ELSEVIER

Inorganica Chimica Acta 229 (1995) 95–100

Inorganica Chimica Acta

Synthesis and crystal structure of the unique chiral anion $[Re_2Cl_7PBzMePh]^-$ and the direct determination of its δ-bond energy by molecular modelling ☆

Patrick McArdle, Mary Rabbitte, Desmond Cunningham

Chemistry Department, University College, Galway, Ireland

Received 22 March 1994; revised 30 May 1994

Abstract

The quadruply bonded chiral anion $[Re_2Cl_7PBzMePh]^-$ (Bz = CH_2Ph) was synthesized and its crystal structure was determined. It crystallized in space group $P\bar{1}$ with unit cell dimensions $a = 10.677(2)$, $b = 12.220(2)$, $c = 18.220(4)$ Å, $\alpha = 85.66(2)$, $\beta = 75.98(2)$ and $\gamma = 80.07(2)°$. The Re–Re distance was 2.2196(8) Å. The average twist angle χ was 11.6°. The δ-bond energy was determined by molecular modelling to be 9 kcal mol^{-1} and 5% greater than the energy required to eclipse $[Re_2Cl_8]^{2-}$.

Keywords: Crystal structures; Rhenium complexes; Chloride complexes; Chiral complexes; Dinuclear complexes

---

1. Introduction

Despite its widespread use in organic chemistry molecular modelling of inorganic and organometallic systems is still far from a routine procedure. This is undoubtedly due both to the difficulty of obtaining suitable parameters and the inability of most of the common modelling packages to handle the unusual geometries encountered. There has been only one report describing the application of molecular modelling to quadruply bonded systems. Boeyens has used molecular mechanics to measure the equilibrium strain values of eclipsed quadruply bonded complexes [1]. Plots of these strain values versus the twist angle (χ), Fig. 1, gave potential energy curves, and at $\chi = 45°$ a potential energy minimum was observed for $[M_2X_8]^{n-}$ complexes. The difference in potential energy was used to estimate a minimum value for the δ-bond contribution. This method did not provide an upper limit for the δ-bond energy. However, Boeyens has crudely estimated the upper limit, based on the non-existence of $[Cr_2Br_8]^{4-}$ (assumed non-existent due to excessive strain energy), to be 11 kcal mol^{-1}.

Compounds containing M–M quadruple bonds have a preference for eclipsed conformations because of the nature of the angular dependence of the δ bond. The δ bond, being due to d_{xy}–d_{xy} overlap, has a $\cos(2\chi)$ dependence. In species such as $[M_2X_8]^{n-}$ this tendency is dominant over repulsive forces and fully eclipsed structures are observed. Experimental support for this δ-bond model has come from the demonstrated linear relationship between M–M bond strength (as measured by M–M bond length) and $\cos(2\chi)$ for the series $M_2X_4(L\text{-}L)_2$, which have χ values in the range 0–40° [2].

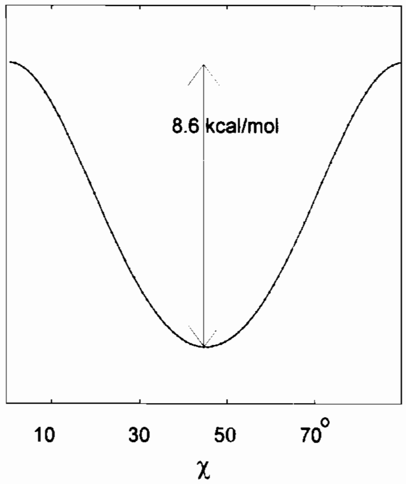

Fig. 1. Strain energy for $[Re_2Cl_8]^{2-}$.

It was the aim of this work to try to obtain the energy of the δ bond directly by modelling suitable

---

☆ This paper is dedicated to Professor F.A. Cotton on the occasion of his 65th birthday.

SSDI 0020-1693(94)04232-K

non-eclipsed complexes using a torsional M–M force constant based on cos(2χ). The systems examined were the known $Mo_2X_4(L\text{-}L)_2$ complexes and the more recently reported unsymmetrical rhenium anions $[Re_2Cl_7L]^-$ [3].

2. Discussion

2.1. $Mo_2X_4(L\text{-}L)_2$ complexes

The neutral complexes $Mo_2X_4(L\text{-}L)_2$ where L-L is a bridging bidentate phosphine ligand exhibit a wide range of twist angles around the Mo–Mo bond due to the conformational preference and specific bite size of the L-L ligand. Attempts were made to model these non-eclipsed complexes in an effort to obtain a direct measure of the δ-bond energy.

The torsional twist, χ, varies from $\chi = 0°$ for eclipsed $Mo_2Cl_4(dppm)_2$ to $\chi = 40°$ for $Mo_2Cl_4(dmpe)_2$ [4,5]. While the fully eclipsed complex $Mo_2Cl_4(dppm)_2$ ($\chi = 0°$) was modelled successfully no δ-bond energy could be extracted as the torsional force constant k_{tor} is zero at $\chi = 0$.

All attempts to model the non-eclipsed $Mo_2X_4(L\text{-}L)_2$ complexes were unsuccessful for the following reasons. First, in the non-eclipsed complexes the bridging ligand, which is of the general type $R_2P(CH_2)_nPR_2$ ($n >/= 2$), forms a ring containing the Mo–Mo unit and interconversion between boat and chair type conformations can take place. An example of this can be seen in the crystal structure of $Mo_2Cl_4(dmpe)_2$ which has two conformations with different values of χ, 33.8 and 40°, for boat and chair forms. Here the chair conformation is only slightly more favoured than the boat conformation. From a modelling point of view chair, boat and any twist boat conformations need to be modelled separately. Secondly, the observed twist angles depend to a considerable extent upon crystal packing forces and this could not be included in the model. The space filling shape of these complexes is particularly prone to this problem as the phenyl rings (of which there are eight) reach far into the lattice and can act as 'levers' on the M–M bond thereby producing a packing force dependant twist.

2.2. $[Re_2Cl_7L]^-$ complexes

Due to the failure of $Mo_2X_4(L\text{-}L)_2$ complexes to provide suitable systems for modelling the space filling properties, the $[Re_2Cl_7L]^-$ systems were examined. In these complexes the M-M unit is not involved in a ring system and the $ReCl_4$ unit while essentially square in shape is clearly going to suffer far less from crystal packing forces than the Mo_2 system and therefore twist angles should depend largely on asymmetry at P.

$[Re_2Cl_8]^{2-}$ was first modelled for comparison with the work of Boeyens and force field parameters were adjusted until deviations in bond distances, bond angles and bond torsions were 0.1 Å, 1° and 1°, respectively. The strain energy of the staggered conformation of $[Re_2Cl_8]^{2-}$ was obtained by setting $k_{tor} = 0$ and optimizing the geometry, while the strain energy of the eclipsed conformation was obtained by setting k_{tor} to a large value and then optimizing the geometry. An identical eclipsed strain energy can also be obtained by setting the k_{tor} parameter to zero and then optimizing the eclipsed geometry (starting from eclipsed geometry). This was done to ensure that the k_{tor} value did not in fact contribute to the energy at $\chi = 0°$. This latter procedure is possible because the molecular modelling optimization procedure looks at very small atom movements and the system does not always 'fall off' the exact top of the curve. The difference in potential energy between the staggered and eclipsed conformations estimated in this way was 8.6 kcal mol^{-1} for $[Re_2Cl_8]^{2-}$. This is close to that of 7.5 kcal mol^{-1} for $[Re_2Me_8]^{2-}$ reported by Boeyens. The minimum torsional parameter necessary to render a stable eclipsed conformation was $k_{tor} = 4.75$.

The known quadruply bonded complexes $[Re_2Cl_7L]^-$, where L is PBu_2Ph, $PBuPh_2$ and $PMePh_2$, all have non-zero χ values and show no disorder of the M–M unit [3a,b,c]. For example $[Re_2Cl_7PBu_2P]^-$ has two formula units per asymmetric unit with average torsional twists away from an eclipsed geometry of 8.68 and 1.72°, and $[Re_2Cl_7PBuPh_2]^-$ and $[Re_2Cl_7PMePh_2]^-$ have average χ values of 4.7 and 4.9°. In each of these cases it is possible to associate the observed twist with intramolecular contacts involving asymmetrically folded phosphine substituents. Attempts to model the observed twists in these complexes were also unsuccessful due to the small value of χ. An examination of the curve of χ versus torsional energy, k_{tor}, Fig. 2 clearly shows that χ values of less than 10° have only a very small effect on torsional energy. For successful modelling a complex with $\chi > 10°$ is required, that is a complex with greater (built in) asymmetry at phosphorus.

Attempts were made to synthesize complexes containing the ligands $PPhBzPr^i$ and PBzMePh. Only in the latter case was it possible to obtain crystals of $[AsPh_4]^+[Re_2Cl_7(PBzMePh)]^-$ (**1**) suitable for crystallography. The crystal structure of the anion in **1** is shown in Fig. 3 and crystal data, fractional atomic coordinates and selected bond lengths and angles are given in Tables 1, 2 and 3. The structure in Fig. 3 has the following features in common with the other known disorder free structure of the $[Re_2Cl_7L]^-$ type and $Re_2Cl_6(PMePh_2)_2$ [6]. There is a lengthening of the Re(1)–Cl(2) bond *trans* to P. The Re(1)–Re(2)–Cl(4) angle is greater than all other Re–Re–Cl angles and about 8° larger than Re(2)–Re(1)–P. This latter angle

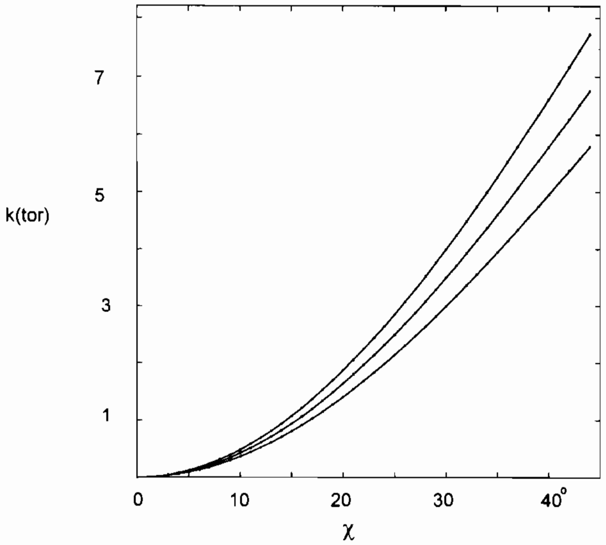

Fig. 2. k_{tor} vs. χ.

at 101° is virtually constant in all the complexes in this group and clearly indicates a strong steric interaction between the phosphine and Cl(4). This in turn clearly implies a larger force constant for P–Re–Re than Cl–Re–Re. The M–M distance, 2.2196(8), is close to that of other $[Re_2Cl_7L]^-$ systems, and is shorter than that of $Re_2Cl_6(PMePh_2)_2$, 2.227(1); this is probably due to higher steric pressure in the latter. The twist angle in **1** was 12° and the structure was suitable for modelling. The observed structure was modelled, using different values of k_{tor}, by twisting the $ReCl_4$ unit to $\chi = 45°$ and allowing geometry optimization until convergence. The results are given in Table 4. The average of the observed torsional angles in the crystal structure is $\chi = 11.6°$ and in the best modelled structure, $k_{tor} = 5.0$, the average torsional angle is also $\chi = 11.6°$, with no single torsional angle out by more than 5°. The largest deviations are due to differences between the acute angles subtended at Re(1) by its ligands. This is in contrast to the Cl–Re(2)–Cl angles which are all within 1° of each other. The Re(1) angles which involve P are more than 4° smaller than those which do not. This effect is also observed in other $[Re_2Cl_7L]^-$ anions and it could be due to the *trans* influence of the phosphine. No allowance was made for phosphine *trans* influence in the model.

Since $k_{tor} = 4.75$ was required to eclipse $[Re_2Cl_8]^{2-}$ giving a minimum δ-bond contribution of 8.6 kcal mol^{-1}, we can estimate the upper limit of the δ-bond contribution in this case to be about 9 kcal mol^{-1} or 5% greater than the energy required to eclipse $[Re_2Cl_8]^{2-}$. It is interesting to compare this result with δ-bond energies obtained by theoretical methods. The modified generalized valence bond method (specially adapted for M–M multiple bonds) gives an intrinsic δ-bond strength of 6±3 kcal mol^{-1} for $[Re_2Cl_8]^{2-}$ [7], while a recent ab initio CASSCF study of $Mo_2Cl_4(PH_3)_4$ concluded that the δ-bond energy in that case was 16.8 kcal mol^{-1} [8]. The present work gives a value intermediate between these two results but closer to the result of the valence bond calculation on $[Re_2Cl_8]^{2-}$.

3. Experimental

3.1. Molecular modelling parameters

Suitable values for some of the stretching force constants were obtained from the literature [9]. It has been shown for square planar platinum systems that

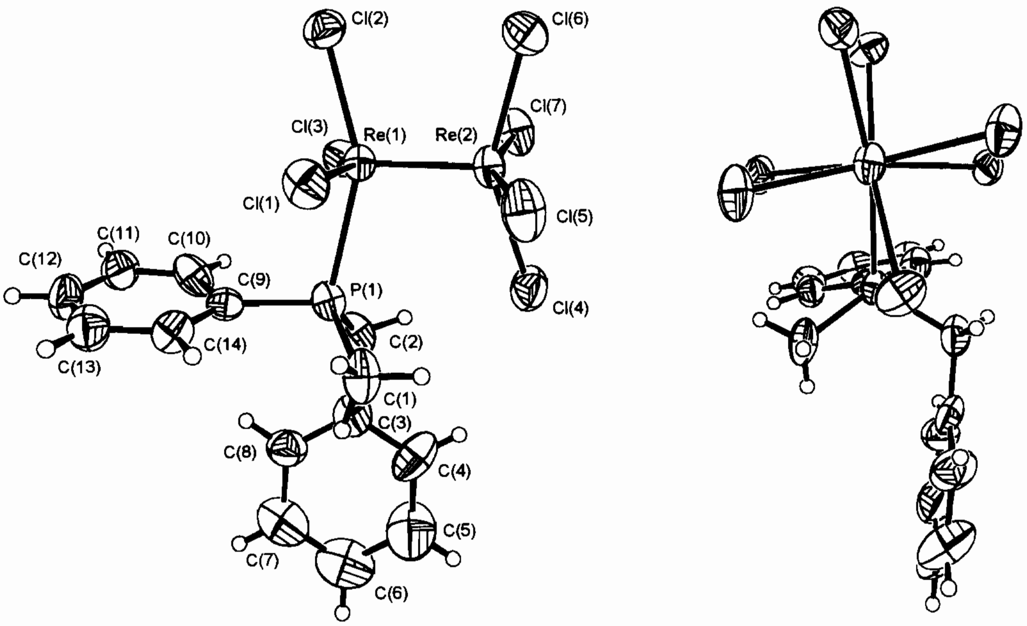

Fig. 3. ORTEP drawing of the anion in 1.

Table 1
Crystal data and structure refinement for **1**

Empirical formula	$C_{39}H_{37}AsCl_9PRe_2$
Formula weight	1303.03
Temperature (K)	293(2)
Wavelength (Å)	0.71069
Crystal system	triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a (Å)	10.677(2)
b (Å)	12.220(2)
c (Å)	18.220(4)
α (°)	85.66(2)
β (°)	75.98(2)
γ (°)	80.07(2)
Volume (Å^3)	2270.4(8)
Z	2
Density (calc.) (Mg m^{-3})	1.906
Absorption coefficient (mm^{-1})	6.642
F(000)	1244
Crystal size (mm)	0.22×0.20×0.11
θ Range for data collection (°)	2.01–24.91
Index ranges	$0< =h< =11$ $-12< =k< =12$ $-18< =l< =18$
Reflections collected	7920
Independent reflections	7405 (R(int) = 0.0226)
Refinement method	full-matrix least-squares on F^2
Data/restraints/parameters	7405/0/314
Goodness-of-fit on F^2 [a]	1.000
Final R indices ($I>2\sigma(I)$)	
R_1 [b]	0.0616
wR_2 [c]	0.1558
R indices (all data)	
R_1 [b]	0.1003
wR_2 [c]	0.1718
Largest difference peak and hole (e Å^{-3})	0.531 and −0.360

[a] Goodness-of-fit $= [\Sigma w(|F_o^2| - |F_c^2|)^2/(N_{obs} - N_{param})]^{1/2}$.
[b] $R_1 = [\Sigma||F_o| - |F_c||]/\Sigma|F_o|$ (based on F).
[c] $wR_2 = [[\Sigma w(|F_o - F_c|)^2]/[\Sigma w(|F_o|)^2]]^{1/2}$ (based on F^2); $w = q/[(\sigma F_o)^2 + (a^*P)^2 + b^*P + d + e^* \sin(\theta)]$.

bending force constants for X–M–X bond angles (where X = Cl or P) are usually about 40% of the corresponding M–X stretching value [10]. This general rule was applied and a set of values for X–M–X bending force constants was assumed. However, the X–M–M bending force constants proved more difficult to calculate, as no clear literature values were available for X–M–M bending frequencies. Their values were obtained by a process of trial and error, that is an ideal value for the angle θ_0, was assumed (90°) and k_{bend} was adjusted until a suitable (k, θ_0) reproduced the observed structure after energy minimization. The P–M–M bending force constant was increased above the Cl–M–M value to reproduce the observed bond angles which are the result of the steric pressure discussed above. The Chem-X program was used for all molecular modelling calculations [11].

Table 2
Atomic coordinates (×10^4) and equivalent isotropic displacement parameters (Å^2×10^3)

	x	y	z	U_{eq} [a]
Re(1)	4758(1)	2471(1)	8373(1)	43(1)
Re(2)	4309(1)	1435(1)	7550(1)	47(1)
As(1)	8410(1)	3338(1)	4544(1)	46(1)
P(1)	2809(3)	2464(3)	9425(2)	46(1)
Cl(1)	5709(4)	1207(3)	9161(2)	64(1)
Cl(2)	6802(3)	2950(3)	7815(2)	67(1)
Cl(3)	3798(3)	4260(3)	8108(2)	57(1)
Cl(4)	2131(4)	1209(4)	7925(2)	73(1)
Cl(5)	4807(4)	−351(3)	8041(2)	73(1)
Cl(6)	6289(4)	1085(3)	6669(2)	65(1)
Cl(7)	3648(4)	2742(3)	6660(2)	67(1)
C(1)	2471(15)	1118(10)	9794(8)	61(4)
C(2)	1286(14)	3273(12)	9270(8)	62(4)
C(3)	47(8)	3048(9)	9866(5)	61(4)
C(4)	−796(11)	2415(10)	9689(6)	95(6)
C(5)	−1897(11)	2199(10)	10231(9)	114(8)
C(6)	−2154(9)	2616(12)	10951(8)	102(7)
C(7)	−1311(12)	3250(11)	11128(5)	95(6)
C(8)	−211(10)	3466(9)	10586(6)	73(4)
C(9)	3189(12)	3144(10)	10170(7)	46(3)
C(10)	3113(15)	4310(13)	10134(8)	67(4)
C(11)	3511(15)	4847(14)	10642(9)	70(4)
C(12)	3926(16)	4253(15)	11232(9)	72(5)
C(13)	4011(16)	3126(14)	11280(9)	72(4)
C(14)	3646(14)	2567(12)	10752(8)	58(4)
C(15)	7432(8)	2375(7)	4232(5)	53(3)
C(16)	7718(8)	2071(8)	3483(4)	60(4)
C(17)	6995(9)	1368(8)	3260(4)	64(4)
C(18)	5985(9)	969(8)	3787(5)	72(4)
C(19)	5699(9)	1272(9)	4537(5)	74(4)
C(20)	6422(9)	1975(8)	4759(4)	61(4)
C(21)	7310(12)	4480(10)	5166(7)	46(3)
C(22)	6511(15)	4220(13)	5828(8)	68(4)
C(23)	5766(15)	5078(12)	6288(8)	63(4)
C(24)	5824(15)	6132(13)	6061(9)	69(4)
C(25)	6628(15)	6377(14)	5403(9)	71(4)
C(26)	7408(14)	5573(11)	4948(8)	58(4)
C(27)	9380(13)	4051(11)	3676(7)	50(3)
C(28)	8668(14)	4660(11)	3176(7)	55(3)
C(29)	9346(17)	5201(15)	2577(10)	83(5)
C(30)	10667(17)	5195(14)	2430(10)	78(5)
C(31)	11327(17)	4591(14)	2938(9)	78(5)
C(32)	10677(14)	4047(12)	3556(8)	62(4)
C(33)	9545(13)	2503(11)	5122(8)	53(3)
C(34)	10408(17)	1518(14)	4756(10)	81(5)
C(35)	11245(19)	948(16)	5174(10)	91(5)
C(36)	11273(19)	1298(16)	5876(11)	89(5)
C(37)	10535(19)	2235(16)	6167(11)	92(6)
C(38)	9641(17)	2857(14)	5779(9)	76(4)
Cl(8)	1420(8)	1592(7)	2602(4)	122(2)
Cl(9)	446(10)	206(8)	1777(5)	147(3)
C(39)	1551(23)	275(20)	2258(13)	91(7)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor

Non-bonded van der Waals interactions were described by the Buckingham potential, $Vnb = a\ \exp(-br) - c/r^6$ where c is the attractive constant, b a shielding function and a was chosen to balance the attractive

Table 3
Selected bond lengths (Å) and angles (°)

Re(1)–Re(2)	2.2196(8)
Re(1)–Cl(1)	2.304(3)
Re(1)–Cl(3)	2.317(3)
Re(1)–Cl(2)	2.328(4)
Re(1)–P(1)	2.464(4)
Re(2)–Cl(4)	2.317(4)
Re(2)–Cl(6)	2.319(4)
Re(2)–Cl(5)	2.321(4)
Re(2)–Cl(7)	2.335(3)
P(1)–C(1)	1.791(12)
P(1)–C(9)	1.803(13)
P(1)–C(2)	1.825(14)
C(2)–C(3)	1.55(2)
C(9)–C(14)	1.37(2)
C(9)–C(10)	1.41(2)
C(10)–C(11)	1.36(2)
C(11)–C(12)	1.37(2)
C(12)–C(13)	1.36(2)
C(13)–C(14)	1.39(2)
Re(2)–Re(1)–Cl(1)	104.47(1)
Re(2)–Re(1)–Cl(3)	104.45(1)
Re(2)–Re(1)–Cl(2)	106.06(10)
Cl(1)–Re(1)–Cl(2)	89.29(14)
Cl(3)–Re(1)–Cl(2)	89.38(13)
Re(2)–Re(1)–P(1)	101.19(9)
Cl(1)–Re(1)–P(1)	82.64(12)
Cl(3)–Re(1)–P(1)	85.06(12)
Re(1)–Re(2)–Cl(4)	109.32(10)
Re(1)–Re(2)–Cl(6)	102.69(10)
Re(1)–Re(2)–Cl(5)	102.26(10)
Cl(4)–Re(2)–Cl(5)	87.0(2)
Cl(6)–Re(2)–Cl(5)	87.1(2)
Re(1)–Re(2)–Cl(7)	103.27(10)
Cl(4)–Re(2)–Cl(7)	85.8(2)
Cl(6)–Re(2)–Cl(7)	86.13(14)
C(1)–P(1)–C(9)	107.0(6)
C(1)–P(1)–C(2)	107.5(7)
C(9)–P(1)–C(2)	105.2(6)
C(1)–P(1)–Re(1)	115.5(5)
C(9)–P(1)–Re(1)	104.0(4)
C(2)–P(1)–Re(1)	116.6(5)
C(3)–C(2)–P(1)	114.6(9)

and repulsive parts to produce a minimum at a separation corresponding to the sum of the van der Waals radii [12]. Literature values were used for *b* and *c*, and *a* was increased slightly (17%) above the literature value for C–Cl bonds [13]. This is reasonable, because when bonded to less electronegative Re, Cl is expected to have more charge and a larger radius.

The torsional parameters were described by the torsional energy term V_{tor}, $V_{tor} = k_{tor}\,(1-\cos(2\chi))$.

A partial charge of -0.25 was placed on the Cl ligands for $[Re_2Cl_8]^{2-}$ and $[Re_2Cl_7(PMePhBz)]^-$. It was necessary to include the Columbic interaction to obtain the observed geometry as the non-bonded observed Cl...Cl distance of 3.3 Å in $[Re_2Cl_8]^{2-}$ is slightly attracting without it, and clearly the method is not capable of modelling the existing geometry without a charge contribution. A private communication with Boeyens has revealed that in his work this charge was also included.

The force field parameters used are summarized in Tables 5–7.

3.2. Syntheses

All phosphines, solutions of phosphines and Grignard reagents were prepared and handled in an atmosphere of dry nitrogen to prevent air oxidation. Dichloromethane was dried over calcium hydride and then slowly distilled. Methanol was purified by refluxing with magnesium methoxide for one hour prior to distillation. Petroleum spirit 40/60 and diethyl ether were dried over calcium hydride, distilled and stored over sodium wire. UV–Vis spectra were recorded on either Shimadzu UV-260 or Carey 1 spectrometers. IR spectra were obtained on a Perkin-Elmer 983G spectrometer. NMR spectra were recorded on a Jeol GX-270 spectrometer. Deuterated solvents, $CDCl_3$ and DMSO-d_6, were deoxygenated with nitrogen. The method of Bailey et al. was used to synthesize PBzMePh and $PBzPhPr^i$ [14]. The ^{31}P NMR spectra of these phosphines showed singlets at -29.43 and 1.217 ppm, respectively, in diethyl ether solution relative to external $(CH_3O)_3PO$.

3.2.1. $Re_2Cl_6L_2$ complexes

These complexes were prepared by the method of San Fillipo [15]. $[Bu_4N]_2{}^+[Re_2Cl_8]^{2-}$ (100 mg) was suspended in 5–10 ml of methanol containing 0.2–0.4 ml of concentrated hydrochloric acid and (250 mg) of phosphine was added. The solution turned green immediately. After stirring for 30 min the green precipitate was isolated by filtration and dried under vacuum. The isolated yields were >85%. $Re_2Cl_6(PPhBzMe)_2$ δ–δ^* CH_2Cl_2 solution: 726 nm. *Anal.* Calc. for $C_{28}H_{30}Cl_6P_2Re_2$: C, 33.18; H, 2.98. Found: C, 32.75; H, 3.30%. $Re_2Cl_6(PBzPhPr^i)_2$ δ–δ^* CH_2Cl_2 solution: 726 nm. *Anal.* Calc. for $C_{32}H_{38}Cl_6P_2Re_2$: C, 35.93; H, 3.58. Found: C, 35.43; H, 3.51%.

3.2.2. $[Re_2Cl_7L]^-$ complexes

$Re_2Cl_6L_2$ (40 mg) and Ph_4AsCl (20 mg) were stirred in 2 ml of dichloromethane for 5 min. The resulting dark green solution was then placed in a narrow glass tube (3 mm i.d.) and carefully covered with a layer of n-heptane. Dark green crystals formed at the interface and these were isolated after 2–3 days. $[Ph_4As]^+[Re_2Cl_7PPhBzMe]^-\cdot CH_2Cl_2$ δ–δ^* CH_2Cl_2 solution: 716 nm. *Anal.* Calc. for $C_{39}H_{37}AsCl_9PRe_2$: C, 35.95; H, 2.86. Found: C, 35.75; H, 3.21%. $[Ph_4As]^+[Re_2Cl_7PPhBzPr^i]^-$ δ–δ^* CH_2Cl_2 solution: 718 nm. *Anal.* Calc. for $C_{40}H_{39}AsCl_7PRe_2$: C, 38.55; H, 3.15. Found: C, 38.24; H, 2.97%.

Table 4
Torsional angles

k_{tor}	Torsional (twist) angles, χ (°)				Average twist, χ (°)
	$Cl_2ReReCl_6$	$Cl_1ReReCl_7$	$Cl_3ReReCl_5$	Cl_4ReReP	
4.0	16.3	16.7	17.0	20.4	17.6
4.25	14.1	15.1	14.6	18.4	15.5
4.5	11.8	12.3	13.0	16.1	13.3
4.75	10.8	11.1	12.1	14.9	12.2
5.0	10.4	10.5	11.6	14.0	11.6
5.25	9.0	9.1	10.4	12.8	10.3
5.5	7.5	7.7	9.0	11.6	8.9
Observed	10.8	15.5	7.0	13.1	11.6

Table 5
Bond stretching force constants

Bond	k_s (kcal mol^{-1} $Å^2$)	r_0 (Å)
$Re–Cl^{-1/4}$	100	2.29 [a], 2.327
Re–Re	598	2.283 [a], 2.219
Re–P	100	2.462

[a] $[Re_2Cl]^{2-}$ values.

Table 6
Angle bending force constants

Angle	k_θ (kcal mol^{-1} rad^2)	θ_0 (rad)
$Cl^{-1/4}–Re–Cl^{-1/4}$	40	1.571
$Cl^{-1/4}–Re–Re$	35	1.571
$Cl^{-1/4}–Re–P$	40	1.571
P–Re–Re	95	1.571

Table 7
Parameters for non-bonded interactions

Interaction	a (kcal mol^{-1})	b ($Å^{-1}$)	c (kcal mol^{-1} $Å^2$)
Re...Cl	4.692×10^4	2.99	1548
Re...P	6.906×10^4	3.09	1512.4
Cl...Cl	3.7×10^5	3.75	2520
Cl...P	4.02×10^5	3.87	1980
Cl...C	2.55×10^5	1.81	684
Cl...H	4.05×10^4	3.85	265.2
C...C	2.36×10^5	4.32	298.1
C...H	4.48×10^4	2.04	125
C...P	2.55×10^5	1.81	684
H...H	6.595×10^3	4.08	49.2
H...P	4.05×10^4	3.85	265.2

3.3. X-ray crystallography

Data were collected on a CAD4 diffractometer. The structure was solved by direct methods, SHELX86, and refined by full-matrix least-squares using SHELXL-93 [16,17]. Data were corrected for Lorentz and polarization effects but not for absorption. The crystal contained a molecule of dichloromethane of crystallization. Hydrogen atoms were included in calculated positions with thermal parameters 20% larger than the atom to which they were attached. Two of the aromatic rings were refined as rigid hexagons (C(3) and C(15). Carbon atoms of $[AsPh_4]^+$ were refined isotropically; all other non-hydrogen atoms were refined anisotropically. All calculations were performed on a VAX 6610 computer. The ORTEX program was used to obtain the drawings [18].

References

[1] J.C.A. Boeyens, *Inorg. Chem., 24* (1985) 4149.

[2] F.L. Campbell, F.A. Cotton and G.L. Powell, *Inorg. Chem., 24* (1985) 4384.

[3] (a) J. Ferry, J. Gallagher, D. Cunningham and P. McArdle, *Inorg. Chim. Acta, 172* (1990) 79; (b) *164* (1989) 185; (c) J. Gallagher, *Ph.D. Thesis* National University of Ireland, 1990.

[4] E.H. Abbott, K.S. Bose, F.A. Cotton, W.T. Hall and J. Sekutowski, *Inorg. Chem., 17* (1978) 3240.

[5] F.A. Cotton and G.L. Powell, *Inorg. Chem., 22* (1983) 1507.

[6] F.A. Cotton, M.P. Diebold and W.J. Roth, *Inorg. Chim. Acta, 144* (1988) 17.

[7] D.C. Smith and W.A. Goddard, *J. Am. Chem. Soc., 109* (1987) 5580.

[8] F.A. Cotton and X. Feng, *J. Am. Chem. Soc., 115* (1993) 1074.

[9] N.L. Allinger, D. Hindman and H. Honig, *J. Am. Chem. Soc., 99* (1977) 3282.

[10] V.S. Allured, C.M. Kelly and C.R. Landis, *J. Am. Chem. Soc., 113* (1991) 1.

[11] *Chem-X*, Chemical Design Limited, Oxford, UK.

[12] R.A. Buckingham, *Proc. R. Soc. London, Ser. A, 264,* (1938) 168.

[13] R.A. Scott and H.A. Scheraga, *J. Chem. Phys., 42* (1965) 2209.

[14] W.J. Bailey, S.A. Buckler and F. Marktscheffel, *J. Org. Chem., 25* (1960) 1996.

[15] J. San Fillipo, *Inorg. Chem., 11* (1972) 3140.

[16] G.M. Sheldrick, *SHELX86*, a computer program for crystal structure determination, University of Göttingen, Germany, 1986.

[17] G.M. Sheldrick, *SHELXL-93*, a computer program for crystal structure determination, University of Göttingen, Germany, 1993.

[18] P. McArdle, *J. Appl. Crystallogr., 26* (1993) 752.