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Mixed chloride-phosphine complexes of the dirhenium core 9. The first mixed monodentate phosphine complex, 1,2,7,8-Re₂Cl₄(PMe₂Ph)₃(PEt₂H)

Panagiotis A. Angaridis^a, F. Albert Cotton^{a,*}, Evgeny V. Dikarev^{a,b}, Marina A. Petrukhina^{a,b}

^a Department of Chemistry, Laboratory for Molecular Structure and Bonding, Texas A&M University, College Station, P.O. Box 30012,

Texas, TX 77842-3012, USA

^b Department of Chemistry, State University of New York at Albany, Albany, NY 12222, USA

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Dedicated to the memory of Professor Luigi Venanzi

Abstract

The reduction of the $\text{Re}_2^{5^+}$ core in 1,2,7- $\text{Re}_2\text{Cl}_5(\text{PR}_3)_3$ molecules, followed by addition of 1 equiv. of a different phosphine ligand, PR_3' , allows the preparation of the mixed monodentate phosphine compounds of the $\text{Re}_2^{4^+}$ type, namely 1,2,7,8- $\text{Re}_2\text{Cl}_4(\text{PR}_3)_3(\text{PR}_3')$. The stereochemistry of the starting materials dictates the stereochemistry of the final products. The one-electron reduction of the 1,2,7-isomer of $\text{Re}_2\text{Cl}_5(\text{PMe}_2\text{Ph})_3$ with KC₈ to the corresponding anion, $[1,2,7-\text{Re}_2\text{Cl}_5(\text{PMe}_2\text{Ph})_3]^-$ (1), followed by non-redox substitution of one chloride ion by one diethylphosphine, PEt_2H , afforded the first mixed monodentate phosphine compound of the dirhenium(II) core, $\text{Re}_2\text{Cl}_4(\text{PMe}_2\text{Ph})_3(\text{PEt}_2\text{H})$ (2), in good yield. Crystal structure determination as well as other physical methods and elemental analysis unambiguously confirmed the formation of 2. The related system 1,2,7- $\text{Re}_2\text{Cl}_5(\text{PMe}_3)_3$ - $\text{Co}(\text{C}_5\text{H}_5)_2$ - PEt_2H leads to several products, one of which is 1,2,7,8- $\text{Re}_2\text{Cl}_4(\text{PMe}_3)_3(\text{PEt}_2\text{H})$ (3). © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Dirhenium(II,II) complex; cis-Isomer; Mixed phosphine complex; Crystal structures

1. Introduction

A classic type of problem often encountered in inorganic chemistry involves the stepwise control of substitution reactions while at the same time preserving cis or trans geometry of the products. In dirhenium chemistry





* Corresponding author. Tel.: + 1-979-845 4432; fax: + 1-979-845 9351.

E-mail address: cotton@tamu.edu (F.A. Cotton).

only a few mixed phosphine complexes have been reported, all of which have been prepared by stepwise substitution reactions of $Re_2Cl_4P_4$ core compounds. The first of these triply bonded Re_2^{4+} species, having both mono- and bidentate phosphine ligands, Re₂Cl₄(PEt₃)₂(dppm), was prepared by heating a mixture of Re₂Cl₄(PEt₃)₄ and dppm in benzene [1]. Later, the PMe₃ complexes $\text{Re}_2\text{Cl}_4(\text{PMe}_3)_2(\text{P}-\text{P})$ (P-P = dppm and dppa) were obtained by a closely related procedure [2]. ¹H and ³¹P NMR spectroscopy were used to show [3] that they possess the type of structure drawn in Scheme 1, and only much later this was confirmed [4] by X-ray analysis performed on Re₂Cl₄(PMe₃)₂- $(\mu$ -dppm). So, to date, the mixed phosphine dirhenium chemistry is dominated by the $Re_2Cl_4(PR_3)_2(P-P)$ type core in which the Re2 unit is bridged by bidentate phosphine groups. No mixed monodentate phosphine analogues of the dirhenium core have yet been re-

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ported. Although the mechanism of the substitutional lability of the monodentate phosphine groups at metal-metal bonded units in solutions has been examined [5], synthetically the problem of controlled substitution of PR₃ ligands and the isolation of the desired mixed phosphine compounds has not been solved. The work reported here affords an interesting example of solving such a problem with the result that the first dimetal complex containing a mixed set of monodentate phosphine ligands has been synthesized. This is done by the one-electron reduction of an Re₂Cl₅(PR₃)₃ species to the corresponding [Re₂Cl₅(PR₃)₃]⁻ anions followed by substitution of a chloride ion by a different phosphine group PR₃'.

2. Experimental

2.1. General procedures

All syntheses and purifications were carried out under an atmosphere of N₂ in standard Schlenkware. All solvents were freshly distilled under N₂ from suitable drying agents. Chemicals were purchased from the following commercial sources and used as received: PMe₃, PMe₂Ph, PEt₂H, and Co(C₅H₅)₂, Strem Chemicals; [Bu₄ⁿN]₂[Re₂Cl₈], [Bu₄ⁿN]Cl, Aldrich, Inc. 1,2,7-Re₂Cl₅(PMe₂Ph)₃ [6], 1,2,7-Re₂Cl₅(PMe₃)₃ [7], and KC₈ [8] were prepared by literature procedures.

2.2. Physical measurements

Electrochemical measurements were carried out on dichloromethane solutions that contained 0.1 M tetra*n*-butylammonium hexafluorophosphate (TBAH) as the supporting electrolyte. A stream of nitrogen was bubbled through the solution during the measurements. $E_{1/2}$ values, determined as $(E_{p,a} + E_{p,c})/2$, were referenced to the Ag/AgCl electrode at room temperature (r.t.). Under our experimental conditions, $E_{1/2} = +0.47$ V versus Ag/AgCl for the ferrocenium/ferrocene couple. Voltammetric experiments were done with the use of a Bioanalytical Systems Inc. electrochemical analyzer, Model 100. The scan rate was 100 mV s⁻¹ at a Pt disk electrode. Elemental analyses were done by Canadian Microanalytical Services Ltd. The positive and negative FAB/DIP mass spectra were acquired using a VG Analytical 70S high-resolution, double-focusing, sectored (EB) mass spectrometer. Samples for mass spectral analysis were prepared by mixing a solution of each compound in CH2Cl2 or CHCl3 with an NBA matrix on the direct insertion probe tip. The ${}^{31}P{}^{1}H$ NMR data were recorded at r.t. on a UNITY-plus 300 multinuclear spectrometer operated at 121.4 MHz and using 85% H₃PO₄ as an external standard.

2.3. Preparation of $[Bu_4^n N][1,2,7-Re_2Cl_5(PMe_2Ph)_3]$ (1)

1,2,7-Re₂Cl₅(PMe₂Ph)₃ (0.101 g, 0.10 mmol) was mixed with KC₈ (0.022 g, 0.16 mmol). Toluene (5 ml) was added to the mixture of solids, followed by CH₂Cl₂ (5 ml). The suspension was stirred for 30 min at r.t., after which all volatile components were removed under reduced pressure. The residue was washed with C₆H₁₄ $(3 \times 10 \text{ ml})$ and then dried overnight. It was dissolved in 7 ml of CH₂Cl₂ containing [Bu₄ⁿ N]Cl (0.025 g, 0.09 mmol), the mixture was filtered and the green filtrate was layered with 15 ml of C₆H₁₄. Large brown blockshaped crystals came out in a few days in the freezer. Yield: 0.069 g (57%). For $[1,2,7-\text{Re}_2\text{Cl}_5(\text{PMe}_2\text{Ph})_3]^-$ (1): CV (CH₂Cl₂, 22 °C, V versus Ag/AgCl): $E_{1/2}(ox)(1) =$ $-0.42, E_{1/2}(\text{ox})(2) = +0.76. - \text{FAB/DIP MS}$ (NBA, $CH_2Cl_2, m/z$): 965 ([M]⁻), 929 ([M - Cl]⁻), 828 ([M - $PMe_{2}Ph]^{-}$, 791 ([$M - PMe_{2}Ph - Cl]^{-}$).

2.4. Preparation of $1,2,7,8-Re_2Cl_4(PMe_2Ph)_3(PEt_2H)$ (2)

1,2,7-Re₂Cl₅(PMe₂Ph)₃ (0.202 g, 0.21 mmol) was mixed with KC_8 (0.042 g, 0.31 mmol). Toluene (8 ml) was added to the mixture of solids, followed by CH₂Cl₂ (10 ml) and approximately 30 µL of PEt₂H. The suspension was stirred for 30 min at r.t., after which all volatile components were removed under reduced pressure. The residue was washed with C_6H_{14} (3 × 10 ml) and then dried overnight. It was dissolved in 7 ml of CH₂Cl₂, the solution was filtered, and the green filtrate was layered with 20 ml of C_6H_{14} . The green-brown (dichroic) crystals of 2·CH₂Cl₂ came out in a few days in the freezer. Yield: 0.123 g (53%). For 1,2,7,8-Re₂Cl₄(PMe₂Ph)₃(PEt₂H) (2): CV (CH₂Cl₂, 22 °C, V versus Ag/AgCl): $E_{1/2}(ox)(1) = +0.37$, $E_{1/2}(ox)(2) =$ + 1.22. ³¹P NMR {CD₂Cl₂, 20 °C}: δ 3.19 (s), -13.65 (t), -16.55 (t), -24.83 (s). + FAB/DIP MS (NBA, $CH_2Cl_2, m/z$): 1018 ([M]⁺), 880 ([M - PMe_2Ph]⁺), 742 $([M - 2PMe_2Ph]^+), 652 ([M - 2PMe_2Ph - PEt_2H]^+).$ Anal. Calc. for C₂₉H₄₆Cl₆P₄Re₂: C, 31.59; H, 4.12. Found, C, 31.76; H, 4.19%.

2.5. Preparation of $1, 2, 7, 8-Re_2Cl_4(PMe_3)_3(PEt_2H)$ (3)

1,2,7-Re₂Cl₅(PMe₃)₃ (0.101 g, 0.13 mmol) was dissolved in 10 ml of CH₂Cl₂ and cobaltocene, Co(C₅H₅)₂, (0.024 g, 0.13 mmol) was added to the solution. The reaction mixture was stirred for about 30 min, after which 0.1 ml of PEt₂H was added to the mixture and the solution was stirred for 2 h at r.t. The volume of the solution was reduced by half, and 5 ml of benzene was added to precipitate cobaltocenium chloride. After filtration the solution was evaporated to leave a brown residue. The solid was washed with hexanes, redissolved in dichloromethane and the solution was layered with Table 1

 $\label{eq:crystallographic data for $[Bu_1^4N][1,2,7-Re_2Cl_5(PMe_2Ph)_3]$ (1) and $1,2,7,8-Re_2Cl_4(PMe_2Ph)_3(PEt_2H)$-CH_2Cl_2$ ($\mathbf{2}$-CH_2Cl_2$)$

	1	$2 \cdot CH_2Cl_2$
Empirical formula	$C_{40}H_{69}Cl_5N_1P_3Re_2$	$C_{29}H_{46}Cl_6P_4Re_2$
Formula weight	1206.52	1103.64
Temperature (K)	213(2)	213(2)
Radiation (λ , Å)	Mo Ka (0.71073)	Mo Ka (0.71073)
Crystal system	monoclinic	triclinic
Space group	$P2_1/n$	$P\overline{1}$
a (Å)	9.958(3)	11.336(4)
b (Å)	36.879(6)	12.431(3)
c (Å)	13.096(2)	15.507(5)
α (°)		104.70(2)
β (°)	91.92(2)	105.54(6)
γ (°)		103.44(3)
V (Å ³)	4807(2)	1928(1)
Ζ	4	2
$\rho_{\rm calc} \ ({\rm g} \ {\rm cm}^{-3})$	1.667	1.901
$\mu (mm^{-1})$	5.438	6.876
Transmission factors	0.389-0.580	0.397-0.584
Unique data	5916	4592
Observed data $[I > 2\sigma(I)]$	5455	4187
Parameters refined	460	374
$R_1^{a}, wR_2^{b} [I > 2\sigma(I)]$	0.0403, 0.1018	0.0374, 0.0917
R_1^{a} , wR_2^{b} (all data)	0.0454, 0.1056	0.0431, 0.0975
Quality-of-fit ^c	1.264	1.159

^a
$$R_1 = \Sigma ||F_0| - |F_c|| / \Sigma |F_0|$$

^b $wR_2 = [\Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2]]^{1/2}.$

^c Quality-of-fit = $[\Sigma [w(F_o^2 - F_c^2)^2]/(N_{obs} - N_{params})]^{1/2}$, based on all data.

hexanes. Brown, block shaped crystals were found at the bottom of the Schlenk tube after a week. The product was shown by X-ray crystallography to be a mixture of species, two known complexes [9]: 1,2,7,8- $Re_2Cl_4(PMe_3)_4$ and $[Bu_4^n N][1,2,7-Re_2Cl_5(PMe_3)_3]$; and a new product, $Re_2Cl_4(PMe_3)_3(PEt_2H)$ (3).

2.6. X-ray structure determination

Single crystals of compounds 1 and $2 \cdot CH_2Cl_2$ were obtained as described above. The X-ray diffraction experiments were carried out on a Nonius FAST diffractometer with an area detector using Mo Ka radiation. The crystals were mounted on the tip of a quartz fiber with silicone grease, and the setup was quickly placed in the cold N₂ stream (-60 °C) of a low temperature controller. Fifty reflections were used in cell indexing and about 250 reflections in cell refinement. The data were corrected for Lorentz and polarization effects by the MADNES program [10]. Reflection profiles were fitted and values of F^2 and $\sigma(F^2)$ for each reflection were obtained by the program PROCOR [11]. The intensities were also corrected for anisotropy effects using a local adaptation of the program SORTAV [12]. All calculations were done on a DEC Alpha running VMS. The coordinates of rhenium atoms were found in direct E maps using the structure solution program SHELXTL [13]. The positions of the remaining atoms were located by means of alternating series of least-squares cycles and difference Fourier maps [14].

Anisotropic displacement parameters were assigned to all non-hydrogen atoms. Hydrogen atoms were included in the structure factor calculations at idealized positions. The hydrogen atom connected to the phosphorus atom of diethylphosphine in **2** was found in a difference Fourier map and then refined independently with an isotropic thermal parameter.

Relevant crystallographic data for 1 and $2 \cdot CH_2Cl_2$ are summarized in Table 1, and selected bond distances and angles are given in Table 2.

Table 2

Selected distances (Å), angles (°), and torsion angles (°) for $[1,2,7-Re_2Cl_5(PMe_2Ph)_3]^-$ in (1) and $1,2,7,8-Re_2Cl_4(PMe_2Ph)_3(PEt_2H)$ (2)

	1	2
Bond lengths		
Re(1) - Re(2)	2.2388(7)	2.247(1)
Re(1) - P(1)	2.380(3)	2.399(3)
Re(1) - P(2)	2.360(3)	2.390(3)
Re(1)-Cl(1)	2.422(3)	2.407(3)
Re(1)-Cl(2)	2.424(3)	2.419(2)
$\operatorname{Re}(2)-\operatorname{P}(3)$	2.352(3)	2.392(3)
Re(2)–P(4)		2.348(3)
Re(2)Cl(3)	2.401(3)	2.422(3)
Re(2)–Cl(4)	2.401(3)	2.411(3)
Re(2)-Cl(5)	2.386(3)	
Bond angles		
P(1)-Re(1)-P(2)	95.7(1)	94.57(9)
P(1)-Re(1)-Cl(1)	151.3(1)	146.10(9)
P(1)-Re(1)-Cl(2)	83.6(1)	83.50(9)
P(2)-Re(1)-Cl(1)	86.6(1)	84.47(9)
P(2)-Re(1)-Cl(2)	153.7(1)	151.02(9)
Cl(1)-Re(1)-Cl(2)	82.0(1)	81.47(9)
Re(2)-Re(1)-P(1)	97.17(7)	102.66(9)
Re(2)-Re(1)-P(2)	96.88(8)	94.22(7)
$\operatorname{Re}(2)-\operatorname{Re}(1)-\operatorname{Cl}(1)$	111.00(8)	111.21(9)
$\operatorname{Re}(2)$ - $\operatorname{Re}(1)$ - $\operatorname{Cl}(2)$	109.30(8)	114.46(7)
P(3)-Re(2)-P(4)		94.31(9)
P(3)-Re(2)-Cl(5)	85.0(1)	
P(3)-Re(2)-Cl(3)	149.9(1)	153.2(1)
P(3)-Re(2)-Cl(4)	86.9(1)	85.0(1)
P(4)-Re(2)-Cl(3)		80.4(1)
Cl(3)-Re(2)-Cl(5)	84.9(1)	
P(4)-Re(2)-Cl(4)		141.2(1)
Cl(4)-Re(2)-Cl(5)	142.8(1)	00.0(1)
Cl(3) - Re(2) - Cl(4)	84.2(2)	83.0(1)
Re(1)-Re(2)-P(3)	97.77(7)	95.94(9)
Re(1) - Re(2) - P(4)	110 01 (0)	102.98(7)
Re(1) - Re(2) - CI(3)	112.21(8)	110.9(1)
Re(1)-Re(2)-Cl(4)	112.38(9)	115.73(8)
Re(1) - Re(2) - CI(5)	104.70(9)	20.4(1)
P(1)-Re(1)-Re(2)-Cl(3)	28.0(1)	30.4(1)
P(2)-Re(1)-Re(2)-Cl(4)	24.2(1)	27.0(1)
CI(1) - Re(2) - Re(1) - P(3)	25.1(1)	28.68(9)
CI(2) - Re(2) - Re(1) - P(4)	22.2(1)	34.4(1)
CI(2) - Ke(1) - Ke(2) - CI(5)	23.3(1)	



3. Results and discussion

It was first shown in 1985 by Dunbar and Walton [15] that one-electron reduction of a 1,3,6-Re₂Cl₅(PR₃)₃ molecule, followed by reaction of the resulting anion with a molar equivalent of PR₃ leads to the product 1,3,6,8-Re₂Cl₄(PR₃)₄, as shown in Scheme 2. More recently, after we learned to make 1,2,7-Re₂Cl₅(PR₃)₃ molecules [6,9], we discovered the existence of 1,2,7,8-Re₂Cl₄(PR₃)₄ molecules by a similar reaction sequence (Scheme 3, where PR₃' = PR₃) starting with a 1,2,7-Re₂Cl₅(PR₃)₃ compound. However, because of the cis relationship of the PR₃ ligands in both starting compound and the product, reactions of this second type can occur only when the phosphines have small cone angles [16], that is, with PMe₃ [9], PMe₂Ph [6], and PEt₂H [17].

We then recognized that by employing Scheme 3, with PR_3' not the same as PR_3 , it might be possible to make the first compounds with different phosphines in the same $\text{Re}_2\text{Cl}_4(\text{PR}_3)_4$ type molecule. We first accomplished such a synthesis by using 1,2,7-Re₂Cl₅-(PMe₂Ph)₃ as a starting material, KC₈ as a reducing agent and diethylphosphine as the entering phosphine ligand affording the complex 1,2,7,8-Re₂Cl₄(PMe₂Ph)₃- (PEt_2H) (2). We confirmed that the intermediate after one-electron reduction is indeed the [1,2,7-Re₂Cl₅- $(PMe_2Ph)_3$ ⁻ anion (1). It has been isolated in crystalline form as its tetrabutylammonium salt. An analogous reaction scheme has also been applied for the related system $1,2,7-\text{Re}_2\text{Cl}_5(\text{PMe}_3)_3-\text{Co}(\text{C}_5\text{H}_5)_2-$ PEt₂H. However, this resulted in a mixture of products, but one of them was a new mixed monodentate phosphine dirhenium complex, $1,2,7,8-\text{Re}_2\text{Cl}_4(\text{PMe}_3)_3$ -(PEt₂H) (3).

Complex 2 has been obtained in pure form in moderate yield, and it has been fully characterized by massspectrometry, elemental analysis and cyclic voltammetry. We have not detected any side-products in this system. The reaction affording 3 was not so clean and less efficient, yielding a mixture of dirhenium complexes with the Re_2^{4+} core, from which crystals of 3 were separated manually for X-ray diffraction study.

In addition to stereochemical suitability of the ligands for the synthesis of cis products, it is also important that the entering monodentate phosphine have the same or lower basicity than the three in the starting material, in order to avoid phosphine ligand redistribution. For both of these reasons, the system Re₂Cl₅(PMe₂Ph)₃-PEt₂H was found to be unique. When we tried to introduce the sterically suitable but most basic ligand, PMe₃, to [Re₂Cl₅(PMe₂Ph)₃]⁻, even at a ratio $Re_2 - PMe_3 = 1:1$, uncontrolled side reactions were observed, including complete substitution of PMe₂Ph by PMe₃. Conversely, it might seem that trimethylphosphine ligands in the starting material should be resistant to replacement by any other phosphine, including PMe₂Ph and PEt₂H. However, when we tried to extend our approach by using 1,2,7- $Re_2Cl_5(PMe_3)_3$ as the starting material and PEt₂H as the entering phosphine, we isolated the target mixed phosphine complex, 1,2,7,8-Re₂Cl₄(PMe₃)₃(PEt₂H) (3), only in a low yield.

The tetrabutylammonium salt of anion 1 forms crystals in the monoclinic space group $P2_1/n$ with two pairs of enantiomeric dimetal molecules in the unit cell. The dirhenium(II,II) anion has C_1 virtual symmetry and exhibits a staggered conformation (Fig. 1). All dimensions of the $[1,2,7\text{-Re}_2\text{Cl}_5(\text{PMe}_2\text{Ph})_3]^-$, including the Re-Re bond length and the P-Re-P angle, have small deviations from the corresponding dimensions of the



Fig. 1. A drawing of the anion $[1,2,7-\text{Re}_2\text{Cl}_5(\text{PMe}_2\text{Ph})_3]^-$ (1). Atoms are represented by thermal ellipsoids at the 40% probability level. Hydrogen atoms are shown as spheres of arbitrary radii.



Fig. 2. A drawing of 1,2,7,8-Re₂Cl₄(PMe₂Ph)₃(PEt₂H) (**2**). Atoms are represented by thermal ellipsoids at the 35% probability level. Only the hydrogen atom connected to the phosphorus atom of the PEt₂H group is shown.

neutral dirhenium(II,III) molecule, 1,2,7-Re₂Cl₅(PMe₂-Ph)₃ [6]. The staggered conformation is also retained with the torsion angles in the range $23.3(1)-28.0(1)^{\circ}$.

Compound 2 crystallizes in triclinic group $P\overline{1}$ with two Re₂Cl₄(PMe₂Ph)₃(PEt₂H) molecules in the unit cell.

Selected bond distances (Å) and angles (°) for 1,2,7,8-Re₂Cl₄(PR₃)₄ type complexes

Table 3



Fig. 3. A drawing of 1,2,7,8-Re₂Cl₄(PMe₃)₃(PEt₂H) (3). Only the major orientation of the Re₂ unit is shown. Rhenium and phosphorus atoms are represented by thermal ellipsoids at the 30% probability level; other atoms are shown as spheres of arbitrary radii.

Each molecule has C_1 virtual symmetry. The structure determination on Re₂Cl₄(PMe₂Ph)₃(PEt₂H) (2) confirmed that a *cis*-type of geometry of phosphine groups had indeed been retained on both rhenium atoms upon reduction and addition of the diethylphosphine ligand to yield an 1,2,7,8-isomer (Fig. 2). The P-Re-P angles at both ends of the dirhenium unit are almost identical (94.57(9) and 94.31(9)°). The bond distances and angles in the mixed phosphine complex 2 are compared with respective characteristics of other 1,2,7,8-species listed in Table 3. In fact all geometrical parameters are in good agreement with the corresponding values for the whole 1,2,7,8-class of molecules. The essential feature of the molecule 2 is a 'half-staggered' conformation as in the parent anion 1 (Table 2) with the P-Re-Re-Cl torsion angles spanning the range $27.0(1)-34.4(1)^{\circ}$. That contrasts with all other complexes of this type (and Re₂Cl₄(PR₃)₄ complexes with monodentate phosphines in general) which are known to have an eclipsed conformation.

The structure determination on $\text{Re}_2\text{Cl}_4(\text{PMe}_3)_3$ -(PEt₂H) (3) [18] also proved that a *cis*-type of phosphine disposition is preserved (Fig. 3). The structure solution of 3 was complicated by the disorder

(PR ₃) ₄ , (Reference)	(PMe ₃) ₄ ([9])	(PMe ₂ Ph) ₄ ([6])	(PEt ₂ H) ₄ ([17])	$(PMe_2Ph)_3(PEt_2H)$ (2) (this work)	$(PMe_3)_3(PEt_2H)$ (3) (this work)
Bond distances					
Re–Re	2.2414 (8)	2.260 (1)	2.2533 (8)	2.247 (1)	2.253 (2)
Re–P	2.373 (7)	2.407 (3)	2.366 (2)	2.382 (3)	2.353 (8)
Re-Cl	2.410 (9)	2.411 (3)	2.414 (2)	2.415 (3)	2.416 (7)
Bond angles					
P-Re-P	93.2 (7)	93.6 (1)	93.12 (6)	94.44 (9)	95.8 (3)
P-Re-Re-Cl	1.1–3.7	1.8-4.4	0.11-1.16	27.0-34.4	3.0

of the phosphine groups. Each phosphine position is occupied by 3/4 of PMe₃ and 1/4 of PEt₂H. Such a distribution stems from the fact that trimethyl and diethyl phosphines match closely in size. Unfortunately, we were unable to completely model the location of partially occupied carbon atom positions in the crystal structure of **3**. However, the positions of the heavy atoms (Re, Cl, and P) were well-refined and the principal dimensions shown in Table 3 are reliable. As expected, the core distances and angles in the structure of 1,2,7,8-Re₂Cl₄(PMe₃)₃(PEt₂H) are very close to those in corresponding homo-phosphine complexes.

In conclusion, complexes 2 and 3 constitute the first structurally characterized examples of mixed monodentate phosphine compounds of the multiply bonded dinuclear core for $M_2X_4(PR_3)_{4-x}(PR_3')_x$, where M = Mo, W, Tc, Re; X = halide. The suggested synthetic route is an alternative strategy to a stepwise substitution [19,20], and opens a door for further research on synthetic techniques that will allow the formation of mixed phosphine derivatives of the dimetal core with controlled stoichiometry and stereochemistry. We also note that while the two-step procedure described here might also be thought to allow conversion of 1,3,6-Re₂Cl₅(PR₃)₃ compounds to 1,3,6,8-Re₂Cl₄(PR₃)₃(PR₃') compounds, more complex and not well understood reactions occur instead.

4. Supplementary material

Crystallographic data (excluding structure factors) for **1** and $2 \cdot CH_2Cl_2$ have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 163592 and 163591. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam. ac.uk or www:http://www.ccdc.cam.ac.uk).

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