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### New Dinuclear Face- and Edge-Sharing Bioctahedral Ruthenium Compounds Containing 1,2-Bis(diphenylphosphanyloxy)ethane

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The bidentate diphosphinite ligand 1,2-bis(diphenylphosphanyloxy)ethane (L), Ph<sub>2</sub>P–O–(CH<sub>2</sub>)<sub>2</sub>–O–PPh<sub>2</sub>, can be sequentially incorporated into a series of dinuclear chlorobridged ruthenium compounds using [RuCl<sub>2</sub>(DMSO)<sub>4</sub>] as a precursor to give the new bioctahedral compounds [Ru<sub>2</sub>( $\mu$ -Cl)<sub>3</sub>(DMSO)<sub>3</sub>Cl( $\eta^2$ -L)] (1), [Ru<sub>2</sub>( $\mu$ -Cl)<sub>3</sub>(DMSO)Cl( $\eta^2$ -L)<sub>2</sub>] (2) and [Ru<sub>2</sub>Cl<sub>2</sub>( $\eta^2$ -L)<sub>2</sub>{ $\eta^1$ -L(O)}<sub>2</sub>( $\mu$ -Cl)<sub>2</sub>] (3). Compound 3 contains two partially oxidised diphosphinite ligands that act in a monodentate manner. These compounds can also be obtained by direct reaction of [RuCl<sub>2</sub>(DMSO)<sub>4</sub>] with the appropriate stoichiometric amount of L but in the case of 3 (in which prolonged heating is necessary) the reaction affords

### Introduction

Ruthenium complexes continue to attract attention because they can be used in a range of applications in many different fields including catalytic processes<sup>[1]</sup> and bioinorganic processes.<sup>[2]</sup> Moreover, the discovery of the anticancer activity of [RuCl<sub>2</sub>(DMSO)<sub>4</sub>] has increased interest in the properties of new Ru–DMSO complexes.<sup>[3]</sup> A number of chelating diphosphines have been used to stabilise transition-metal complexes but, surprisingly, studies on analogous diphosphinites are rare, although some such compounds have proved to be efficient catalysts.<sup>[4]</sup> Furthermore, the presence of halogeno bridges between the metal centres provides higher reactivity, thus enhancing their possibilities for successful use as new catalysts.<sup>[5]</sup>

We report here the results obtained in the reaction between [RuCl<sub>2</sub>(DMSO)<sub>4</sub>] and 1,2-bis(diphenylphosphanyloxy)ethane (L) to yield a range of new mono- and dinuclear ruthenium complexes (Scheme 1). It is worth mentioning that, in contrast with the behaviour observed for other diphosphinite ligands,<sup>[6]</sup> it was possible to obtain different products when the stoichiometric relationship be-

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two mononuclear compounds  $[RuCl_2(\eta^2-L)(Ph_2POPPh_2)]$  (7) and  $[RuCl(CO)(\eta^2-L)(Ph_2POCH_2)]$  (8), with ligand fragments coordinated to the metal probably originating in metal-mediated disruptions of L. Reaction of **2** with the monodentate ligands  $PPh_{3-n}(OEt)_n$  (n = 1-3) (L') affords the dinuclear doubly chloro-bridged compound  $[Ru_2(\mu-Cl)_2Cl_2(\eta^2-L)_2(L')_2]$  (4), the dinuclear triply chloro-bridged compound  $[{Ru(\eta^2-L)(L')}_2 - (\mu-Cl)_3]Cl$  (5) and the mononuclear compound  $[RuCl_2(\eta^2-L)-(L')_2]$  (6). The solid-state structures of **2** (*transoid* isomer), **5** (*transoid* isomer), **6**, **7** and **8** are reported.

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tween the metal-containing precursor and the ligand was varied.

### **Results and Discussion**

# Reaction of $[RuCl_2(DMSO)_4]$ with L – Preparation of $[Ru_2(\mu-Cl)_3(DMSO)_3Cl(L)]$ (1)

Reaction of [RuCl<sub>2</sub>(DMSO)<sub>4</sub>] with 1,2-bis(diphenylphosphanyloxy)ethane (L) in a 2:1 molar ratio in refluxing toluene for 1/2 h gave a yellow solid. The analytical data for this compound are consistent with the empirical formula Ru<sub>2</sub>LCl<sub>4</sub>(DMSO)<sub>3</sub>. The IR spectrum shows a strong band at 1093 cm<sup>-1</sup>, which is consistent with the presence of the  $\eta^{1}$ -S (DMSO) ligands.<sup>[7]</sup> The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum in CDCl<sub>3</sub> shows a singlet at  $\delta = 158.2$  ppm, indicating the magnetic equivalence of the two phosphorus atoms of the bidentate ligand L. The <sup>1</sup>H NMR spectrum shows, in the same solvent, three singlets at  $\delta = 3.04$ , 3.12 and 3.43 ppm (integrating to 6 protons each), which can be assigned to the three DMSO ligands, and two multiplets at  $\delta = 3.72$ and 4.26 ppm (integrating to 2 protons each) corresponding to the methylene groups of L. Further evidence for the dinuclear nature of 1 comes from the FAB-MS spectrum, which shows signals corresponding to the molecular ion  $[M^+]$  and to the fragments  $[M^+ - Cl]$ ,  $[M^+ - (DMSO)]$ ,  $[M^+ - 3(DMSO)], [M^+ - 3(DMSO) - Cl] and [M^+ - Ru -$ 3(DMSO) - 2Cl]. Two of the three isomers shown in Scheme 2 are compatible with this structural information.



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#### Scheme 2.

Isomer C can be ruled out because the two P nuclei are not equivalent. Isomer A is our preferred choice between isomers A and B because the chemical shift of P is similar to that observed for compounds with the same environment<sup>[8]</sup> and the methyl groups of each DMSO do not appear as two diastereotopic singlets (we carried out a 2D <sup>1</sup>H, <sup>13</sup>C HSQC experiment to confirm this, see Supporting Information) as one would expect them to if they were in proximity to a bidentate ligand. Moreover, the 2D <sup>1</sup>H, <sup>31</sup>P NMR HMBC experiments do not show any evidence of an interaction between the P atoms and the CH<sub>3</sub> protons of the DMSO ligands (although such negative evidence is not conclusive).

## Reaction of Compound 1 with L – Preparation of $[Ru_2(\mu-Cl)_3(DMSO)Cl(L)_2]$ (2)

Reaction of **1** with L in a 1:1 molar ratio in refluxing toluene for 1/2 h gave a yellow solid. The analytical data for this product are consistent with the formulation  $[Ru_2(\mu-Cl)_3-(\eta^2-L)_2Cl(DMSO)]$  (**2**).<sup>[9]</sup> The IR spectrum shows a strong band at 1093 cm<sup>-1</sup>, which is consistent with the presence of a  $\eta^1$ -*S* sulfoxide ligand.<sup>[7]</sup>

The  ${}^{31}P{}^{1}H$  NMR spectrum in CDCl<sub>3</sub> shows two sets of signals. The first set (indicated in Figure 1 by an asterisk) consists of a pair of doublets and a quartet [consistent with

an AX spin system ( $\delta = 160.7$ , 151.9 ppm,  $J_{AX} = 54$  Hz) and an AB spin system ( $\delta = 148.3$  ppm,  $J_{AB} = 44$  Hz), respectively]. This is a characteristic pattern of compounds of the type [RuCl(PP)( $\mu$ -Cl)<sub>3</sub>Ru(PP)L]<sup>[10]</sup> and can be assigned to the *transoid* form of **2** in which the four P atoms are not equivalent (see Scheme 3).



Figure 1.  ${}^{31}P{}^{1}H$  NMR spectrum in CDCl<sub>3</sub> for compound 2.



Scheme 3.

The second set of signals consists of two singlets [ $\delta$  = 156.9, 146.4 ppm] (indicated by a double asterisk in Figure 1) and corresponds to the *cisoid* structure **2b** (see

Scheme 4) in which both phosphorus nuclei, belonging to each bidentate ligand, are magnetically equivalent.



#### Scheme 4.

The <sup>1</sup>H NMR spectrum in CDCl<sub>3</sub> also presents signals that correspond to both structures. For example, two singlets at  $\delta = 2.54$  and 2.87 ppm can be assigned to the two diastereotopic methyl groups of DMSO corresponding to the transoid structure. At 3.22 ppm a singlet with a lower intensity can be assigned to the methyl groups of the DMSO ligand corresponding to the *cisoid* structure (there are no diastereotopic signals in this case because of its higher symmetry). A similar situation occurs with the signals corresponding to the methylene groups of the bidentate ligand. As observed in other halide compounds bearing this ligand,<sup>[11]</sup> these groups usually display one multiplet for each proton. In our case different multiplets were observed that integrate as one proton each and these coexist with other signals of lower intensity that may correspond to the cisoid structure.

An HMBC <sup>1</sup>H,<sup>31</sup>P{<sup>1</sup>H} NMR study (see Supporting Information) shows that there is a correlation between the signal at  $\delta$  = 148.3 ppm (in CDCl<sub>3</sub>) and that at  $\delta$  = 2.54 ppm attributed to one of the DMSO methyl groups. This indicates that – in agreement with the assignment made by Bianchini for a similar complex – this resonance corresponds to the bidentate ligand coordinated to the Ru atom that bears the DMSO molecule.<sup>[8a]</sup> The relative intensities of the signals of the two isomers change significantly when benzene is used as the solvent, with the signals of the *cisoid* structure almost residual in this case. This must be due to the different solubility of the two isomers, because a VT NMR study carried out in CDCl<sub>3</sub> from 25 °C to –50 °C and

in  $C_6D_6$  from 25 °C to 45 °C did not provide any evidence for interconversion between them.

Finally, the <sup>13</sup>C{<sup>1</sup>H} spectrum in CD<sub>2</sub>Cl<sub>2</sub> shows two singlets at  $\delta = 50.5$  and 51.0 ppm, which can be assigned to the two inequivalent methyl groups of the DMSO ligand corresponding to the *transoid* structure. A signal with a lower intensity was also observed at  $\delta = 51.3$  ppm and this can be assigned to the two equivalent methyl groups of the *cisoid* structure.

We were able to obtain single crystals of the *transoid* isomer of compound **2** (**2a**) to carry out an X-ray diffraction analysis. Selected bond lengths and angles are reported in Table 1 and an ORTEP view is shown in Figure 2.

Table 1. Bond lengths [Å] and angles [°] for 2a.

Bond lengths			
Ru(1)–P(2)	2.203(5)	Ru(1)–P(1)	2.228(5)
Ru(1)-Cl(4)	2.377(5)	Ru(1)-Cl(1)	2.422(4)
Ru(1)-Cl(2)	2.502(5)	Ru(1)-Cl(3)	2.551(5)
Ru(2) - P(3)	2.267(5)	Ru(2) - P(4)	2.258(5)
Ru(2)-S(1)	2.260(5)	Ru(2)-Cl(3)	2.515(5)
Ru(2)-Cl(1)	2.495(4)	Ru(2)–Cl(2)	2.395(5)
Bond angles			
P(2)-Ru(1)-P(1)	91.21(19)	P(2)-Ru(1)-Cl(4)	91.86(19)
P(1)-Ru(1)-Cl(4)	90.28(18)	P(2)-Ru(1)-Cl(1)	96.88(17)
P(1)-Ru(1)-Cl(1)	100.39(17)	Cl(4)-Ru(1)-Cl(1)	166.02(18)
P(2)-Ru(1)-Cl(2)	174.95(18)	P(1)-Ru(1)-Cl(2)	92.70(17)
Cl(4)-Ru(1)-Cl(2)	91.30(17)	Cl(1)-Ru(1)-Cl(2)	79.28(15)
P(2)-Ru(1)-Cl(3)	98.52(18)	P(1)-Ru(1)-Cl(3)	170.27(17)
Cl(4)-Ru(1)-Cl(3)	89.63(17)	Cl(1)-Ru(1)-Cl(3)	78.32(15)
Cl(2)-Ru(1)-Cl(3)	77.57(15)	P(4)-Ru(2)-S(1)	93.51(19)
P(4)-Ru(2)-P(3)	90.14(19)	S(1)-Ru(2)-P(3)	93.99(18)
P(4)-Ru(2)-Cl(2)	9515(18)	S(1)-Ru(2)-Cl(2)	169.72(17)
P(3)-Ru(2)-Cl(2)	91.52(17)	P(4)-Ru(2)-Cl(1)	172.99(18)
S(1)-Ru(2)-Cl(1)	90.95(17)	P(3)-Ru(2)-Cl(1)	94.94(16)
Cl(2)-Ru(2)-Cl(1)	79.93(15)	P(4)-Ru(2)-Cl(3)	96.65(18)
S(1)-Ru(2)-Cl(3)	93.26(17)	P(3)-Ru(2)-Cl(3)	169.73(18)
Cl(2)-Ru(2)-Cl(3)	80.25(16)	Cl(1)-Ru(2)-Cl(3)	77.68(15)
Ru(1)-Cl(1)-Ru(2)	86.56(14)	Ru(2)-Cl(2)-Ru(1)	86.97(15)
Ru(2)-Cl(3)-Ru(1)	83.43(15)		

Complex 2 adopts a triply chloride-bridged diruthenium *transoid* structure (2a) in which the coordination geometry



Figure 2. ORTEP view of  $[Ru_2(\mu-Cl)_3(DMSO)Cl(L)_2]$  (2a). The phenyl groups are omitted for clarity.

at each metal centre is a distorted octahedron. The structure is unsymmetrical, with Ru(2) bearing a DMSO and Ru(1) a chloride ligand. The structural features are similar to those found in previously reported face-sharing bioctahedral Ru<sup>II</sup>–Ru<sup>II</sup> complexes.<sup>[7b,12]</sup> The Ru–Cl<sub>terminal</sub> distance is shorter than the Ru–Cl<sub>bridge</sub> distances. Of all the Ru–Cl<sub>bridge</sub> distances, those that are *trans* to a phosphorus atom are the longest. The shortest Ru–Cl<sub>bridge</sub> distance is that with the DMSO ligand in the *trans* position. It is worth noting that the Ru(1)–P distances (with Ru bound to a terminal chloro ligand) are significantly shorter than the Ru(2)–P distances (with Ru bound to the DMSO ligand).

The seven-membered chelate rings allow P–Ru–P angles of 91.21(19) and 90.14(19)°. The Cl<sub>bridge</sub>–Ru–Cl<sub>bridge</sub> angles have values between 77.57(15) and 80.25(16)°, with this being the main source of distortion of the octahedron. As shown in Figure 3, the environment of the metal atoms corresponds with the  $C_1$ -symmetric *transoid* isomer, with the dihedral torsion angle Cl(4)–Ru(1)–Ru(2)–S(1) having a value of 122.4(2)°. The Ru–Ru distance of 3.371(2) Å lies in the range expected for this type of dinuclear Ru<sup>II</sup> complex (3.28–3.44 Å).<sup>[12a]</sup>



Figure 3. Environment of the Ru atoms in 2a.

## Reaction of Compound 2 with L – Preparation of $[{RuCl(\eta^2-L)[\eta^1-L(O)]}_2(\mu-Cl)_2]$ (3)

The reaction of 2 with L (1:2 molar ratio) in refluxing toluene for 1 h gave the new compound 3. The  ${}^{31}P{}^{1}H{}$ NMR spectrum in CDCl<sub>3</sub> displays a doublet at  $\delta$  = 159.0 ppm (J = 46 Hz), a triplet at  $\delta = 138.3$  ppm and a singlet at  $\delta = 32.5$  ppm with an intensity ratio of 2:1:1, respectively. The singlet at higher field is consistent with the existence of a P=O group (corresponding to a partially oxidised molecule of L) that is not coordinated to the metal. The other two signals can be assigned to the P atoms of  $\eta^2$ -L and  $\eta^1$ -L(O), respectively. The <sup>1</sup>H NMR spectrum in CDCl<sub>3</sub> displays four multiplets at 3.68, 3.73, 4.17 and 4.49 ppm with an integral ratio 1:1:1:1. These signals correspond to the  $CH_2$  groups of the two ligands. The 2D <sup>1</sup>H, <sup>1</sup>H COSY and the 2D <sup>1</sup>H, <sup>31</sup>P HMQC spectra allow full assignment of those signals (see Exp. Sect.). The FAB mass spectrum contains peaks at mass values for fragments of dinuclear species  $[M^+ - Cl - L(O)]$ ,  $[M^+ - 2Cl - L(O)]$ ,  $[M^+ - 2Cl - 2L(O)]$  and, interestingly, the strongest fragment was found at 1013, which corresponds exactly to the monomeric unit [RuClLL(O)]. Finally, treatment of a sample of 3 with excess NaBPh<sub>4</sub> in ethanol resulted in the precipitation of a new product, 3'. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of this compound contains two sets of signals: three pseudotriplets integrating in a 1:1:1 ratio, and a triplet and a doublet integrating in a 1:2 ratio (the first set integrates to three times the second one) coexisting with traces of the original compound (very small signals at 159 and 138 ppm). When the sample in the NMR tube was stored for five days, evidence was observed that the reaction had gone backwards and the small signals had increased in intensity to levels similar to those observed at the beginning of the experiment.

All these data suggest the formation of neutral edgesharing bioctahedra with two chloro bridges [{RuCl( $\eta^2$ -L)[ $\eta^1$ -L(O)]}<sub>2</sub>( $\mu$ -Cl)<sub>2</sub>] for compound **3** and this converts into the cationic face-sharing bioctahedral compound **3**' by reaction with NaBPh<sub>4</sub> – as depicted in Scheme 5.



Scheme 5.

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#### Reaction of 2 with L' $[L' = PPh_{3-n}(OEt)_n; n = 1-3]$

In an effort to complement the results described above and to gather more information about the reactivity of complex **2**, we investigated the reaction of **2** with the monodentate phosphinite, phosphonite and phosphite ligands of formulae  $PPh_{3-n}(OEt)_n$  (n = 1-3) (L'). Unexpectedly, different results were obtained when L' was changed from a phosphinite (n = 1) to a phosphite (n = 3).

## $L' = PPh_2(OEt) - Preparation of [ {RuCl(\eta^2 - L)[PPh_2(OEt)]_2}_2(\mu - Cl)_2] (4)$

When a mixture of 2 and PPh<sub>2</sub>(OEt) in a 1:2 molar ratio was heated under reflux in toluene for 1 h, the new compound [{RuCl( $\eta^2$ -L)[PPh<sub>2</sub>(OEt)]<sub>2</sub>}<sub>2</sub>( $\mu$ -Cl)<sub>2</sub>] (4) was obtained. Compound 4 shows spectral features that are very similar to those of compound 3. The  ${}^{31}P{}^{1}H{}$  NMR spectrum shows a doublet at  $\delta = 159.7$  ppm and a triplet at  $\delta =$ 136.3 ppm (integrating to 2:1, J = 46 Hz), which are very similar to the signals of 3. The <sup>1</sup>H NMR spectrum also contains a set of signals that is consistent with this formulation. The signals at 4.31 (m, 4 H) and 3.86 (m, 4 H) ppm can be assigned to the -CH2- groups of the bidentate ligand L, and those at 3.50 (m, 4 H) and 1.22 (t, 6 H) can be assigned to the ethoxy group of L'. The FAB mass spectrum of 4 displays (as observed for compound 3) peaks that indicate the dinuclear nature of the compound: 1630  $(M^+ - Cl)$ , 1435  $(M^+ - L')$ , 1400  $(M^+ - L' - Cl)$ , 830 [RuCl<sub>2</sub>LL']<sup>+</sup>, 797 [RuClLL']<sup>+</sup>.

Treatment of a sample of **4** with excess NaBPh<sub>4</sub> in ethanol gave similar results to those obtained in the case of complex **3**, with a new dinuclear face-shared bioctahedral complex, **4'**, formed as a mixture of both *cisoid* and *transoid* isomers.<sup>[13]</sup> However, in this case the proportion of the *transoid* isomer for the face-shared bioctahedra is significantly greater than in the case of compound **3**. In agreement

with this situation, the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of 4' in CDCl<sub>3</sub> displays three pseudotriplets at 134.1, 141.9 and 145.7 ppm (corresponding to a *transoid* isomer) along with a doublet at  $\delta = 143.3$  ppm (the triplet is probably obscured by the signal at  $\delta = 134.1$  ppm) that corresponds to the *cisoid* form.

### $L' = PPh(OEt)_2 - Preparation of [ {Ru(\eta^2-L) [PPh(OEt)_2]}_2(\mu-Cl)_3]Cl (5)$

When a mixture of 2 and  $PPh(OEt)_2$  in a 1:2 molar ratio was heated under reflux in toluene for 1.5 h, we obtained a solid with <sup>31</sup>P{<sup>1</sup>H} and <sup>1</sup>H NMR spectra consistent with a mixture (approx. 1:3) of both cisoid and transoid isomers of the cationic trichloro-bridged dinuclear compound [{ $Ru(\eta^2 -$ L)[PPh(OEt)<sub>2</sub>] $_{2}(\mu$ -Cl)<sub>3</sub>]Cl (5) (see Scheme 1). The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum displays a doublet at  $\delta = 151.7$  ppm and a triplet at  $\delta = 158.2$  ppm (J = 53 Hz) (*cisoid* isomer) and three pseudotriplets at 149.7, 153.0 and 156.1 ppm (transoid isomer). Careful inspection of the <sup>1</sup>H NMR spectrum also enables the signals of both isomers to be assigned (see Exp. Sect.). The mass spectrum shows the  $[M^+]$  peak at m/z =1567, which is consistent with a dinuclear formulation. Moreover, treatment of a solution of this complex with excess NaBPh<sub>4</sub> in ethanol gave a tan solid with spectral features identical to those of the original product, thus confirming its ionic nature. We were also able to obtain suitable crystals for an X-ray diffraction study. The structure of the complex cation and the most relevant distances and angles are shown in Figure 4 and in Tables 2 and 3, respectively.

It can be seen that the cation complex 5a adopts a *transoid* [dihedral torsion angle P(1)–Ru(1)–Ru(2)–P(2) of 115.5(2)°] triply chloride-bridged diruthenium structure similar to 2a (Figure 5). The coordination geometry around each metal centre is a distorted octahedron, with the same coordination sphere at each ruthenium atom (three bridging chlorine atoms and three phosphorus atoms). The two met-



Figure 4. The cation of  $[{Ru(\eta^2-L)[PPh(OEt)_2]}_2(\mu-Cl)_3]Cl$  (5a) drawn at 20% probability level. The phenyl rings were replaced by spheres of arbitrary radius.

Bond lengths			-
Ru(1)–Cl(3)	2.478(3)	Ru(1)–Cl(4)	2.482(2)
Ru(1)–Cl(2)	2.535(3)	Ru(1) - P(1)	2.241(3)
Ru(1)–P(12)	2.261(3)	Ru(1) - P(11)	2.274(3)
Ru(2)–Cl(3)	2.495(3)	Ru(2)-Cl(2)	2.511(3)
Ru(2)–Cl(4)	2.473(2)	Ru(2)-P(2)	2.253(3)
Ru(2)–P(21)	2.284(3)	Ru(2)–P(22)	2.265(3)
Ru(2)–Ru(1)	3.4417(12)		
Bond angles			
P(1)–Ru(1)–P(12)	89.78(12)	P(1)–Ru(1)–P(11)	93.54(11)
P(12)-Ru(1)-P(11)	89.89(11)	P(1)-Ru(1)-Cl(3)	95.13(11)
P(12)-Ru(1)-Cl(3)	94.82(11)	P(11)-Ru(1)-Cl(3)	170.14(10)
P(1)-Ru(1)-Cl(4)	169.52(10)	P(12)-Ru(1)-Cl(4)	99.34(10)
P(11)-Ru(1)-Cl(4)	91.65(10)	P(1)-Ru(1)-Cl(2)	93.28(11)
P(12)-Ru(1)-Cl(2)	171.16(11)	P(11)-Ru(1)-Cl(2)	98.19(11)
Cl(3)-Ru(1)-Cl(2)	76.66(9)	Cl(4) - Ru(1) - Cl(2)	76.95(8)
Cl(3)-Ru(1)-Cl(4)	79.05(8)	P(2)-Ru(2)-P(22)	94.45(11)
P(2)-Ru(2)-P(21)	90.66(11)	P(22)-Ru(2)-P(21)	90.05(10)
P(2)-Ru(2)-Cl(4)	94.10(10)	P(22)-Ru(2)-Cl(4)	170.80(10)
P(21)-Ru(2)-Cl(4)	93.22(9)	P(2)-Ru(2)-Cl(3)	168.04(11)
P(22)-Ru(2)-Cl(3)	92.09(10)	P(21)-Ru(2)-Cl(3)	99.34(10)
P(2)-Ru(2)-Cl(2)	92.30(11)	P(22)-Ru(2)-Cl(2)	98.72(10)
P(21)-Ru(2)-Cl(2)	170.49(9)	Cl(4)-Ru(2)-Cl(2)	77.56(8)
Cl(3)-Ru(2)-Cl(2)	76.80(9)	Cl(4)-Ru(2)-Cl(3)	78.90(8)
Ru(2)-Cl(2)-Ru(1)	86.02(8)	Ru(1)-Cl(3)-Ru(2)	87.59(9)
Ru(2)- $Cl(4)$ - $Ru(1)$	87.99(8)		

Table 2. Selected bond lengths [Å] and angles  $[\circ]$  for complex cation **5a**.

Table 3. Hydrogen bonding parameters for complex cation 5a [Å and °].

D–H···A	<i>d</i> (D–H)	<i>d</i> (H···A)	<i>d</i> (D····A)	blab- la(DHA)
C(3)–H(3B)····Cl(1A)	0.97	2.79	3.500(9)	131.1
C(1)–H(1A)····Cl(1)	0.97	2.93	3.586(10)	125.7
$C(2)-H(2A)\cdots Cl(1)$	0.97	2.89	3.610(10)	131.3

als maintain the same oxidation state (+II) as a disordered chloride ion is acting as a counterion. Two of the phosphorus atoms coordinated to each metal atom come from the bidentate phosphinite ligand L, and the third one comes from the monodentate ligand L'. In contrast to complex **2a**, the environment around each ruthenium atom is quite similar, with similar values for bond lengths and angles. The Ru–P bonds are slightly shorter, by 0.01 Å, when the ligand is the monodentate phosphonite ligand. The Ru–Cl bond lengths range from 2.473(2) to 2.535(3) Å, with the longer ones corresponding to those including the labelled Cl(2) atom, the only one that is simultaneously *trans* to two phosphinite phosphorus atoms. The Ru(1)–Cl(2)–Ru(2) angle, 86.02(8)°, is also the most acute of the three Ru–Cl–Ru angles.

The seven-membered chelate rings allows P–Ru–P angles of 89.89(11) and  $90.05(10)^\circ$ , which are virtually identical to one another and similar to those found in **2a**. The Cl–Ru–Cl angles involving the triple bridge have values between 76.66(9) and 79.05(8)° and once again this is the main source of distortion of the octahedron. The Ru–Ru separation of 3.4417(12) Å is in the upper limit of the range ex-



Figure 5. Environment of the Ru atoms in the complex cation 5a.

pected for this type of dinuclear  $Ru^{II}$  complex, 3.28–3.44 Å.<sup>[12a]</sup>

# $L' = P(OEt)_3 - Preparation of [RuCl_2(\eta^2-L) \{P(OEt)_3\}_2]$ (6)

When a mixture of 2 and  $P(OEt)_3$  in a 1:2 molar ratio was heated under reflux in toluene for 1 h, we obtained a solid that has NMR features consistent with a mononuclear species of formula  $[RuCl_2(\eta^2-L){P(OEt)_3}_2]$  (6), in which one bidentate ligand and two phosphite ligands (mutually cis) are present. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum consists of four double doublets of doublets at 97.8 (P1), 122.0 (P4), 129.8 (P<sub>2</sub>) and 150.7 (P<sub>3</sub>) ppm ( $J_{12} = 48$ ,  $J_{13} = 24$ ,  $J_{14} =$ 544,  $J_{23} = 47$ ,  $J_{24} = 64$  and  $J_{34} = 46$  Hz). The <sup>1</sup>H NMR spectrum displays two triplets at  $\delta = 0.90$  and 1.22 ppm (J = 7 Hz), which integrate to 9 protons each, and these signals can be assigned to the methyl groups of L'. These signals demonstrate the nonequivalence of the two ligands. The signals corresponding to the methylene protons of both L and L' appear as seven multiplets of different intensity. These signals were fully characterised by 2D  $^{1}H$ ,  $^{13}C{^{1}H}$ HSQC correlation (see Figure 6). The methylene protons of the bidentate ligand L appear as four multiplets at 3.43, 3.98, 4.40 and 5.67 ppm, integrating to one proton each. On the other hand, the methylene protons of both L' ligands appear as four multiplets centred at 3.26, 3.43, 4.23 and 4.46 and these signals integrate to three protons each because of the nonequivalence of the two L' ligands and the diastereotopic nature of each pair of geminal CH<sub>2</sub> protons.

Crystals suitable for X-ray analysis were obtained. The structure of the complex is shown in Figure 7 and the most relevant distances and angles are given in Table 4. The compound consists of discrete units in which the ruthenium atom is in a slightly distorted octahedral environment, coordinated to two mutually *cis* chlorine atoms, two phosphorus atoms of a diphosphinite ligand and two phosphorus atoms of two monodentate phosphite ligands, which are also mutually *cis*. The *cis* angles range from 84.78(5) to 97.28(6)°, with the latter value corresponding to the chelate angle allowed by the seven-membered chelate ring. The *trans* angles range from 170.42(6) to 177.02(6)° and these show the regu-



Figure 6. 2D <sup>1</sup>H,<sup>13</sup>C{<sup>1</sup>H} HSQC experiment in CDCl<sub>3</sub> for compound **6**. Signals in the <sup>13</sup>C spectrum can be assigned as follows:  $\delta$  = 65.9, 62.6 (br. s, CH<sub>2</sub>, L), 62.9, 61.9 (d,  $J_{CP}$  = 10 Hz, CH<sub>2</sub>, L'). Signals marked with an asterisk correspond to an impurity.

larity of the octahedron, which is probably only distorted due the steric hindrance of the diphosphinite ligand. The *cis* Cl–Ru–Cl angle, 86.81(5)°, is similar to those found in *cis* complexes RuCl<sub>2</sub>P<sub>4</sub>.<sup>[14]</sup> The Ru–Cl distances are similar to one another but the Ru–P distances show small differences in the order Ru–P4 < Ru–P1 < Ru–P3 < Ru–P2. This order is consistent with the greater *trans* influence of phosphorus ligands than Cl and the higher  $\pi$ -acceptor character of phosphite ligands as compared with phosphinites.

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Table 4. Selected bond lengths [Å] and angles [°] for complex 6.					
Bond lengths					
Ru–P(4)	2.2333(17)	Ru-P(1)	2.2777(15)		
Ru-P(3)	2.3040(17)	Ru-P(2)	2.4406(16)		
Ru-Cl(2)	2.4633(15)	Ru–Cl(1)	2.4675(15)		
Bond angles					
P(4)-Ru-P(1)	93.48(6)	P(4)–Ru–P(3)	91.09(6)		
P(1)-Ru-P(3)	92.24(6)	P(4)-Ru-P(2)	89.36(6)		
P(1)-Ru-P(2)	97.28(6)	P(3)-Ru-P(2)	170.42(6)		
P(4)-Ru-Cl(2)	177.02(6)	P(1)-Ru- $Cl(2)$	85.91(5)		
P(3)-Ru-Cl(2)	91.85(6)	P(2)-Ru-Cl(2)	87.82(5)		
P(4)– $Ru$ – $Cl(1)$	93.95(5)	P(1)-Ru- $Cl(1)$	172.04(6)		
P(3)-Ru-Cl(1)	84.78(5)	P(2)-Ru- $Cl(1)$	85.65(5)		
Cl(2)-Ru-Cl(1)	86.81(5)				

#### Reaction of [RuCl<sub>2</sub>(DMSO)<sub>4</sub>] with L in a 1:2 Molar Ratio

A mixture of [RuCl<sub>2</sub>(DMSO)<sub>4</sub>] and L in a 1:2 molar ratio was heated under reflux in toluene for 2 h and the progression of the reaction was followed by <sup>31</sup>P NMR spectroscopy. A complicated spectrum was observed with different sets of signals, suggesting the presence of a mixture of several new compounds. The solution was evaporated to dryness and the residue was treated with Et<sub>2</sub>O. An orange solid and a yellow solution were obtained. The solid was filtered off, washed with Et<sub>2</sub>O and dried to afford the same compound, [{RuCl( $\eta^2$ -L)[ $\eta^1$ -Ph<sub>2</sub>PO(CH<sub>2</sub>)<sub>2</sub>OP(O)Ph<sub>2</sub>]}<sub>2</sub>( $\mu$ -Cl)<sub>2</sub>] (**3**), as was already obtained in the reaction of complex **2** with L.<sup>[15]</sup> The yellow solution was purified by column chromatography to yield the two new compounds [RuCl<sub>2</sub>(L)(Ph<sub>2</sub>POPPh<sub>2</sub>)] (**7**) and [RuCl(CO)(L)(Ph<sub>2</sub>PO-



Figure 7. ORTEP representation of complex  $[RuCl_2(\eta^2-L){P(OEt)_3}_2]$  (6) drawn at the 30% probability level. The phenyl rings were replaced by spheres of arbitrary radius.

 $CH_2$ ] (8) (see Exp. Sect. for details). We were able to obtain single crystals of both compounds that were suitable for X-ray analysis.

### $[RuCl_2(L)(Ph_2POPPh_2)] (7)$

The reaction probably involves a metal-promoted disruption of the bidentate ligand to tetraphenyldiphosphoxane,<sup>[16]</sup> although in a somewhat similar reaction between  $[Rh(COE)_2Cl]_2$  (COE = cyclooctene) and P(NMe<sub>2</sub>)<sub>3</sub> in toluene, the generation of a diphosphoxane complex was attributed to a hydrolysis impurity present in the commercial P(NMe<sub>2</sub>)<sub>3</sub>.<sup>[17]</sup> This is probably not the situation in our case because we did not observe such a process in reactions between the same ligand and other metals such as Re and Mn.<sup>[18]</sup> Other authors have observed the same product (POP) and suggested a P-P(O) to P-O-P thermal rearrangement prior to metal coordination,<sup>[19]</sup> a process that is favoured when R groups bonded to P are inductively electron-withdrawing groups like OR groups (as in our case). A likely mechanism involves partial hydrolysis of the ligand due to the prolonged heating and the presence of adventitious moisture, followed by a tautomeric rearrangement from the P-P(O) to the P-O-P form.

The <sup>1</sup>H NMR spectrum of 7 in CDCl<sub>3</sub> shows a multiplet centred at  $\delta = 4.30$  ppm, which is assigned to the methylene protons of the bidentate diphosphinite ligand, and signals between 6.90 and 7.50 ppm corresponding to the phenyl groups of the two chelating ligands. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum in CDCl<sub>3</sub> shows two doublets of multiplets centred at  $\delta = 106.8$  and 133.0 ppm, corresponding to the two phosphorus nuclei of each bidentate ligand. The signal at lower field can be assigned to the bisphosphinite ligand L (as shown in the 2D <sup>1</sup>H, <sup>31</sup>P{<sup>1</sup>H} HMBC correlation experiment by the cross-peak present with the methylene signal of L at  $\delta = 4.30$  ppm, see Supporting Information) and the multiplet at  $\delta = 106.8$  ppm can be assigned to the phosphorus nuclei of the tetraphenyldiphosphoxane ligand. The IR spectrum contains a strong band at 791 cm<sup>-1</sup> and this is assigned to the P–O–P asymmetric stretching mode in accordance with its chelating nature (reported values of 775–800 cm<sup>-1</sup>).<sup>[16,20]</sup>

An ORTEP view of compound 7 is shown in Figure 8 along with the labelling scheme. Selected distances and angles are given in Table 5. The compound consists of discrete units, although some intermolecular nonclassical Cl···HC hydrogen bonds can be found (Table 6). The ruthenium atom is in a distorted octahedral environment and is coordinated to two chlorine atoms that are mutually *trans*, two phosphorus atoms of a tetraphenyldiphosphoxane ligand and two phosphorus atoms of a diphosphinite ligand.

Table 5. Bond lengths [Å] and angles [°] for compound 7.

Bond lengths			
Ru(1)–P(2)	2.3271(7)	Ru(1)–P(1)	2.3423(7)
Ru(1) - P(3)	2.3783(7)	Ru(1) - P(4)	2.4119(7)
Ru(1)-Cl(1)	2.4237(7)	Ru(1)-Cl(2)	2.4280(7)
O(1)–P(4)	1.6593(17)	O(1)–P(3)	1.6652(17)
Bond angles			
P(1)-Ru(1)-P(2)	92.43(3)	P(3)-Ru(1)-P(4)	66.37(2)
P(2)-Ru(1)-P(3)	98.56(2)	P(1)-Ru(1)-P(4)	102.76(3)
P(1)-Ru(1)-P(3)	168.91(2)	P(2)-Ru(1)-P(4)	164.42(3)
P(2)-Ru(1)-Cl(1)	98.32(3)	P(1)-Ru(1)-Cl(1)	92.53(3)
P(3)-Ru(1)-Cl(1)	84.41(2)	P(4)-Ru(1)-Cl(1)	84.58(2)
P(2)-Ru(1)-Cl(2)	90.25(3)	P(1)-Ru(1)-Cl(2)	87.69(3)
P(3)-Ru(1)-Cl(2)	93.75(3)	P(4)-Ru(1)-Cl(2)	86.99(2)
Cl(1)-Ru(1)-Cl(2)	171.40(2)	P(4)–O(1)–P(3)	104.14(9)



Figure 8. ORTEP drawing of the complex [RuCl<sub>2</sub>(L)(Ph<sub>2</sub>POPPh<sub>2</sub>)] (7).

The four phosphorus atoms are located in the equatorial plane (rms = 0.057). The chelate ring angle of the tetraphenyldiphosphoxane ligand is only 66.37(2)° and is the main source of distortion. To the best of our knowledge, this is the first example of a ruthenium complex with this type of chelating ligand, but the chelate angle is similar to that found in the chromium, molybdenum and rhodium complexes.<sup>[17,21]</sup> The chelate angle allowed by the sevenmembered chelate ring is close to the theoretical value of 90° [92.43(3)°] and, consequently, the other two angles in the equatorial plane increase to 98.56(2) and  $102.76(3)^{\circ}$ . The trans Cl-Ru-Cl angle is also slightly different than the expected value of  $180^{\circ}$  [171.40(2)°] and this is due to a small deviation of the chlorine atom labelled as Cl(1), as shown by the P-Ru-Cl angles. The four-membered chelate ring is almost planar, with the O(1) atom only 0.103(2) Å out of the P(3)-Ru-P(4) plane.

Table 6. Hydrogen bond parameters for 7 [Å and °].<sup>[a]</sup>

<i>d</i> (D–H)	<i>d</i> (H•••A)	<i>d</i> (D•••A)	blab- la(DHA)
0.97	2.61	3.397(3)	138.8
0.93	2.61	3.234(3)	124.8
0.93	2.69	3.506(3)	147.2
0.93	2.69	3.302(3)	124.3
0.93	2.82	3.423(3)	123.8
0.93	2.87	3.738(3)	156.5
	d(D-H) 0.97 0.93 0.93 0.93 0.93 0.93 0.93	d(D-H)         d(H···A)           0.97         2.61           0.93         2.69           0.93         2.69           0.93         2.69           0.93         2.82           0.93         2.87	d(D-H)         d(H···A)         d(D···A)           0.97         2.61         3.397(3)           0.93         2.61         3.234(3)           0.93         2.69         3.506(3)           0.93         2.69         3.302(3)           0.93         2.82         3.423(3)           0.93         2.87         3.738(3)

[a] Symmetry transformations used to generate equivalent atoms: 1 - x, y + 1/2, 1/2 - z.

The angle P(4)-O(1)-P(3) has a value of  $104.14(9)^{\circ}$ , which is slightly less acute than those reported for the aforementioned complexes.<sup>[17,21]</sup> The ruthenium atom is only 0.0184(4) Å out of the equatorial plane defined by the four phosphorus atoms (rms = 0.057). The plane defined by the two phosphorus atoms and the two oxygen atoms of the diphosphinite ligand (rms = 0.088) forms a dihedral angle with the equatorial plane of 41.73(6)°. However, the plane P(3)–Ru–P(4) forms a dihedral angle of only  $6.00(7)^\circ$  with the equatorial plane and can essentially be considered as coplanar [the oxygen atom O(1) is only 0.096(2) Å out of the equatorial plane].

### $[RuCl(CO)(L)(Ph_2POCH_2)] (8)$

Compound 8 has a surprising structure in which the ruthenium centre is coordinated by an intact ligand L, Cl and CO ligands, and an anionic fragment Ph<sub>2</sub>POCH<sub>2</sub><sup>-</sup> of this ligand. This arrangement stabilises, in spite of the strain, a ruthena-phospha-oxa-cyclobutane ring. As the only source of CO is the bis(phosphinite) L ligand, and we did not observe similar behaviour for L with other metals,<sup>[18]</sup> these fragments must come from a metal-promoted disruption of the bidentate ligand. Moreover, although the yields are low, the reaction is perfectly reproducible. The complex was characterised in solution by multinuclear NMR spectroscopy. The  ${}^{31}P{}^{1}H{}$  NMR spectrum of 8 in CDCl<sub>3</sub> shows three doublet of doublets, which is consistent with a structure presenting two mutually *trans* phosphorus atoms [one on the Ph<sub>2</sub>POCH<sub>2</sub><sup>-</sup> fragment ( $\delta$  = 76.0 ppm) and one on the L ligand ( $\delta$  = 133.3 ppm),  $J_{trans}$  = 341 Hz] and the other in a *cis* disposition ( $\delta = 131.5$  ppm),  $J_{cis} = 14$  and 31 Hz. The <sup>1</sup>H NMR spectrum of 8 in CDCl<sub>3</sub> shows two groups of multiplets, one in the range 3.80-4.80 ppm that integrates to six protons and corresponds to the methylene groups of the two ligands, and other between 7.20-7.80 (30 H) that corresponds to the phenyl groups. An HMBC  ${}^{31}P{}^{1}H{}^{-1}H$  correlation enabled identification of the dif-



Figure 9. ORTEP drawing of complex 8.

ferent proton signals, showing that the multiplets at  $\delta = 3.97$ and 4.77 ppm (integrating to 2 protons each) can be assigned to the methylene groups of L, and the multiplets at  $\delta = 4.52$  and 4.68 ppm (integrating to one proton each) correspond to the CH<sub>2</sub> group bonded to the ruthenium. This observation shows that these two protons are diastereotopic.

An ORTEP view of compound 8 is shown in Figure 9 along with the labelling scheme. Selected distances and angles are given in Table 7. The compound consists of discrete units, although some intermolecular nonclassical Cl···HC hydrogen bonds can be found (see Table 8). The ruthenium atom is in a distorted octahedral environment, coordinated to one chlorine atom, two phosphorus atoms of a diphosphinite ligand, one phosphorus atom, a carbon atom of the diphenyl(oxymethyl- $\kappa C$ )phosphinite- $\kappa P$  ligand and a carbon atom of a carbonyl ligand. Two of the ligands act as bidentate systems (diphosphinite and phosphinite ligand) and these can be considered to be in the equatorial plane. The four-membered chelate ring is one of the main sources of distortion in the octahedron, with an angle of  $62.9(3)^{\circ}$ . The opposite seven-membered chelate angle in the equatorial plane is slightly larger than one would expect for this ligand, 93.59(9)°, but the two adjacent angles in the equatorial plane do not increase to the same extent [P(1)- $Ru(1)-P(3) = 110.85(9)^{\circ}, C(1)-Ru(1)-P(2) = 92.4(3)^{\circ}$ ]. The differences found in these angles are due to the steric effects of the phenyl rings on the phosphorus atoms. For the same reason, all the axial angles in the octahedron are close to the expected 180°, except for the P(2)-Ru(1)-P(1) angle [155.26(9)°]. The plane formed by the four atoms in the chelate ring (rms = 0.069) forms a dihedral angle of only  $7.2(2)^{\circ}$  with the equatorial plane of the donor atoms (rms = 0.047). The ruthenium atom is only 0.096(3) Å out of this plane.

Table 7. Selected bond lengths [Å] and angles [°] for complex 8.

Bond lengths			
Ru(1)–C(2)	1.835(11)	Ru(1)–C(1)	2.181(10)
Ru(1)-P(2)	2.336(3)	Ru(1) - P(1)	2.346(3)
Ru(1) - P(3)	2.378(3)	Ru(1)-Cl(1)	2.467(2)
P(1)–O(1)	1.582(6)	O(1)–C(1)	1.465(11)
Bond angles		·	
C(2)-Ru(1)-C(1)	89.8(4)	C(2)–Ru(1)–P(2)	91.9(3)
C(1)-Ru(1)-P(2)	92.4(3)	C(2)-Ru(1)-P(1)	88.8(3)
C(1)-Ru(1)-P(1)	62.9(3)	P(2)-Ru(1)-P(1)	155.26(9)
C(2)-Ru(1)-P(3)	97.3(3)	C(1)-Ru(1)-P(3)	170.5(3)
P(2)-Ru(1)-P(3)	93.59(9)	P(1)-Ru(1)-P(3)	110.85(9)
C(2)-Ru(1)-Cl(1)	174.0(3)	C(1)-Ru(1)-Cl(1)	84.3(3)
P(2)-Ru(1)-Cl(1)	87.09(8)	P(1)-Ru(1)-Cl(1)	89.60(8)
P(3)-Ru(1)-Cl(1)	88.64(8)	O(2)–C(2)–Ru(1)	176.2(9)

To the best of our knowledge, the diphenyl(oxymethyl- $\kappa C$ )phosphinite- $\kappa P$  ligand has only previously been found to show this behaviour in the manganese complex tetracarbonyl-2,2-diphenyl-1-oxa-2-phospha-3-manganacyclobutane.<sup>[22]</sup>

Table 8. Hydrogen-bonding parameters for complex 8 [Å and °].<sup>[a]</sup>

D–H•••A	d(D–H)	<i>d</i> (H•••A)	<i>d</i> (D····A)	blab- la(DHA)
C(43)-H(43)-Cl(1')	0.93	2.95	3.743(10)	143.8
C(36)–H(36)····O(4)	0.93	2.48	2.854(11)	104.1
C(56)-H(56)···O(3)	0.93	2.46	2.871(11)	107.2

[a] Symmetry transformations used to generate equivalent atoms: ' x - 1, y, z.

### Conclusions

New dinuclear ruthenium complexes bearing the 1,2bis(diphenylphosphinite)ethane ligand in different proportions were prepared and characterised. The compounds  $[Ru_2(\mu-Cl)_3(DMSO)_3Cl(\eta^2-L)]$  (1) and  $[Ru_2(\mu-Cl)_3(DMSO) Cl(\eta^2-L)_2$  (2) present a face-sharing bioctahedral structure while compound  $[Ru_2Cl_2(\eta^2-L)_2\{\eta^1-L(O)\}_2(\mu-Cl)_2]$  (3) has an edge-sharing bioctahedral structure with two chelating L units and two monodentate ligands in which a phosphorus atom is oxidised and remains uncoordinated. Reaction of compound 2 [a mixture of both cisoid (2a, minor component) and *transoid* (2b, major component) isomers] with the monodentate ligands  $PPh_{3-n}(OEt)_n$  (n = 1-3) (L') affords different compounds depending on the structure of L'. When L' is structurally similar to L (both phosphinites), the resulting compound is the dinuclear doubly chlorobridged complex [{RuCl( $\eta^2$ -L)(L')}( $\mu$ -Cl)<sub>2</sub>] (4), which is very similar to compound 3 – obtained by reacting compound 2 with L. Reaction of compound 2 with the phosphonite L' (n = 2) gave the face-sharing octahedral compound  $[{Ru(\eta^2-L)(L')}_2(\mu-Cl)_3]Cl$  (5) as a mixture of both cisoid (5a) and transoid (5b) isomers. On the other hand, when L' is a phosphite (n = 3) the reaction with compound 2 yields the mononuclear compound  $[RuCl_2(\eta^2-L)(L')_2]$  (6). Finally, compound 3 can also be obtained by reaction of  $[RuCl_2(DMSO)_4]$  with L, but in this case two more products with formulae  $[RuCl_2(L)(Ph_2POPPh_2)]$  (7) and  $[RuCl(CO)(L)(Ph_2POCH_2)]$  (8) were also obtained. In these products a chelating diphosphinite L coexists with new phosphorus ligands formed in situ by metal-mediated disruptions of L.

### **Experimental Section**

**General:** All experimental manipulations were carried out under argon using Schlenk techniques. All solvents were purified by conventional procedures<sup>[23]</sup> and distilled prior to use. [RuCl<sub>2</sub>-(DMSO)<sub>4</sub>]<sup>[24]</sup> and 1,2-bis(diphenylphosphanyloxy)ethane<sup>[18c]</sup> were prepared using published methods. All the other chemicals were commercial products and were used as received without further purification. 1D and 2D NMR spectra ( $\delta$ , ppm) were recorded in CDCl<sub>3</sub>, CD<sub>2</sub>Cl<sub>2</sub> or C<sub>6</sub>D<sub>6</sub> (as indicated) with a Bruker ARX-400 spectrometer (161 MHz for <sup>31</sup>P{<sup>1</sup>H}, 100 MHz for <sup>13</sup>C{<sup>1</sup>H}, 400 MHz for <sup>1</sup>H) using the solvent as the internal lock. <sup>31</sup>P{<sup>1</sup>H} chemical shifts are referred to 85% H<sub>3</sub>PO<sub>4</sub> with downfield values reported as positive. <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} signals are referred to residual protonated solvents as internal standards. IR spectra of samples in KBr pellets were obtained with a Bruker Vector IFS28 FT spectrophotometer. Mass spectra were recorded with a Micromass Autospec M LSIMS (FAB<sup>+</sup>) system with 3-nitrobenzyl alcohol as matrix. Microanalyses were carried out with a Fisons EA-1108 apparatus. Merck silica gel 60 (0.040-0.063 mm) was used for column chromatography.

Synthesis of [Ru<sub>2</sub>( $\mu$ -Cl)<sub>3</sub>(DMSO)<sub>3</sub>Cl(L)] (1): A solution of L (2.0 mL, 0.56 mmol) in toluene was added to a solution of [RuCl<sub>2</sub>(DMSO)<sub>4</sub>] (0.5 g, 1.03 mmol) in toluene (20 mL). The solution was heated under reflux for 1/2 h, cooled to room temperature and concentrated under vacuum. The residue was treated with EtOH to give a yellow solid, which was washed with EtOH and dried under vacuum. Yield: 0.40 g (77%). C<sub>32</sub>H<sub>42</sub>Cl<sub>4</sub>O<sub>3</sub>P<sub>2</sub>Ru<sub>2</sub>S<sub>3</sub> (108.77): calcd. C 38.10, H 4.20, S 9.54; found C 37.97, H 4.19, S 9.50. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 3.04 (s, 6 H, DMSO), 3.12 (s, 6 H, DMSO), 3.43 (s, 6 H, DMSO), 3.72 (m, 2 H, CH<sub>2</sub>), 4.26 (m, 2 H, CH<sub>2</sub>), 7.29 (m, 12 H, Ph), 7.49 (m, 4 H, Ph), 7.78 (m, 4 H, Ph). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  = 158.2 (s). IR (KBr):  $\nu$ (SO) 1093 (s) cm<sup>-1</sup>. FAB<sup>+</sup>/MS: *m*/*z* (calculated for the most abundant isotopes) = 1010, (M<sup>+</sup>), 975 (M<sup>+</sup> - Cl), 932 (M<sup>+</sup> - DMSO), 776 (M<sup>+</sup> - 3DMSO), 741 (M<sup>+</sup> - 3DMSO - Cl), 602 [RuCl<sub>2</sub>L]<sup>+</sup>.

Synthesis of [Ru<sub>2</sub>(µ-Cl)<sub>3</sub>(DMSO)Cl(L)<sub>2</sub>] (2): Method (a): A solution of L (1.8 mL, 0.50 mmol) in toluene was added to a solution of 1 (0.50 g, 0.49 mmol) in toluene (20 mL). The solution was heated under reflux for 1/2 h and then cooled to room temperature. The solvent was removed under vacuum and EtOH was added to the oily residue. The resulting yellow precipitate was filtered off, washed with EtOH and dried under vacuum. Yield: 0.43 g (68%). Method (b): A solution of L (4.0 mL, 1.14 mmol) in toluene was added to a solution of [RuCl<sub>2</sub>(DMSO)<sub>4</sub>] (0.5 g, 1.03 mmol) in toluene (20 mL). The reaction mixture was heated under reflux for 1 h and then cooled to room temperature. The solvent was removed under vacuum and EtOH was added to the oily residue. The resulting yellow precipitate was filtered off, washed with EtOH and dried under vacuum. Yield: 0.39 g (59%). C54H54Cl4O5P4Ru2S (1282.92): calcd. C 50.55, H 4.24, S 2.50; found C 50.32, H 4.26, S 2.55. <sup>1</sup>H NMR (CDCl<sub>3</sub>) (intensity ratio 1:4 *cisoid/transoid* isomers):  $\delta$  = 2.54 (s, 3 H, CH<sub>3</sub>'SO, transoid), 2.87 (s, 3 H, CH<sub>3</sub>''SO, transoid), 3.22 (s, 6 H, DMSO, cisoid), 3.57-4.13 [m, (5 H, CH<sub>2</sub>, transoid + 5 H, CH<sub>2</sub>, cisoid)], 4.33 [m, (1 H, CH<sub>2</sub>, transoid + 1 H, CH<sub>2</sub>, cisoid)], 4.50 (m, 1 H, CH<sub>2</sub>, cisoid), 4.59 (m, 1 H, CH<sub>2</sub>, cisoid), 4.76 (m, 1 H, CH<sub>2</sub>, transoid), 4.90 (m, 1 H, CH<sub>2</sub>, transoid), 6.80-8.30 [m, (40 H, Ph, *cisoid* + 40 H, Ph, *transoid*)] ppm.  ${}^{31}P{}^{1}H$ NMR (CDCl<sub>3</sub>):  $\delta$  = 146.4 (s, *cisoid*), 148.3 (q, J<sub>AB</sub> = 44 Hz, transoid), 151.9 (d,  $J_{AX}$  = 55 Hz), 156.9 (s, cisoid), 160.7 (d, J = 55 Hz, transoid) ppm. C<sub>54</sub>H<sub>54</sub>Cl<sub>4</sub>O<sub>5</sub>P<sub>4</sub>Ru<sub>2</sub>S: calcd. C 50.55, H 4.24, S 2.50; found C 49.82, H 4.28, S 2.67. FAB+/MS: m/z (calculated for the most abundant isotopes) 1284 (M<sup>+</sup>), 1249 (M<sup>+</sup> - Cl), 1206 (M<sup>+</sup> – DMSO). X-ray quality crystals were obtained by slow evaporation of a CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O (1:10 v/v) solution.

Synthesis of  $[Ru_2(\mu-Cl)_2Cl_2(L)_2\{L(O)\}_2]$  (3): Method (a): A solution of compound 2 (0.150 g, 0.12 mmol) in toluene (20 mL) was added to a solution of L (0.75 mL, 0.26 mmol) in toluene and the mixture was heated under reflux for 1 h, cooled to room temperature and the solvent removed under vacuum. Et<sub>2</sub>O was added to the residue and the resulting yellow solid was filtered off, washed with Et<sub>2</sub>O and dried under vacuum. Yield: 0.18 g (92%). Method (b): A mixture of  $[RuCl_2(DMSO)_4]$  (0.5 g, 1.03 mmol) and a solution of L (7.5 mL, 2.14 mmol) in toluene (20 mL) was heated under reflux for 2 h with stirring. The solution was cooled to room temperature and the solvent was removed under vacuum to give an oily residue. Et<sub>2</sub>O (5 mL) was added and the resulting yellow solid was filtered off. Compounds 7 and 8 were obtained from the filtrate (see below). The solid was washed with Et<sub>2</sub>O and dried under vacuum. Yield: 0.72 g (42%).  $C_{104}H_{96}Cl_4O_{10}P_8Ru_2$  (2097.61): calcd. C 59.55, H 4.61; found C 59.20, H 4.63. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 3.68 (m, 4 H, CH<sub>2</sub>, L), 3.73 [m, 4 H, CH<sub>2</sub>, L(O)], 4.17 [m, 4 H, CH<sub>2</sub>, L(O)], 4.49 (m, 4 H, CH<sub>2</sub>, L), 6.80–8.00 (m, 80 H, Ph) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  = 32.5 [s, (P=O), L(O)], 138.3 [t, *J* = 46 Hz, P, L(O)], 159.0 (d, *J* = 46 Hz, 2P, L) ppm. FAB<sup>+</sup>/MS: *m/z* (calculated for the most abundant isotopes) 1617 [M<sup>+</sup> – Cl – L(O)], 1580 [M<sup>+</sup> – 2Cl – L(O)], 1013 [RuClLL(O)]<sup>+</sup>.

Synthesis of  $[Ru_2(\mu-Cl)_2Cl_2(L)_2\{PPh_2(OEt)\}_2]$  (4): PPh<sub>2</sub>(OEt) (0.05 mL, 0.24 mmol) was added to a solution of compound **2** (0.150 g, 0.12 mmol) in toluene (20 mL). The mixture was heated under reflux for 1 h and the solvent was removed under vacuum. Addition of Et<sub>2</sub>O gave an orange-yellow precipitate and this was filtered off, washed with Et<sub>2</sub>O and dried under vacuum. Yield: 0.15 g (75%). C<sub>80</sub>H<sub>78</sub>Cl<sub>4</sub>O<sub>6</sub>P<sub>6</sub>Ru<sub>2</sub> (1665.27): calcd. C 57.70, H 4.72; found C 57.53, H 4.71. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta = 1.22$  (t, J = 7 Hz, 6 H, CH<sub>3</sub>), 3.50 (m, 4 H, OCH<sub>2</sub>), 3.86 (m, 4 H, CH<sub>2</sub>), 4.31 (m, 4 H, CH<sub>2</sub>), 6.50–7.90 (m, 60 H, Ph) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta = 136.3$  (t, J = 46 Hz, P, L'), 159.7 (d, J = 46 Hz, 2P, L) ppm. FAB<sup>+</sup>/MS: *m/z* (calculated for the most abundant isotopes) 1631 (M<sup>+</sup> – Cl), 1436 (M<sup>+</sup> – L'), 1401 (M<sup>+</sup> – L' – Cl), 832 [RuCl<sub>2</sub>-LL']<sup>+</sup>, 797 [RuClLL']<sup>+</sup>.

Synthesis of  $[Ru_2(\mu-Cl)_3(L)_2\{PPh(OEt)_2\}_2|Cl$  (5): PPh(OEt)\_2 (0.07 mL, 0.24 mmol) was added to a solution of compound 2 (0.150 g, 0.12 mmol) in toluene (20 mL). The mixture was heated under reflux for 1.5 h and the solvent was removed under vacuum. Addition of Et<sub>2</sub>O gave a yellow precipitate and this was filtered off, washed with Et<sub>2</sub>O and dried under vacuum. Yield: 0.13 g (67%). C<sub>72</sub>H<sub>78</sub>Cl<sub>4</sub>O<sub>8</sub>P<sub>6</sub>Ru<sub>2</sub> (1601.18): calcd. C 54.01, H 4.91; found C 53.81, H 4.88. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 0.83 (t, 6 H, J = 7 Hz, CH<sub>3</sub>, transoid), 0.97 (t, 6 H, J = 7 Hz, CH<sub>3</sub>, transoid), 1.25 (m, 12 H, CH<sub>3</sub>, cisoid), 3.50–3.90 [m, 16 H, CH<sub>2</sub> (L + L'), transoid], 4.01 [m, 8 H, CH<sub>2</sub> (L'), cisoid], 4.26 [m, 4 H, CH<sub>2</sub>, (L)], 4.51 [m, 4 H, CH<sub>2</sub>, (L)], 6.40-8.00 [m, (50 H, Ph, cisoid) + (50 H, Ph, transoid)] ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  = 149.6 [ $t_{apparent}$ ,  $J_{app}$  = 48 Hz, 2P (L), transoid], 151.7 [d, J = 53 Hz, 4P (L), cisoid], 153.0 [t<sub>apparent</sub>,  $J_{app}$ = 48 Hz, 2P (L), transoid], 156.1 [ $t_{apparent}$ ,  $J_{app}$  = 53 Hz, 2P (L'), transoid], 158.2 [t, J = 53 Hz, 2P (L'), cisoid] ppm. FAB<sup>+</sup>/MS m/z (calculated for the most abundant isotopes) 1567 ( $M^+$ ), 1530 ( $M^+$  – Cl), 765 [RuClLL']+. X-ray quality crystals were obtained by slow evaporation of a CH2Cl2/Et2O (1:10 v/v) solution.

Synthesis of [RuCl<sub>2</sub>L{P(OEt)<sub>3</sub>}] (6): P(OEt)<sub>3</sub> (0.08 mL, 0.48 mmol) was added to a solution of compound 2 (0.150 g, 0.12 mmol) in toluene (20 mL). The mixture was heated under reflux for 1 h and the solvent was removed under vacuum. Addition of Et<sub>2</sub>O gave a pale yellow precipitate and this was filtered off, washed with Et<sub>2</sub>O and dried under vacuum. Yield: 0.14 g (62%). C<sub>38</sub>H<sub>54</sub>Cl<sub>2</sub>O<sub>8</sub>P<sub>4</sub>Ru (934.71): calcd. C 48.83, H 5.82; found C 49.05, H 5.85. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 0.90 (t, J = 7 Hz, 9 H, CH<sub>3</sub>), 1.22 (t, J = 7 Hz, 9 H, CH<sub>3</sub>), 3.26 [m, 3 H, CH<sub>2</sub> (L')], 3.43 [m, 3 H, CH<sub>2</sub> (L') + 1 H, CH<sub>2</sub> (L)], 3.98 [m, 1 H, CH<sub>2</sub> (L)], 4.23 [m, 3 H, CH<sub>2</sub> (L')], 4.40 [m, 1 H, CH<sub>2</sub> (L)], 4.46 [m, 3 H, CH<sub>2</sub> (L')], 5.67 [m, 1 H, CH<sub>2</sub> (L)] ppm. <sup>31</sup>P{<sup>1</sup>H}NMR (CDCl<sub>3</sub>):  $\delta$  = 97.8 (ddd,  $J_{cis}$  = 24, 48 Hz,  $J_{trans}$  = 544 Hz, P<sub>1</sub>), 122.0 (ddd,  $J_{cis}$  = 46, 64 Hz,  $J_{trans}$  = 544 Hz, P<sub>4</sub>), 129.8 (ddd,  $J_{cis}$  = 47, 48, 64 Hz, P<sub>2</sub>), 150.7 (ddd,  $J_{cis}$  = 24, 46, 47 Hz,  $P_3$ ) ppm. FAB<sup>+</sup>/MS: m/z (calculated for the most abundant isotopes) 899 (M<sup>+</sup> – Cl), 733 [M<sup>+</sup> – Cl – P(OEt)<sub>3</sub>]. X-ray quality crystals were obtained by slow evaporation of a CH2Cl2/Et2O (1:10 v/ v) solution.

Synthesis of [RuCl<sub>2</sub>(L)(Ph<sub>2</sub>POPPh<sub>2</sub>)] (7) and [RuCl(CO)(L)-(PPh<sub>2</sub>OCH<sub>2</sub>)] (8): From the ether solution obtained during the synthesis of compound 3 [Method (b), see above], the solvent was re-

moved under vacuum, and the residue was treated with MeOH to give a yellow solid, which was washed with MeOH and dried under vacuum. This solid was a mixture of compounds 7 and 8 and these were separated by column chromatography using silica gel as the stationary phase. Complex 7 was eluted first using a mixture of CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O (10:1, v:v). The eluent was removed under vacuum and the residue was treated with EtOH to give a yellow solid, which was filtered off, washed with EtOH and dried under vacuum. Yield: 0.012 g (12%). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 4.30 (m, 4 H, CH<sub>2</sub>), 6.90– 7.50 (m, 40 H, Ph) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  = 106.8 (m, P<sub>3,4</sub>), 133.0 (m, P<sub>1,2</sub>) ppm. C<sub>50</sub>H<sub>44</sub>Cl<sub>2</sub>O<sub>3</sub>P<sub>4</sub>Ru (988.75): calcd. C 60.74, H 4.49; found C 60.60, H 4.50. FAB+/MS: m/z (calculated for the most abundant isotopes) 988 (M<sup>+</sup>), 953 (M<sup>+</sup> - Cl), 602 [RuCl<sub>2</sub>L]<sup>+</sup>. X-ray quality crystals were obtained by slow evaporation of a CH<sub>2</sub>Cl<sub>2</sub>/EtOH (1:10 v/v) solution. Complex 8 was eluted using CH<sub>2</sub>Cl<sub>2</sub> as eluent. The solvent was removed under vacuum and the residue was treated with EtOH. The resulting white solid was filtered off, washed with EtOH and dried under vacuum. Yield: 0.013 g (1.5%). IR (KBr disc): 1953 (s) ( $v_{co}$ ) cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 3.80–4.80 (m, 6 H, CH<sub>2</sub>), 7.20–7.80 (m, 30 H, Ph) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  = 76.0 (dd,  $J_{12}$  = 341,  $J_{13}$  = 14 Hz,  $P_1$ ), 131.5 (dd,  $J_{23} = 31$  Hz,  $P_3$ ), 133.3 (dd,  $P_2$ ) ppm.  $C_{40}H_{36}ClO_{4-}$ P<sub>3</sub>Ru (810.15): calcd. C 59.30, H 4.48; found C 59.46, H 4.46. FAB<sup>+</sup>/MS: m/z (calculated for the most abundant isotopes) 782 (M<sup>+</sup> - CO), 775 (M<sup>+</sup> - Cl), 747 (M<sup>+</sup> - CO - Cl), 595 [RuCl(CO)- L]<sup>+</sup>. X-ray quality crystals were obtained by slow evaporation of a CH<sub>2</sub>Cl<sub>2</sub>/EtOH (1:10 v/v) solution.

CCDC-297717 to -297721 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif.

Details of crystal data and structural refinement are given in Table 9. The data were collected with a SIEMENS Smart CCD area-detector diffractometer with graphite-monochromated Mo- $K_{\alpha}$ radiation. Absorption correction was carried out using SAD-ABS.<sup>[25]</sup>

The structures of 5a and 8 were solved by Patterson methods and the structures of 2a, 6 and 7 were solved by direct methods. All of the structures were refined by a full-matrix least-squares based on  $F^{2,[26]}$  In the case of **5a** and **7** the compounds crystallised with a solvent molecule and the Squeeze program was used to correct the reflection data for the diffuse scattering due to disordered solvent.<sup>[27]</sup> Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in idealised positions and refined with isotropic displacement parameters. Atomic scattering factors and anomalous dispersion corrections for all atoms were taken from International Tables for X-ray Crystallography.<sup>[28]</sup>

Table 9. Crystallographic data for 2a, 5a, 6, 7 and 8.

Compound	2a	5a	6	7	8
Empirical formula	C54H54Cl4O5P4Ru2S	C72H78Cl4O8P6Ru2	C38H54Cl2O8P4Ru	C <sub>50</sub> H <sub>44</sub> Cl <sub>2</sub> O <sub>3</sub> P <sub>4</sub> Ru	C40H36ClO4P3Ru
Formula mass	1282.85	1601.10	934.66	988.70	810.12
Temperature [K]	293(2)	293(2)	293(2)	293(2)	293(2)
Wavelength [Å]	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	triclinic	triclinic	monoclinic	monoclinic	monoclinic
Space group	PĪ	ΡĪ	$P2_{1}/c$	$P2_1/c$	$P2_1/c$
a [Å]	13.089(2)	12.312(4)	19.068(4)	18.2857(15)	10.3989(19)
b [Å]	14.520(3)	16.121(5)	13.511(3)	10.9637(9)	30.417(5)
c [Å]	19.143(3)	24.310(7)	17.006(4)	23.896(2)	14.4224(19)
a [°]	110.211(4)	73.483(8)	90	90	90
β [°]	93.650(4)	81.195(6)	102.146(5)	94.062(2)	125.777(9)
γ [°]	99.004(4)	83.280(7)	90	90	90
Volume [Å <sup>3</sup> ]	3344.8(10)	4558(2)	4283.4(17)	4778.6(7)	3701.0(10)
Ζ	2	2	4	4	4
$D_{\text{calcd}} [\text{Mg/m}^3]$	1.274	1.167	1.449	1.374	1.454
Absorption coefficient [mm <sup>-1</sup> ]	0.776	0.596	0.688	0.614	0.666
F(000)	1300	1640	1936	2024	1656
Crystal size [mm]	$0.24 \times 0.14 \times 0.09$	$0.29 \times 0.214 \times 0.23$	$0.34 \times 0.21 \times 0.20$	$0.50 \times 0.33 \times 0.26$	$0.25 \times 0.27 \times 0.15$
$\theta$ range for data collection [°]	1.52-28.11	1.68-28.19	1.86-28.07	1.71-28.03	1.34-28.08
Index ranges	$-17 \le h \le 17$	$-16 \le h \le 15$	$-25 \le h \le 20$	$-16 \le h \le 23$	$-13 \le h \le 13$
	$-19 \le k \le 19$	$-21 \le k \le 13$	$-16 \le k \le 17$	$-13 \le k \le 14$	$-40 \le k \le 25$
	$-16 \le l \le 25$	$-31 \le l \le 30$	$-17 \le l \le 22$	$-31 \le l \le 31$	$-18 \le l \le 18$
Reflections collected	17668	30329	27353	27535	19695
Independent reflections	12503	21088	10210	10879	8278
	[R(int) = 0.0740]	[R(int) = 0.1186]	[R(int) = 0.1652]	[R(int) = 0.0441]	[R(int) = 0.1512]
Reflections observed (> $2\sigma$ )	3658	3904	3373	6882	2658
Data completeness	0.765	0.939	0.981	0.940	0.918
Max. and min. transmission	1.00000 and 0.81992	1.0000 and 0.7838	1.0000 and 0.711	1.00000 and 0.817076	1.0000 and 0.36612
Data/restraints/parameters	12503/0/598	21088/0/833	10210/0/484	10879/0/541	8278/0/450
Goodness-of-fit on $F^2$	0.969	0.608	0.700	0.849	0.811
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0987$	$R_1 = 0.0724$	$R_1 = 0.0553$	$R_1 = 0.0386$	$R_1 = 0.0732$
	$wR_2 = 0.2866$	$wR_2 = 0.1638$	$wR_2 = 0.0699$	$wR_2 = 0.0673$	$wR_2 = 0.1231$
R indices (all data)	$R_1 = 0.2550$	$R_1 = 0.2650$	$R_1 = 0.1974$	$R_1 = 0.0748$	$R_1 = 0.2516$
	$wR_2 = 0.3317$	$wR_2 = 0.1992$	$wR_2 = 0.0915$	$wR_2 = 0.0728$	$wR_2 = 0.1652$
Largest diff. peak/hole [e/Å3]	2.637/-0.637	0.632/0.451	0.695/-1.054	0.509/-0.371	1.088/-0.617

### FULL PAPER

**Supporting Information** (see also the footnote on the first page of this article): 2D  ${}^{1}H, {}^{1}C{}^{1}H$  HSQC experiment for  $[Ru_{2}(\mu-Cl)_{3}-(DMSO)_{3}Cl(L)]$  (1); 2D  ${}^{1}H, {}^{3}P{}^{1}H$  HMBC experiments for  $[Ru_{2}(\mu-Cl)_{3}(DMSO)Cl(L)_{2}]$  (2) and  $[RuCl_{2}(L)(Ph_{2}POPPh_{2})]$  (7); synthesis and crystal structure of  $[Ru_{2}(\mu-Cl)_{3}(L)_{2}{PPh_{2}(OEt)}_{2}]Cl$ .

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- a) B. M. Trost, M. U. Frederiksen, M. T. Rudd, Angew. Chem. Int. Ed. 2005, 44, 6630–6666; b) J. Gimeno, Curr. Org. Chem. 2006, 10, 113.
- [2] a) S. C. Weatherly, I. V. Yang, H. H. Thorp, J. Am. Chem. Soc.
   2001, 123, 1236–1237; b) C. J. Burrows, J. G. Muller, Chem. Rev. 1998, 98, 1109–1151.
- [3] a) J. Malina, O. Novakova, B. K. Keppler, E. Alessio, V. Bravec, J. Biol. Inorg. Chem. 2001, 6, 435–445; b) M. J. Clark, F. Zhu, D. R. Frasca, Chem. Rev. 1999, 99, 2511–2533.
- [4] a) V. Alezra, G. Bernardinelli, C. Corminboeuf, U. Frey, E. P. Kündig, A. E. Merbach, C. M. Saudan, F. Viton, J. Weber, J. Am. Chem. Soc. 2004, 126, 4843–4853; b) Y.-G. Zhou, X. Zhang, Chem. Commun. 2002, 10, 1124–1125; c) Y.-G. Zhou, W. Tang, W.-B. Wang, W. Li, X. Zhang, J. Am. Chem. Soc. 2002, 124, 4952–4953; d) Z. Csok, G. Szalontai, G. Czira, L. Kollar, J. Organomet. Chem. 1998, 570, 23–29.
- [5] a) L. Quebatte, R. Scopelliti, K. Severin, Angew. Chem. Int. Ed. 2004, 43, 1520–1524; b) B. De Clerq, F. Verpoort, Tetrahedron Lett. 2002, 43, 4687–4690; c) A. C. da Silve, H. Piotrowski, P. Mayer, K. Polborn, K. Severin, Eur. J. Inorg. Chem. 2001, 685–691; d) M. T. Reetz, M. H. Becker, M. Liebl, A. Fürstner, Angew. Chem. Int. Ed. 2000, 39, 1236–1239.
- [6] T. J. Geldbach, A. B. Chaplin, K. D. Hänni, R. Scopelliti, P. J. Dyson, *Organometallics* 2005, 24, 4974–4980.
- [7] a) E. Iengo, E. Zangrando, E. Baiutti, F. Munini, E. Alessio, *Eur. J. Inorg. Chem.* 2005, 1019–1031; b) A. M. Joshi, I. S. Thorburn, S. J. Rettig, B. R. James, *Inorg. Chim. Acta* 1992, *198–200*, 283–296; c) J. S. Jaswal, S. J. Rettig, B. R. James, *Can. J. Chem.* 1990, 68, 1808–1817.
- [8] a) C. Bianchini, P. Barbaro, G. Scapacci, F. Zanobini, Organometallics 2000, 19, 2450–2461; b) see compound 2 in next paragraph.
- [9] Compound 2 can also be obtained by reaction of [RuCl<sub>2</sub>(DMSO)<sub>4</sub>] with L in a 1:1 molar ratio in refluxing toluene for 1 h.
- [10] S. D. Drouin, S. Monfette, D. Amoroso, G. P. A. Yap, D. E. Fogg, *Organometallics* 2005, 24, 4721–4728.
- [11] a) J. Bravo, J. Castro, S. García-Fontán, E. M. Lamas, P. Rodríguez-Seoane, Z. Anorg. Allg. Chem. 2003, 629, 297–302;
  b) F. Fernández-García, S. Bolaño, R. Carballo, S. García-Fontán, J. Bravo, Polyhedron 2001, 20, 2675–2681.

- [12] a) F. A. Cotton, R. C. Torralba, *Inorg. Chem.* 1991, 30, 2196–2207; b) S. Gauthier, L. Quebatte, R. Scopelliti, K. Severin, *Chem. Eur. J.* 2004, 10, 2811–2821.
- [13] The structure of **4**' has been accidentally confirmed by the serendipitous preparation and X-ray structure analysis of  $[{Ru(\eta^2-L)[PPh_2(OEt)]}_2(\mu-Cl)_3]Cl$  (see Supporting Information) that presents spectral features identical to those of the *transoid* isomer of **4**'.
- [14] a) D. J. Darensbourg, F. Joó, M. Kannisto, A. Katho, J. H. Reibenspies, D. J. Daigle, *Inorg. Chem.* 1994, 33, 200–208; b)
  A. R. Chakravarty, F. A. Cotton, W. Schwotzer, *Inorg. Chim. Acta* 1984, 84, 179–185; c) R. F. Winter, B. M. Brunner, T. Scheiring, *Inorg. Chim. Acta* 2000, 310, 21–26; d) A. Keller, B. Jasionka, T. Glowiak, A. Ershov, R. Matusiak, *Inorg. Chim. Acta* 2003, 344, 49–60.
- [15] This compound can be obtained in two other ways using [RuCl<sub>2</sub>(COD)]<sub>n</sub> or [RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub>] as metallic precursors.
- [16] D. J. Irvine, C. Glidewell, D. J. Cole-Hamilton, J. C. Barnes, A. Howie, J. Chem. Soc., Dalton Trans. 1991, 1765–1772.
- [17] K. Wang, T. J. Emge, A. S. Goldman, Organometallics 1994, 13, 2135–2137.
- [18] a) J. Bravo, J. A. Castro, E. Freijanes, S. García-Fontán, E. M. Lamas, P. Rodríguez-Seoane, Z. Anorg. Allg. Chem. 2005, 631, 2067–2074; b) S. Bolaño, J. Bravo, S. García-Fontán, Inorg. Chim. Acta 2001, 315, 81–87; c) S. Bolaño, J. Bravo, R. Carballo, S. García-Fontán, U. Abram, E. M. Vázquez-López, Polyhedron 1999, 18, 1431–1436.
- [19] M. M. Turnbull, E. H. Wong, E. J. Gabe, F. L. Lee, *Inorg. Chem.* 1986, 25, 3189–3194.
- [20] a) C. S. Kraihanzel, C. M. Bartish, J. Am. Chem. Soc. 1972, 94, 3572–3575; b) D. E. C. Corbridge, Phosphorus. An Outline of its Chemistry, Biochemistry and Technology, 5th ed., Elsevier, 1995, chapter 10.
- [21] a) E. H. Wong, L. Prasad, E. J. Gabe, F. C. Bradley, J. Organomet. Chem. 1982, 236, 321–331; b) F. C. Bradley, E. H. Wong, E. J. Gabe, F. L. Lee, Y. Lepage, Polyhedron 1987, 6, 1103–1110; c) D. J. Irvine, D. J. Cole-Hamilton, J. Barnes, P. K. G. Hodgson, Polyhedron 1989, 8, 1575–1577.
- [22] E. Lindner, H.-J. Eberle, S. Hoehne, Chem. Ber. 1981, 114, 413– 422.
- [23] D. D. Perrin, W. L. F. Armarego, *Purification of Laboratory Chemicals*, 3rd ed., Butterworth and Heinemann, Oxford, 1988.
- [24] I. P. Evans, A. Spencer, G. Wilkinson, J. Chem. Soc., Dalton Trans. 1973, 2, 204–209.
- [25] G. M. Sheldrick, SADABS. An empirical absorption correction program for area detector data, University of Göttingen, Germany, 1996.
- [26] G. M. Sheldrick, SHELX-97. Program for the solution and refinement of crystal structures. University of Göttingen, Germany, 1997.
- [27] A. L. Spek, Acta Crystallogr., Sect. A: Found. Cystallogr. 1990, 46, C34.
- [28] International Tables for X-ray Crystallography, vol. C, Kluwer, Dordrecht, 1992.

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