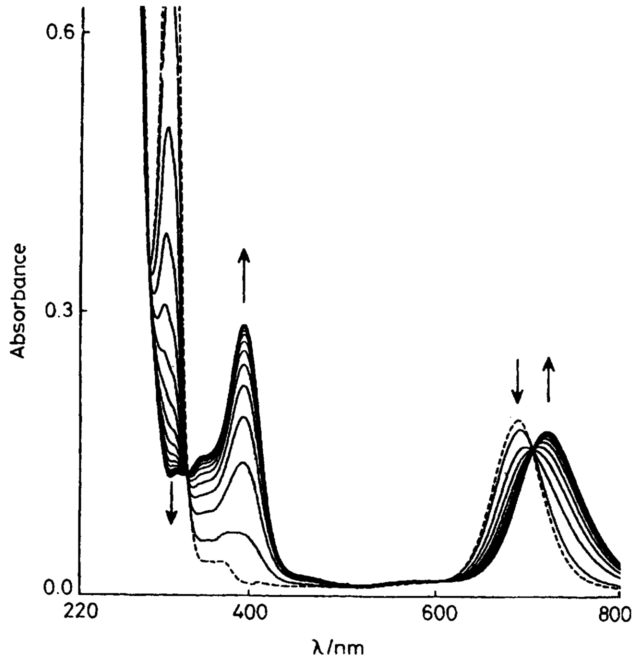


Figure 1. U.v.-visible spectra for the reaction of complex (**1**) with $PBu^n{}_3$ in CH_2Cl_2: - - - -, $[Re_2Cl_8]^{2-}$; ——, $[Re_2Cl_6(PBu^n{}_3)_2]$. Equal time intervals between the solid-line spectra

Diethylphenylarsine reacts with complex (**1**) in a similar manner to PBu^nPh_2 to give $[Re_2Cl_6(AsEt_2Ph)_2]$ (**2e**). The moderate intensity change at 660 nm was used to monitor the reaction.

Triphenylphosphine does not react with complex (**1**) in dichloromethane solution. On the other hand, reaction of (**1**) with an excess of diethylphenylphosphine or tri-n-butylarsine led only to loss of the δ–δ* absorbance at 685 nm. Similar decomposition with loss of the quadruple bond is also observed in the presence of large excesses of the ligands (**a**) to (**e**).

Reaction of $[Re_2Cl_6L_2]$ *with Halide.*—When NBu_4Cl is treated with $[Re_2Cl_6L_2]$ typically two distinct reaction steps

Table 1. Observed rate constants for the reaction of complex (**1**) with L (k_1, Scheme) at 25 °C in CH_2Cl_2 and monitored at 400 nm, except where indicated otherwise

L	$10^2[L]$/mol dm^{-3}	$10^2k_{obs.}$/s^{-1}
$PBu^n{}_3$[a]	0.5	0.314
	1.5	1.01
	2.0	1.34
	2.5	1.69
	3.0	1.97
	$10^3[L]$/mol dm^{-3}	$10^3k_{obs.}$/s^{-1}
$PBu^n{}_2Ph$[b]	3.5	0.471
	5.25	0.693
	7.00	0.952
	8.75	1.168
	12.25	1.634
	$10^3[L]$/mol dm^{-3}	$10^4k_{obs.}$/s^{-1}
PBu^nPh_2[b]	3.51	0.90
	4.21	1.11
	5.61	1.40
	6.31	1.69
	7.01	1.82
	$10^2[L]$/mol dm^{-3}	$10^4k_{obs.}$/s^{-1}
$AsEt_2Ph$[a,c]	2.81	2.15
	4.21	2.68
	5.61	3.38
	7.02	3.93
	8.42	4.58
	9.82	5.70

L = $PBu^n{}_2Ph$, in CCl_4, [complex] = 5×10^{-4} mol dm^{-3}

Temperature/°C	$10^2[L]$/mol dm^{-3}	$10^4k_{obs.}$/s^{-1}
25.2	1.93	0.82
	2.89	1.26
	3.85	1.73
	4.82	2.15
	5.78	2.56
34.8	1.54	1.05
	2.31	1.61
	2.89	1.95
	3.47	2.37
	3.85	2.61
40.0	1.54	1.33
	2.31	2.33
	3.08	2.69
	3.85	3.40
	4.63	4.00
45.4	1.54	1.75
	2.31	2.46
	3.08	3.33
	3.85	4.24
	4.63	5.16
	5.39	5.86

[a] [Complex] = 5×10^{-4} mol dm^{-3}. [b] [Complex] = 4×10^{-4} mol dm^{-3}. [c] Monitored at 660 nm.

are observed. A relatively rapid formation of the intermediate complex $[Re_2Cl_7L]^-$ (**2**) is followed by a slow regeneration of $[Re_2Cl_8]^{2-}$, Figure 2. The rates of these two reactions for complexes (**3b**)—(**3h**) inclusive were measured under pseudo-first-order conditions with NBu_4Cl in excess. The rapid first step was measured by stopped-flow techniques and the second step by conventional u.v.–visible spectrophotometry. In all cases overall second-order rate laws, first order in both metal and chloride concentrations, were followed and the results are given in Tables 2, 3, and 6. The only exception is $[Re_2Cl_6(PBu^n{}_3)_3]$. In this case only one phosphine ligand is replaced to give (**2a**) as the final product.

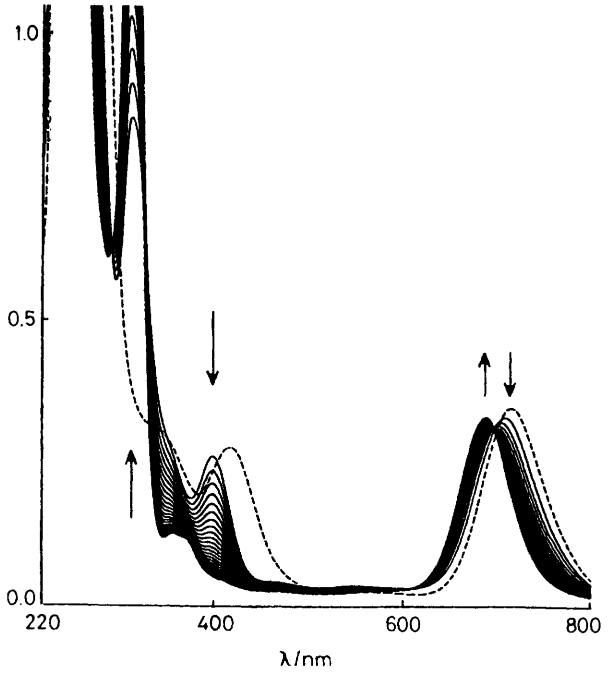


Figure 2. U.v.-visible spectra for the reaction of complex (**3g**) with Cl^- in CH_2Cl_2: – – – –, $[Re_2Cl_6(AsBu_2Ph)_2]$; ——, $[Re_2Cl_8]^{2-}$. The first solid-line spectrum, that closest to the dashed line, is of $[Re_2Cl_7(AsBu_2Ph)]^-$. Subsequent spectra were taken at equal time intervals

Tetra-n-butylammonium bromide reacts with complex (**3c**) in a similar manner to NBu_4Cl above and the results are given in Tables 4 and 6.

Reaction of $[Re_2Cl_7L]^-$ *with Phosphines*.—The availability of the $[AsPh_4][Re_2Cl_7L]$ complexes enabled direct measurement of the rate of the second reaction step, k_2, in the Scheme. The reactions of complexes (**2b**), (**2c**), and (**2d**) with excesses of phosphines (**b**), (**c**), and (**d**) respectively were studied in CH_2Cl_2 solution. The rates for (**2b**) and (**2c**) were measured by the stopped-flow technique and that of (**2d**) by u.v.–visible spectroscopy. The observed rate constants are given in Table 5 and the second-order rate constants in Table 6.

The reactions of complexes (**2a**)—(**2c**) with some phosphines which could give mixed complexes were examined spectroscopically. No attempts were made to isolate the products of these reactions. However, the spectra clearly identified the products formed in solution. Complex (**2a**) reacts with ligands (**b**) and (**c**) to give the mixed $[Re_2Cl_6L(L')]$ complexes. Complex (**2b**) reacts with (**c**) to give the mixed complex but with (**a**) to give only (**3a**); (**2c**) reacts with (**a**) and (**b**) to give only (**3a**) and (**3b**). Thus the most basic phosphine, (**a**), can displace both (**b**) and (**c**) from (**2b**) and (**2c**) to give (**3a**), but (**b**) can displace only (**c**) from (**2c**) to give (**3b**). The rate of the reaction of ligand (**b**) with complex (**2a**) was measured under pseudo-first-order conditions with (**b**) in excess. The observed rate constants are given in Table 5 and the second-order rate constants in Table 6.

Discussion

The observation of but a single step in the reactions of ligands (**a**) and (**b**) with complex (**1**), to yield (**3a**) and (**3b**), clearly implies that step 2 is faster than step 1, *i.e.* that $k_2 > k_1$. In this

Table 2. Observed rate constants for the reaction of complex (**3**) with Cl^- (step 1, k_{-2} Scheme) at 25 °C in CH_2Cl_2. [Complex] = 5×10^{-4} mol dm^{-3} except where indicated otherwise

Complex (λ/nm)	$10^2[Cl^-]$/mol dm^{-3}	$10k_{obs.}$/s^{-1}
(**3b**)	2.00	1.70
(430)	4.00	3.21
	5.00	4.16
	6.25	5.24
	7.50	6.30
(**3c**)	1.96	8.76
(740)	2.24	9.77
	5.50	19.41
	8.25	26.47
	11.00	36.61
	$10^2[Cl^-]$/mol dm^{-3}	$k_{obs.}$/s^{-1}
(**3e**)	0.56	5.26
(440)	0.70	7.07
	0.84	8.60
	1.12	11.95
	2.10	22.14
	3.50	35.66
	$10^2[Cl^-]$/mol dm^{-3}	$10k_{obs.}$/s^{-1}
(**3d**)	1.00	1.55
(420)	2.00	3.07
	3.00	4.46
	3.75	5.25
	5.00	7.07
(**3f**)	1.00	1.44
(420)	2.00	2.62
	3.00	4.08
	4.00	5.75
	5.00	6.91
	8.00	11.37
	$10^2[Cl^-]$/mol dm^{-3}	$k_{obs.}$/s^{-1}
(**3g**)[a]	0.13	1.50
(430)	0.25	2.53
	0.40	3.81
	0.50	5.07
	0.75	7.53
	1.00	10.47
(**3h**)[b]	0.05	0.65
(430)	0.10	1.03
	0.20	1.80
	0.25	2.36
	0.35	3.02

[a] [Complex] = 2×10^{-4} mol dm^{-3}. [b] [Complex] = 1×10^{-4} mol dm^{-3}.

Table 3. Observed rate constants for the reaction of complex (**2**) with Cl^- [k_{-1}, Scheme, second step in the reaction of (**3**) with Cl^-] at 25 °C in CH_2Cl_2 and [complex] = 5×10^{-4} mol dm^{-3} except where stated otherwise

Complex (λ/nm)	$10^2[Cl^-]$/mol dm^{-3}	$10^3k_{obs.}$/s^{-1}
(**3e**)	2.24	1.50
(740)	3.36	2.57
	4.20	2.83
	5.60	3.86
	7.00	4.81
	8.40	5.78
	9.80	6.80

(**3e**), in CCl_4, 740 nm

Temperature/°C	$10^2[Cl^-]$/mol dm^{-3}	$10^4k_{obs.}$/s^{-1}
26.2	2.8	1.22
	4.2	1.71
	5.6	2.27
	7.0	2.75
	8.4	3.21
35.8	2.8	2.42
	4.2	3.80
	5.6	5.18
	7.0	6.17
	8.4	7.27
46.2	2.8	6.25
	4.2	8.39
	5.6	10.58
	7.0	13.33
	8.4	15.52

Complex (λ/nm)	$10^2[Cl^-]$/mol dm^{-3}	$10^3k_{obs.}$/s^{-1}
(**3f**)	3.0	0.057
(400)	4.0	0.075
	5.0	0.095
	6.0	0.118
	8.0	0.151
(**3g**)	0.38	0.296
(410)	1.0	0.895
	2.0	1.72
	4.0	3.53
	5.00	4.49
(**3h**)	0.5	0.46
(316)	1.0	0.86
	1.5	1.29
	2.0	1.72
	2.5	2.19

way only the k_1 value is obtained directly from the reaction. Reaction of (**1**) with the less basic phosphine (**c**) does not lead to the formation of a disubstituted product, only formation of (**2c**) is observed and a k_1 value obtained. Attempts to extend the range of ligands to amines and other phosphines and arsines met with little success. Only diethylphenylarsine, (**e**), gave good kinetic data. All of the tertiary Group 5 ligands (**a**)—(**h**) when used in large excess reduced Re^{III} and destroyed the quadruple bond. Reduction of Re^{III} in $[Re_2Cl_8]^{2-}$ by tertiary phosphines is well known and has been used to synthesise rhenium(II) complexes[6] and the loss of the quadruple bond has also been observed on reaction of $[Re_2Cl_8]^{2-}$ with thiourea and methyl isocyanide.[1,7] If the substitution reaction rate does not exceed the rate of reduction of Re^{III} by at least a factor of ten then clearly good kinetic data cannot be obtained. Reactions with amines gave only brown solutions which were not characterised.

Displacement of the phosphine ligands in complex (**3**) by chloride was also examined. It seemed reasonable that pseudo-first-order experimental conditions, the presence of an excess of halide, would stabilise the reaction products and lead to good kinetic data. This was indeed the case and good kinetic data were obtained for the two observed steps. These steps are clearly the stepwise replacement of the two phosphine ligands in (**3**).

In dichloromethane solution bromide is a weaker nucleophile than chloride and the rate of displacement of phosphine by bromide is lower than for chloride. For this reason it is also possible to isolate pure samples of the mixed halide anion $[Re_2Cl_6Br_2]^{2-}$.

The great difference in the rate measured for the reverse of step 2 and step 1, k_{-2} and k_{-1}, suggested that the intermediate complex (**2b**) could be isolated. This was achieved and using $[AsPh_4]Cl$ as the source of chloride, crystals of the tetraphenylarsonium salts of (**2a**)—(**2c**) were obtained. The availability of

Table 4. Observed rate constants for the reaction of complex (**3c**) (1×10^{-4} mol dm^{-3}) with Br^-, in CH_2Cl_2 solution, steps 1 and 2, at 25 °C

Step	$10^3[Br^-]$/mol dm^{-3}	$10^2k_{obs.}$/s^{-1}
1	0.97	0.33
	1.95	0.69
	2.44	0.88
	2.92	1.05
	3.41	1.26
	3.90	1.41
	$10^2[Br^-]$/mol dm^{-3}	$10^5k_{obs.}$/s^{-1}
2	1.25	1.41
	2.50	2.33
	5.00	4.24
	7.50	6.59
	8.75	7.84

Table 5. Observed rate constants for the reaction of complexes (**2**) with phosphines in CH_2Cl_2 solution, at 25 °C

Complex	$10^2[PBu^n_3]$/ mol dm^{-3}	$k_{obs.}$/s^{-1}
(**2a**)^a	0.25	0.81
	0.50	1.94
	1.00	3.70
	1.50	5.83
	2.50	9.68
	$10^2[PBu^n_2Ph]$/ mol dm^{-3}	$10k_{obs.}$/s^{-1}
	0.50	1.62
	1.00	2.92
	1.50	4.31
	2.00	5.66
	2.50	6.95
	$10^3[PBu^n_2Ph]$/ mol dm^{-3}	$10k_{obs.}$/s^{-1}
(**2b**)^b	0.80	0.45
	1.60	0.79
	2.40	1.36
	3.20	1.80
	4.00	2.32
	4.80	2.77
	6.40	3.75
	$10^2[PBu^nPh_2]$/ mol dm^{-3}	$10^3k_{obs.}$/s^{-1}
(**2c**)^c	0.50	2.55
	1.00	5.29
	1.50	7.50
	2.00	10.12
	2.50	12.54

^{a} [Complex] = 2×10^{-4} mol dm^{-3}. ^{b} [Complex] = 1×10^{-4} mol dm^{-3}. ^{c} [Complex] = 5×10^{-4} mol dm^{-3}.

these compounds provided a method for measuring the rate of step 2 directly. Thus reaction of (**2a**) with an excess of PBu^n_3 followed a second-order rate law and the measured k_2 value is clearly larger than k_1 as predicted above.

Table 6. Second-order rate constants (dm^3 mol^{-1} s^{-1}) in CH_2Cl_2, products as in the Scheme except where indicated

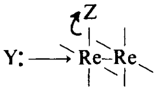
Rate constant		Nucleophile	Complex	Temp./°C
k_1	0.67 ± 0.01	PBu^n_3	(**1**)	25
	0.133 ± 0.002	PBu^n_2Ph	(**1**)	25
	$2.63 \pm 0.15 \times 10^{-2}$	PBu^nPh_2	(**1**)	25
	$4.89 \pm 0.31 \times 10^{-3}$	$AsEt_2Ph$	(**1**)	25
	0.45 ± 0.01	PBu^n_2Ph	(**1**)	25.2^a
	0.67 ± 0.01	PBu^n_2Ph	(**1**)	34.8^a
	0.87 ± 0.02	PBu^n_2Ph	(**1**)	40.0^a
	1.10 ± 0.02	PBu^n_2Ph	(**1**)	45.4^a
k_2	$(3.93 \pm 0.05) \times 10^2$	PBu^n_3	(**2a**)	25
	$(2.68 \pm 0.18) \times 10$	PBu^n_2Ph	(**2a**)	25^b
	$(5.98 \pm 0.10) \times 10$	PBu^n_2Ph	(**2b**)	25
	$(4.96 \pm 0.08) \times 10^{-1}$	PBu^nPh_2	(**2c**)	25
k_{-1}	$(1.09 \pm 0.02) \times 10^{-3}$	Cl^-	(**2b**)	25
	$(3.60 \pm 0.14) \times 10^{-3}$	Cl^-	(**2c**)	25
	$(8.30 \pm 0.34) \times 10^{-4}$	Cl^-	(**2d**)	25
	$(6.84 \pm 0.17) \times 10^{-2}$	Cl^-	(**2e**)	25
	$(1.90 \pm 0.06) \times 10^{-3}$	Cl^-	(**2f**)	25
	$(9.00 \pm 0.09) \times 10^{-2}$	Cl^-	(**2g**)	25
	$(8.64 \pm 0.14) \times 10^{-2}$	Cl^-	(**2h**)	25
	$(3.59 \pm 0.07) \times 10^{-3}$	Cl^-	(**2e**)	26.2^a
	$(8.61 \pm 0.35) \times 10^{-3}$	Cl^-	(**2e**)	35.8^a
	$(1.68 \pm 0.04) \times 10^{-2}$	Cl^-	(**2e**)	46.2^a
k_{-2}	8.43 ± 0.19	Cl^-	(**3b**)	25
	$(3.00 \pm 0.10) \times 10$	Cl^-	(**3c**)	25
	$(1.36 \pm 0.04) \times 10$	Cl^-	(**3d**)	25
	$(1.03 \pm 0.02) \times 10^3$	Cl^-	(**3e**)	25
	$(1.43 \pm 0.25) \times 10$	Cl^-	(**3f**)	25
	$(1.02 \pm 0.03) \times 10^3$	Cl^-	(**3g**)	25
	$(8.04 \pm 0.24) \times 10^2$	Cl^-	(**3h**)	25
k_{-1}	$(8.56 \pm 0.28) \times 10^{-4}$	Br^-	(**2c**)	25^c
k_{-2}	3.75 ± 0.05	Br^-	(**3c**)	25^d

^{a} In tetrachloroethane. ^{b} Product is $[Re_2Cl_6(PBu^n_3)(PBu^n_2Ph)]$. ^{c} Product is $[Re_2Cl_6Br_2]^{2-}$. ^{d} Product is $[Re_2Cl_6Br(PBu^nPh_2)]^-$.

Table 7. Thermodynamic parameters (tetrachloroethane solution)

Reaction	(**1**) + PBu^n_2Ph	(**3d**) + Cl^- (step 2, k_{-1})
E/kJ mol^{-1}	35.27 ± 0.6	61.15 ± 2.81
$\Delta H^\ddagger$/kJ mol^{-1}	30.32 ± 0.6	56.19 ± 2.81
$\Delta S^\ddagger$/J K^{-1} mol^{-1}	-150.04 ± 2.0	-103.64 ± 9.45
$\Delta G^\ddagger$/kJ mol^{-1}	75.03 ± 0.05	87.08 ± 0.12
$k_{25\,C}$/dm^3 mol^{-1} s^{-1}	0.437	3.37×10^{-3}

All of the reactions in this study followed second-order kinetics (first order in the concentrations of both the metal complex and the incoming ligand). This is consistent with an associative mechanism. Further support for this is provided by the thermodynamic parameters measured for step 1 of the reaction of PBu^n_2Ph with complex (**1**) and for the reverse of step 1 in the reaction of (**3d**) with Cl^-, Table 7. In both cases the large negative $\Delta S^\ddagger$ values are indicative of a net increase in bonding in the transition state. The most reasonable position for attack



by an incoming ligand is along the Re–Re axial direction since this allows nucleophilic attack at the only available metal orbital.

The kinetic results may be summarised: $k_2 > k_1$ and $k_{-2} \gg k_{-1}$. It might seem reasonable that the large rate difference in the latter case is due to charge effects, with k_{-1} retarded by the repulsion experienced by the incoming chloride approaching $[Re_2Cl_7L]^-$. It has long been argued, however, that reactions which are largely associative in mechanism are not subject to significant charge effects.[8] Furthermore the reaction steps involving approach by the neutral phosphine ligands, k_1 and k_2, show considerable rate differences. The molar conductivity of $[NBu^n_4]_2[Re_2Cl_8]$ in CH_2Cl_2 and tetrachloroethane solution is also very low, 2.49×10^{-3} and 3.14×10^{-4} Ω^{-1} m^2 mol^{-1} respectively, suggesting tight ion-pair binding which alone would tend to reduce charge effects.

The most reasonable explanation for the rate differences is that phosphine labilises chloride more strongly than chloride labilises phosphine and that the effect is transmitted across the quadruple bond. This is similar to the well known *trans*-labilising effect in square-planar complexes. This transmission of strong electronic effects across the quadruple bond is reasonable since considerable competition for *d* orbitals on Re is expected as all such orbitals are used in bonding.[9] The relative labilising ability is also consistent with the relative positions of phosphines and chloride in the *trans*-effect series. This effect is also found when the rate of chloride displacement by PBu_2Ph from $[Re_2Cl_7(PBu_2Ph)]^-$ is compared with the lower rate of displacement from $[Re_2Cl_7(PBu_3)]^-$. The difference, a factor of two, can be due only to the labilising effect of the phosphine already present in the complex; PBu_2Ph is clearly a stronger π acceptor than PBu_3 and more effectively labilises chloride.

It is interesting to compare the present work with the results of related studies. Webb and Espenson[2] studied the substitution of axial X^- in $[Re_2(O_2CEt)_4X_2]$. This is not directly relevant, since all except the axial positions are inert in these complexes. The isoelectronic quadruply bonded molybdenum systems have been studied. Mureinik[3] has examined the displacement of chloride by acetic acid from $[Mo_2Cl_8]^{4-}$–HX mixtures and concluded that the reactions were dissociative. Andersen and co-workers[4] simplified the molybdenum system by alkyl and phosphine substitution and using n.m.r. spectroscopy were able to follow kinetically two steps of phosphine exchange in $[Mo_2Me_4(PEt_3)_4]$ with PMe_3 and PMe_2Ph. In both cases the reaction was dissociative and the driving force was relief of steric congestion.[4] Kinetic and structural *trans* effects have also been observed for quadruply bonded dimolybdenum(II) systems.[5] However, the present work provides the first evidence that ligand-labilising effects are transmitted across the quadruple bond. At present crystallographic work is in progress on samples of complexes (**2a**)—(**2c**) in an effort to find structural support for this effect.

Experimental

Ultraviolet–visible spectra were recorded either on a Cary 17 or a Shimadzu UV-260 spectrometer, n.m.r. spectra on a JEOL GX-270 spectrometer. Kinetic measurements were made either on these spectrometers or on an Applied Photophysics stopped-flow device. Stopped-flow kinetic data were initially recorded on a Datalab DL901 transient recorder and then downloaded to a BBC microcomputer for all computations. All reaction rates were measured under pseudo-first-order conditions. Reaction rates were checked for reproducibility and repeat runs with different solutions gave second-order rate constants within the experimental errors quoted. Rate constants were determined either from plots of $-\ln(A - A_\infty)$ against time or from Guggenheim plots. Pseudo-first-order rate data were tested by curve fitting to a single exponential. In all cases, good correlation (less than 2% standard deviation) was observed between experimental and theoretical results. Temperature control was ±0.1 °C. The errors quoted were calculated as described by Swinbourne.[10] Thermodynamic activation parameters were calculated using locally developed computer programs.

Tertiary phosphines and arsines were prepared by literature methods.[11] All phosphines and arsines were distilled prior to use and handled under nitrogen. It was especially important to check for the absence of water by i.r. spectroscopy. Dichloromethane was purified by repeated slow distillation, the final distillation under a nitrogen atmosphere being carried out immediately before use. 1,2-Dichloroethane was purified by distillation from P_2O_5 prior to use. All solutions were purged with nitrogen prior to use. The salt $[NBu^n_4]_2[Re_2Cl_8]$ was prepared as described in the literature.[12] The complexes $[Re_2Cl_6L_2]$ (**3**) were prepared by the method of San Filippo.[13] Yields were in the range 80—90%. Elemental analyses of the new complexes are given in Table 8 and u.v.–visible spectra in Table 9.

Table 8. Elemental analysis/% with required values in parentheses

	Found (Required)	
Complex	C	H
(**3b**)	32.80	4.50
	(32.65)	(4.50)
(**3c**)	35.80	3.55
	(35.95)	(3.55)
(**3d**)	26.60	3.75
	(26.15)	(3.30)
(**3e**)	23.40	2.60
	(23.85)	(3.00)
(**3f**)	26.55	4.95
	(26.75)	(5.05)
(**3g**)	30.30	4.20
	(30.10)	(4.15)
(**3h**)	33.55	3.50
	(33.20)	(3.30)
(**2a**)	35.60	3.80
	(35.80)	(3.90)
(**2b**)	36.80	3.50
	(37.20)	(3.55)
(**2c**)	38.20	3.05
	(38.55)	(3.15)

Table 9. U.v.–visible spectra in CH_2Cl_2 solution

Complex	Electronic absorption maxima (nm)
(**2a**)	709s, 390m, 317s, 280 (sh)
(**2b**)	710s, 392m, 320s, 290 (sh)
(**2c**)	712s, 396m, 320s, 290 (sh)
(**2d**)	710s, 390m, 317s, 290 (sh)
(**2e**)	705s, 398m, 316s, 280 (sh)
(**2f**)	702s, 400m, 312s, 290 (sh)
(**2g**)	706s, 400m, 315s, 280 (sh)
(**2h**)	702s, 400m, 315s, 270 (sh)
(**3a**)	720s, 395s, 290 (sh)
(**3b**)	720s, 410m, 338m, 300 (sh)
(**3c**)	722s, 410m, 348m, 300 (sh)
(**3d**)	720s, 405m, 332m, 300 (sh)
(**3e**)	712s, 409m, 350m, 290 (sh)
(**3f**)	712s, 410m, 350m, 300 (sh)
(**3g**)	713s, 419m, 350m, 300 (sh)
(**3h**)	712s, 420m, 360m, 310 (sh)
$[Bu^n_4]^+{}_2$-$[Re_2Cl_6Br_2]^{2-}$	715s, 390m, 320s, 260 (sh)

s = Strong, m = moderate, and (sh) = shoulder. First band is assigned to the δ–δ* transition.

Preparation of $[Re_2Cl_7L]^-$.—Complex (**3a**) (40 mg) was stirred with $[AsPh_4]Cl$ (20 mg) in CH_2Cl_2 (5 cm^3). The dark green solution was placed in a narrow tube and carefully covered with a layer of n-heptane. After 3 d, dark green crystals formed at the interface. They were isolated and characterised by u.v.–visible spectroscopy and elemental analysis as complex (**2a**). Complexes (**2b**) and (**2c**) were prepared similarly.

Preparation of $[NBu^n_4][Re_2Cl_6Br_2]$.—Complex (**3g**) (40 mg) was stirred with $[NBu^n_4]Br$ (0.2 g) in CH_2Cl_2 (6 cm^3) for 10 min. This solution was placed in a narrow glass tube and covered with n-heptane. Overnight, crystals formed at the interface. They were isolated and characterised by elemental analysis and u.v.–visible spectroscopy (Found: C, 31.70; H, 5.80; N, 2.55. $C_{32}H_{72}Br_2Cl_6N_2Re_2$ requires C, 31.25; H, 5.85; N, 2.30%).

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