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Some Aspects of the Structural and Coordination Chemistry of the 2,2′-Biphosphole

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Abstract—The 2,2′-biphosphole which presents axial chirality generated by the biphosphole framework and central chiralities due to the phosphorus atoms leads to the existence of six stereoisomers corresponding to three pairs of enantiomers which have been fully characterised by X-ray diffraction studies. Among these three diastereoisomers, one has a favourable configuration for chelating metals. The synthesis and structure of numerous transition metal complexes are reported. Their X-ray analysis proved that in each complex the 2,2′-biphosphole ligands have the expected configuration.

Introduction

The coordination chemistry of monophospholes has been extensively studied,[1] and the evaluation of their potential in homogenous catalysis has been investigated.[2] In particular, it was proved that phospholes are efficient ligands for hydrogenation and hydroformylation of various unsaturated substrates in conjunction with rhodium.[2c–f] On the other hand, chiral diphosphole ligands associated to rhodium have proved to be moderate asymmetric inductors for these catalytic processes.[3] High enantiomeric excesses (>96%) and high branched to normal (b/n) ratios (77/23) have been obtained in the asymmetric hydroformylation of styrene by the use of platinum complexes in the presence of $SnCl_2$.[4]

In the field of 2,2′-biphosphole chemistry, little work has been done. Indeed, only a few 2,2′-biphosphole compounds, the 1,1′-diphenyl-3,3′,4,4′-tetramethyl-2,2′-biphosphole[5] and its derivatives,[6] and two 2,2′-biphosphole complexes [Mo(2,2′-biphosphole)$(CO)_4$][5] and [Mn_2(2,2′-biphosphole)-$(CO)_8$][5] (Fig. 1) have been reported in the literature by Mathey et al., but no structural information was given.

In 1997, we obtained the X-ray structure of the dinuclear complex [Fe(η^5-C_5H_5)(C_4HMe_2PhP)$(CO)]_2$.[7] It was the first structural report of a complex containing the 2,2′-biphosphole ligand. The molecular structure of this complex presented in Fig. 2 displays a dihedral angle between the two phosphole rings (86°) which generated an axial chirality C_2. This occurrence of C_2-symmetry in the 1,1′-diphenyl-3,3′,4,4′-tetramethyl-2,2′-biphosphole (BIPHOS) in a complex led to a renewed interest in the chemistry of this bidentate ligand.

In this paper we will overview our recent work concerning the structure and stereochemistry of 2,2′-biphosphole compounds as well as their coordination chemistry.

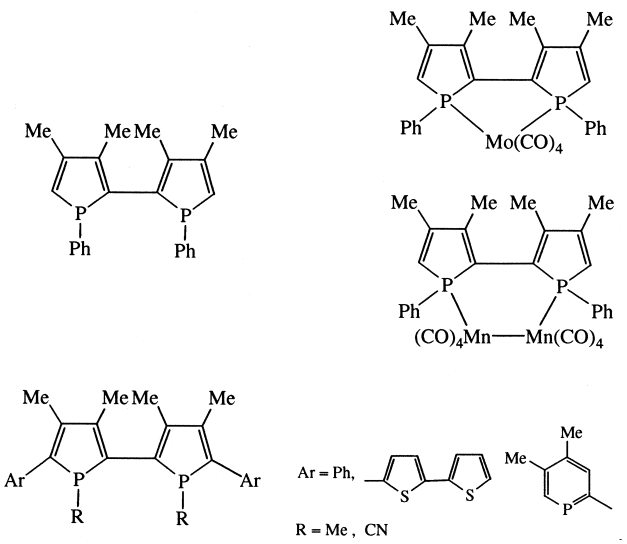

Figure 1.

Keywords: stereoisomers; diastereoisomers; 2,2′-biphosphole complexes; transition metal complexes; enantiomers.

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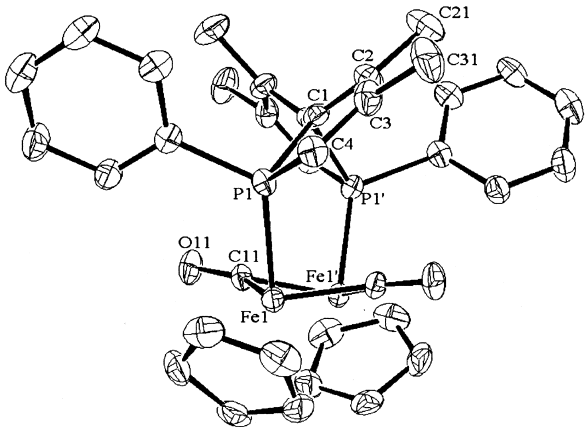


Figure 2. The molecular structure of the dinuclear complex $[Fe(\eta^5\text{-}C_5H_5)(C_4HMe_2PhP)(CO)]_2$.

Results

Structure and stereochemistry of the 2,2′-biphosphole

The 2,2′-biphosphole is a particular diphosphine which presents axial chirality generated by the biphosphole framework and central chirality due to phosphorus atoms. The different possibilities of combining axial and central chiralities in 2,2′-biphosphole are depicted in Fig. 3 using a Newman projection along the C–C axis of the bond linking the phosphole rings.

This stereochemical analysis shows the occurrence of six stereoisomers corresponding to three pairs of enantiomers. Only two isomers were observed in solution for the 2,2′-biphosphole compounds. Using the procedure previously described by F. Mathey and coworkers,[8] we synthesised the 1,1′-diphenyl-3,3′,4,4′-tetramethyl-2,2′-biphosphole **1**[8] which we identified as a mixture of two isomers **1a**, **1b** in the ratio 88/12 as evidenced by ^{1}H-, ^{31}P- and ^{13}C-NMR data analysis.[9] The existence of two isomers was also observed for the 1,1′-dicyano-3,3′,4,4′-tetramethyl-2,2′-biphosphole **2**, obtained from compound **1** (Scheme 1). However, in the solid state, we were able to characterise the three pairs of enantiomers by X-ray diffraction analysis. The diastereoisomer ($[a]^S_{SS}+[a]^R_{RR}$) was identified for the dioxide **3a** and disulfide **4a**[9] obtained by oxidation of the corresponding 2,2′-biphosphole **1** (Scheme 1). The molecular structure of dioxide **3a** is presented in Fig. 4. The diastereoisomer ($[b]^S_{RS}+[b]^R_{SR}$) was characterised for the disulfide derivative **4b**[9] of 2,2′-biphosphole **1b**. Fig. 5 shows the molecular structure of disulfide **4b** in the crystal. The structure of the third isomer ($[a]^S_{RR}+[a]^R_{SS}$) was obtained for free 2,2′-biphosphole **1** and **2**. The molecular structure obtained for compound **2** is shown in Fig. 6.

From these results, we were able to propose a structure for the two isomers of the 2,2′-biphosphole observed in solution. Since the mixture of 2,2′-biphosphole, **1a** and **1b** in the ratio 88/12, leads to the dioxide **3a** and **3b** or to the disulfide **4a** and **4b** in the same ratio 88/12, the major products arise from the major isomer **1a** and the minor product from the minor isomer **1b**. The minor 2,2′-biphosphole stereoisomer

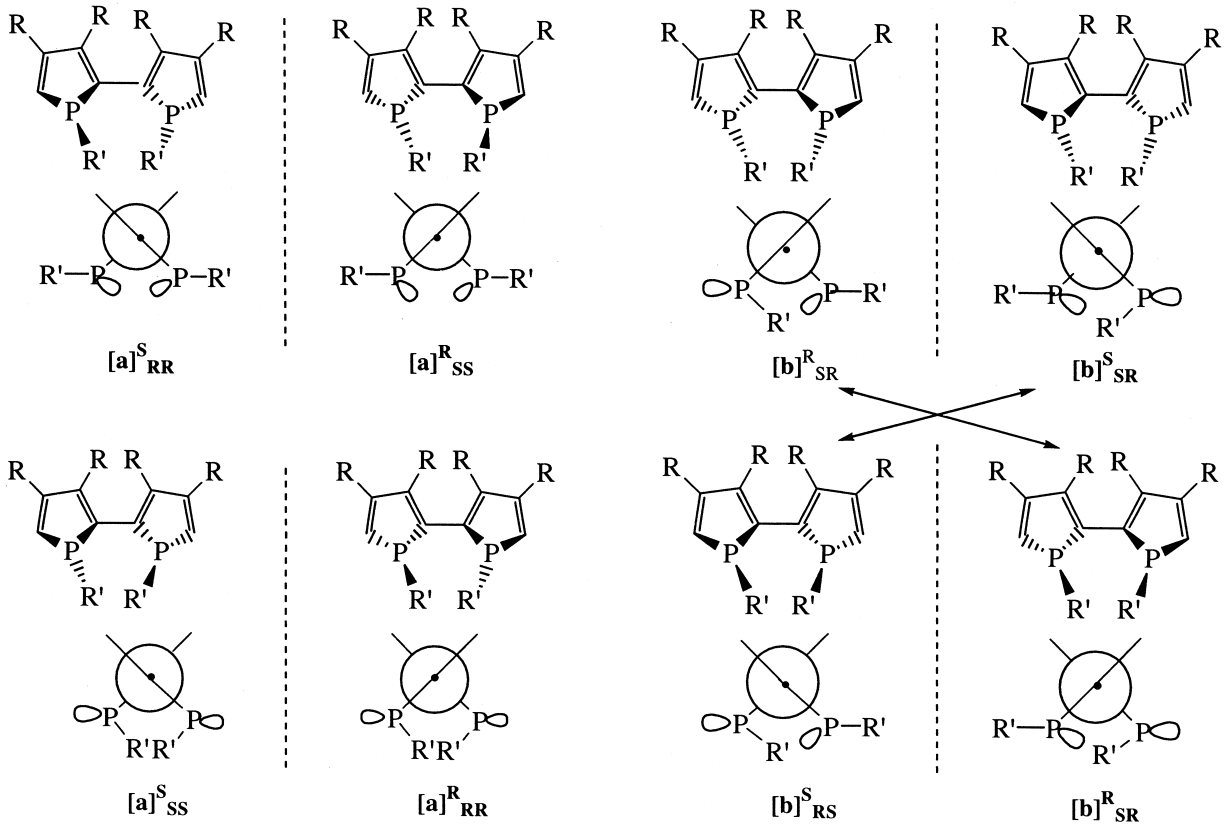
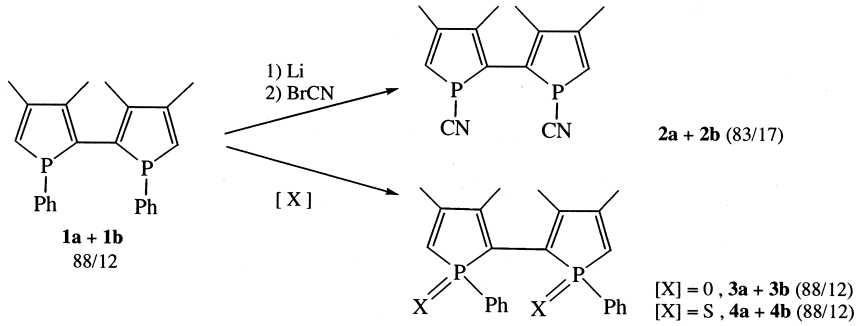


Figure 3. The 2^3 stereoisomers of 2,2′-biphosphole which possess two chiral centres and one chiral axis. Subscript refers to central chirality and superscript to axial chirality. Among these eight stereoisomers, six are really inequivalents.



Scheme 1.

1b or **2b** corresponds to the pair of enantiomers $[b]^{S}_{RS}+[b]^{R}_{SR}$ and presents opposite absolute configuration for the two phosphorus atoms. Thus for the major stereoisomer **1a** or **2a**, both phosphorus atoms have the same absolute configuration. We assume that this isomer exists in solution either in the $[a]^{S}_{RR}+[a]^{R}_{SS}$ form or in the $[a]^{R}_{RR}+[a]^{S}_{SS}$ form or as a mixture of these two pairs of enantiomers interconverting rapidly on the NMR time scale even at low temperature (−70°C) by rotation around the C–C bond bridge and giving only one sharp ^{31}P resonance (δ=15.7). The two isomers **a** and **b** could not be separated by usual methods because 2,2′-biphosphole exists in solution as an equilibrium mixture of two diastereoisomers **a** and **b**, the energetically preferred isomer being **a**. The kinetics studies of the **1b→1a** isomerisation,[9] by ^{31}P NMR at low temperature, shows that the free enthalpy of activation which corresponds to the inversion barrier for the pyramidal phosphorus centre is $\Delta G^{\#}_{218}$=16.5 kcal/mol. This low barrier due to extensive electronic delocalization within the planar transition state is comparable to those observed for the monophosphole series.[10]

However, if we consider the $[a]^{S}_{RR}$ and $[a]^{R}_{SS}$ configurations, the 2,2′-biphosphole presents the phosphorus lone pairs in the right direction to chelate a metal centre. We have explored the coordination behaviour of the 1,1′-diphenyl-3,3′,4,4′-tetramethyl-2,2′-biphosphole ligand (BIPHOS), **1**.

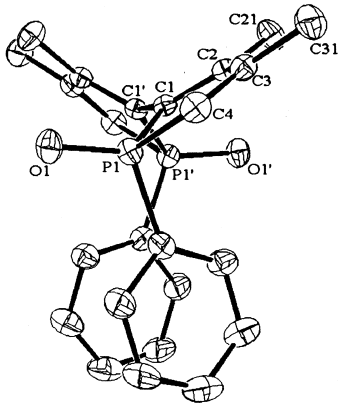


Figure 4. The molecular structure of the dioxide **3a**.

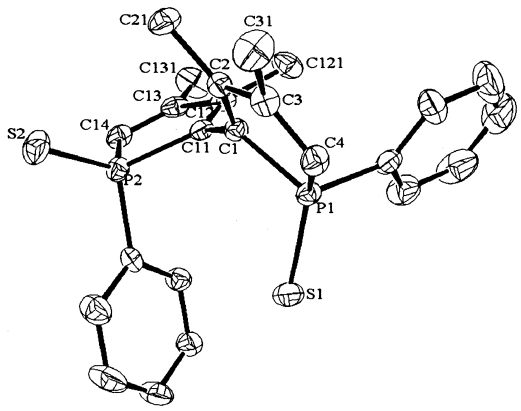


Figure 5. The molecular structure of the disulfide **4b**.

Synthesis and characterisation of 2,2′-biphosphole complexes

The reaction of 2,2′-biphosphole **1** (**1a**+**1b**) with appropriate nickel, palladium and platine precursors produces $[MCl_2(BIPHOS)]$[11] in dichloromethane at room temperature in excellent yield (Scheme 2). The $^{31}P\{^{1}H\}$ NMR spectra of the reaction mixture exhibit in each case a single resonance showing that the conversion of (**1a**+**1b**) into the corresponding complexes **5** is quantitative and that **5** are obtained in a pure diastereoisomer form. Owing to the low pyramidal inversion barrier of the phosphorus atom,[9,10] it is clear that **1b** is quantitatively transformed into **1a** in order to favour coordination onto the metal. These complexes were characterised by elemental analysis, multinuclear NMR spectroscopy, mass spectroscopy and X-ray diffraction studies.

The molecular view of complex **5b** is presented in Fig. 7. In this complex, the P(1), P(1′) and Pd atoms have a square planar environment with slight distortion from

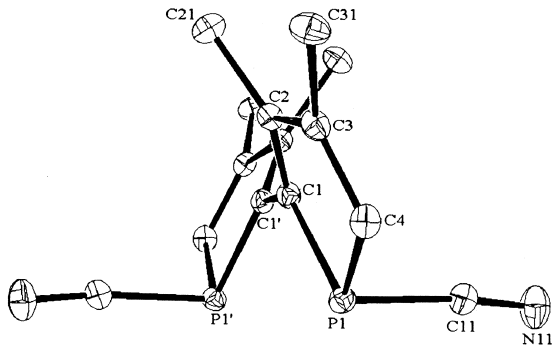
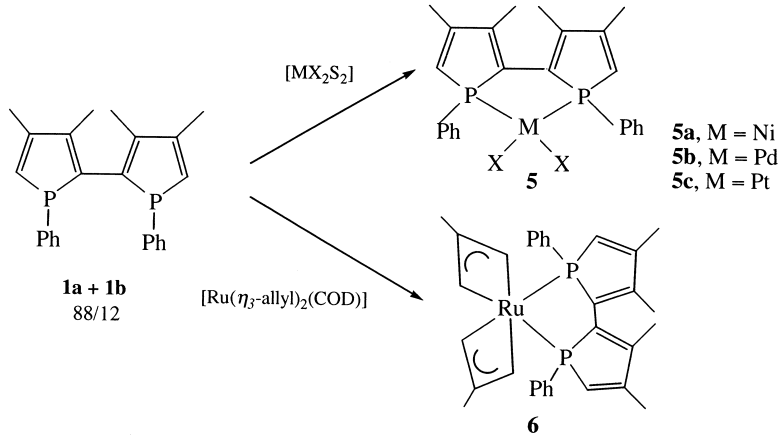


Figure 6. The molecular structure of the 2,2′-biphosphole **2a**.



Scheme 2.

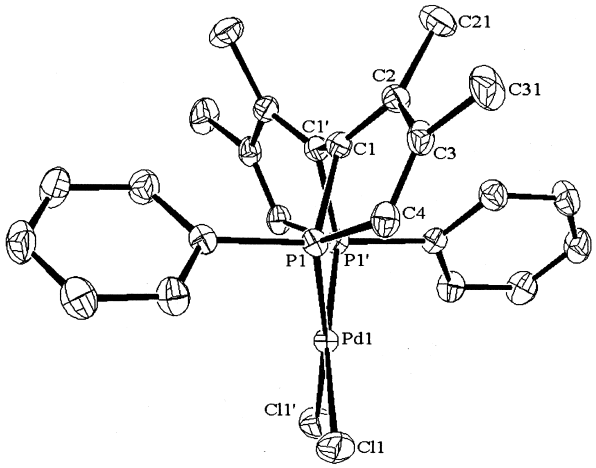


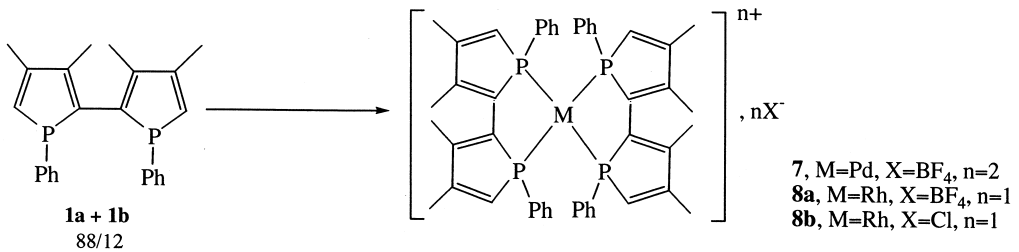
Figure 7. The molecular structure of the palladium complex **5b**.

the idealised situation. The phosphole rings are all planar within experimental error, but they are twisted with respect to each other along the C(1)–C(1′) bond making dihedral angles of 46.8°. This value compares well with the 46.6° observed for the free ligand **1**.[6] As the structure possesses a C_2-symmetry axis passing through the metal atom and crossing the middle of the C(1)–C(1′) bond, the complex **5b** is chiral. The structure determination reveals unambiguously the relative configuration of both central and axial elements of chirality. However, the solid state structure corresponds to a racemic mixture since complex **5b** crystallises in a centrosymmetric space group. This racemic complex corresponds to the two $[a]^S_{RR}$ and $[a]^R_{SS}$ forms of the ligand as expected from the stereochemical analysis (c.f. Fig. 2).

For $[NiCl_2(BIPHOS)]$[11] **5a** and $[PtCl_2(BIPHOS)]$[11] **5c** complexes, X-ray diffraction analysis shows the same stereochemistry of the 2,2′-biphosphole ligand, $[a]^S_{RR}$, $[a]^R_{SS}$, in each complex. This stereochemistry appears to be stable once coordinated to the metal.

The 2,2′-biphosphole ligand **1** can also chelate ruthenium metal. The η^3-allyl-complex, $[Ru(\eta^3\text{-allyl})_2(BIPHOS)]$ **6**, was obtained by reaction of **1** with $[Ru(\eta^3\text{-allyl})_2(COD)]$.[12] In contrast to the formation of nickel, palladium and platinum complexes which are immediate at room temperature, the formation of ruthenium complex is very slow, complete in 8 d at room temperature. Moreover, complex **6** is extremely air and moisture sensitive and has only been characterised by ^1H, ^{31}P-NMR and mass spectroscopy. The NMR spectra indicated the formation of only one diastereoisomer from the two expected if we consider the stereochemistry of the 2,2′-biphosphole ligand, $[a]^S_{RR}$ and $[a]^R_{SS}$, and the stereochemistry of a tris-chelate ruthenium complex, Δ and Λ. This reaction proceeds diastereoselectively but we have not been able to determine on the basis of a single NMR analysis which diastereoisomer has been obtained.

2,2′-biphosphole **1** is a rather good ligand for transition metals as evidenced by the formation of bis-biphosphole complexes. The reaction of **1** with $[Pd(CH_3CN)_4](BF_4)_2$ affords a bis-2,2′-biphosphole–palladium-complex, $[Pd(BIPHOS)_2](BF_4)_2$,[11] **7** (Scheme 3) as indicated by elemental analysis, mass spectroscopy and X-ray analysis.



Scheme 3.

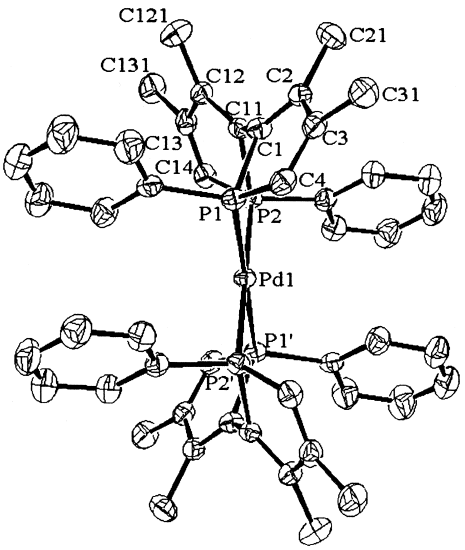


Figure 8. The molecular structure of the *meso*-palladium complex **7**.

The molecular structure of the cation is shown in Fig. 8. As observed in complex **5b**, the phosphole rings are planar within experimental error and they are twisted along the C(1)–C(11) bond making a dihedral angle of 53.3°. Complex **7** contains both the $[a]^{S}_{RR}$ and $[a]^{R}_{SS}$ absolute configurations of the 2,2-biphosphole and it is thus the *meso* diastereoisomer. The same *meso*-palladium complex was later described by Matsuda and coworkers.[13] In addition, these authors observed the formation of another complex, the racemic diastereoisomer. The formation of these two diastereoisomers seems to be solvent dependant. A mixture of *meso* and racemic complexes was obtained in a dichloromethane solution whereas the formation of only the *meso* complex proceeds in a toluene–dichloromethane mixture. These diastereoisomers are stereochemically stable in dichloromethane solution. For example, starting to the *meso*-palladium complex in dichloromethane solution, no interconversion to the racemic complex was observed proving the stereochemistry of the 2,2′-biphosphole ligand is stable once coordinated to the metal.

Similar bis-2,2′-biphosphole–rhodium complexes, [Rh(BIPHOS)$_2$]X,[11] were synthesised from [Rh(COD)$_2$]BF$_4$ or [RhCl(COD)]$_2$ precursors. In these cases, only one diastereoisomer was obtained and identified by mass

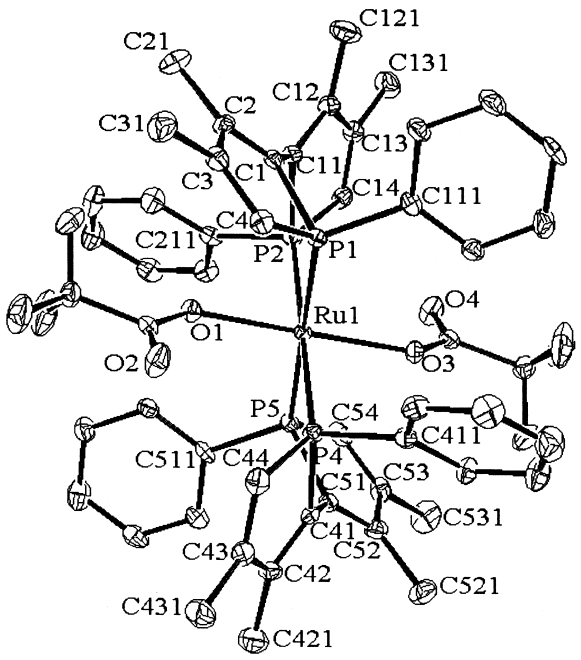
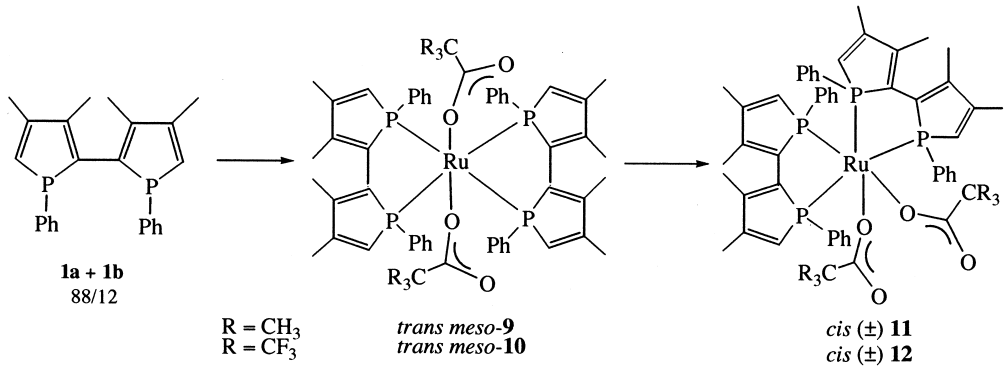


Figure 9. The molecular structure of the *trans*–*meso*-ruthenium complex **10**.

spectroscopy and multinuclear NMR spectroscopy. Unfortunately, we have not yet been able to obtain a crystal structure of these complexes so we cannot determine if it is the *meso* or the racemate.

Bis-2,2′-biphosphole-dicarboxylato–ruthenium complexes, [Ru(O$_2$CCR$_3$)$_2$(BIPHOS)$_2$] R=CH$_3$, CF$_3$, have been surprisingly obtained by reaction of 2,2′-biphosphole **1** with normal precursors of diphosphine-dicarboxylato–ruthenium complexes [Ru(O$_2$CCR$_3$)$_2$(P–P)].[14] The reaction of biphosphole **1** with these ruthenium complexes in dichloromethane at 30 °C gives, in a moderate yield, bis-biphosphole ruthenium complexes **9** and **10**,[15] respectively, (Scheme 4) as indicated by mass spectroscopy.

X-ray structural analysis[15] confirms for complex **10** the formation of [Ru(O$_2$CCF$_3$)$_2$(BIPHOS)$_2$]. The ORTEP plot given in Fig. 9 shows a near-octahedral geometry for ruthenium and mutually *trans* ligated monodentate trifluoroacetate groups. Although unexpected, the monodentate coordination mode of the trifluoroacetate groups is not



Scheme 4.

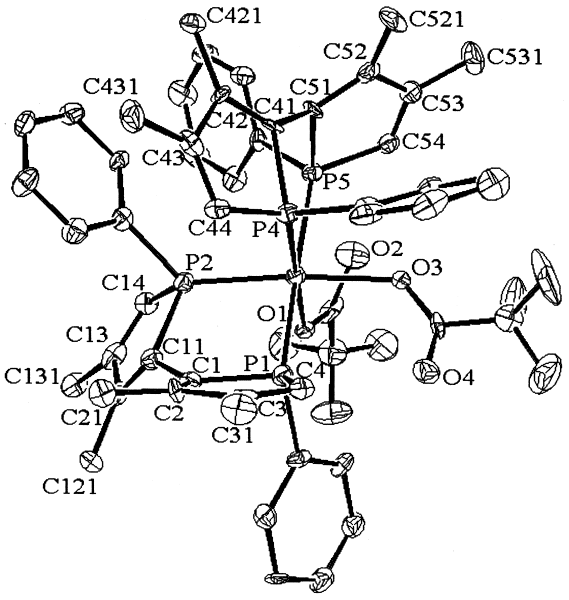


Figure 10. The molecular structure of the *cis*-(±)-ruthenium complex **12**.

unprecedented and there are many examples of such a bonding mode for the trifluoroacetate.[16] The four Ru–P bond distances lie in the range 2.32–2.42 Å found for related ruthenium(II) bisphosphine *trans* disubstituted complexes.[17] This complex contains both the $[a]^{S}_{RR}$ and $[a]^{R}_{SS}$ absolute configurations of the biphosphole **1** (c.f. Fig. 2) and it is then the *meso* diastereoisomer as already observed in the $[Pd(BIPHOS)_2](BF_4)_2$ complex.[11]

However, these *meso*-ruthenium complexes **9** and **10** are stereochemically less stable in dichloromethane solution than the *meso*-palladium complex. Transformation of complexes **9** and **10** proceeded in solution leading to the formation of new complexes **11** and **12**,[15] respectively, (Scheme 4). Remarkable difference was observed for the stability of complexes **9** and **10**: conversion of **9** is complete in 6 h whereas 8 d are necessary for **10**. This conversion, followed using ^{31}P-NMR spectroscopy, displays the disappearance of the singlet (**9**: δ=54.5, **10**: δ=54.5), corresponding to four equivalent phosphorus nuclei in complexes **9** and **10** concomitant with the appearance of an ABCD system corresponding to four non-equivalent phosphorus nuclei in complexes **11** and **12**. Elemental analysis and mass spectroscopy also confirmed the formation of bis-biphosphole–ruthenium complexes for compounds **11** and **12**. The molecular structure of complex **12**,[15] determined by X-ray analysis and represented in Fig. 10, shows a chiral near-octahedral geometry for ruthenium. As in **10**, this complex **12** contains the pair of enantiomers of biphosphole **1** with $[a]^{S}_{RR}$ and $[a]^{R}_{SS}$ absolute configurations but with two *cis* monodentate trifluoroacetate groups leading to a chiral arrangement around the ruthenium atom. However, the solid state structure corresponds to the racemic mixture, $\Delta(([a]^{S}_{RR}+[a]^{R}_{SS})$ and $\Lambda([a]^{R}_{SS}+[a]^{S}_{RR})$, since complex **12** crystallises in a centrosymmetric space group. The two Ru–P bond lengths corresponding to the P atoms *trans* to each other, 2.358(4) and 2.394(4) Å, are similar to those observed for **10**, whereas for the two P atoms *trans* to the trifluoroacetate, the Ru–P distances are much shorter, 2.275(3) and 2.296(4) Å, as also observed in related complexes.[17]

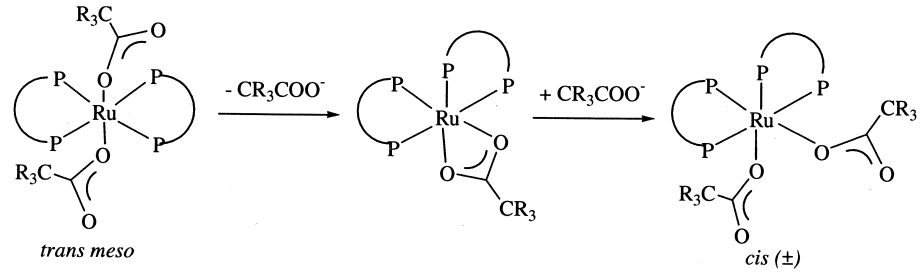
This large difference could be the consequence of a strong *trans* influence of the trifluoroacetate ligands. We assume that the formation of the kinetic product **9** or **10** is probably controlled by steric factors. Indeed, the molecular structures reveal that steric constraints between the two enantiomers of **1** seem to be lower in the *trans–meso* **9** or **10** than in the *cis* (±) **11** or **12**. On the other hand, we assume that the isomerization of the *trans–meso* **9** or **10** into the thermodynamic product *cis* (±) **11** or **12** is triggered by the *trans* influence of the monodentate trifluoroacetate ligands. We may assume that this *trans* influence facilitates a decoordination–recoordination process of one of the trifluoroacetate ligands eventually assisted by the formation of an intermediate with a dihapto coordination of the other (Scheme 5).

We are presently investigating the mechanism of this isomerization reaction.

Conclusion

The 2,2′-biphospholes are peculiar diphosphines presenting axial chirality generated by the biphosphole framework and central chiralities due to the phosphorus atoms. The different possibilities of combining axial and central chiralities imply the existence of three pairs of enantiomers which have been fully characterised by diffraction studies of the 2,2′-biphosphole derivatives. The existence of only two diastereoisomers in solution, as an equilibrium mixture, was explained by the low inversion barrier for the pyramidal phosphorus centre and the free rotation around the C–C bond linking the phosphole rings.

However, the stereochemical and structural analyses reveal that only one configuration, $[a]^{S}_{RR}$ and $[a]^{R}_{SS}$, is favourable for chelating transition metals atoms. Numerous complexes of



Scheme 5.

Ni, Pd, Pt, Rh and Ru with this specific configuration have been obtained with the 1,1′-diphenyl-3,3′,4,4′-tetramethyl-2,2′-biphosphole ligand (BIPHOS) and fully characterised by NMR and X-ray diffraction. Moreover, this stereochemistry of the 2,2′-biphosphole ligand appears to be stable once coordinated to the metal.

These results have highlighted the potential of this ligand in coordination chemistry. More work is currently being done in order to define the evaluation of BIPHOS in catalysis.

Experimental

All reactions were conducted under an inert atmosphere of dry argon using Schlenk glassware and vacuum line techniques. Solvents were freshly distilled from standard drying agents. Preparative column chromatography was performed on Merck silica gel (70–20 μm).

^{1}H, $^{13}C\{^{1}H, ^{31}P\}$ and $^{31}P\{^{1}H\}$ NMR spectra were recorded on a Bruker WMX 400 instrument operating at 400, 162 and 100 MHz, respectively. Chemical shifts are reported in parts per million (ppm) relative to Me_4Si (^{1}H and ^{13}C) or 85% H_3PO_4 (^{31}P). For ^{1}H and ^{13}C data, biphosphole ligands and biphospholes complexes have the same numbering as in the X-ray structures. The following abbreviations are used: s, singlet; d, doublet; t, triplet; m, multiplet. Elemental analyses were performed by the 'Service d'Analyse du Laboratoire de Chimie de Coordination' at Toulouse, France. Mass spectra were obtained on a Mermag R10-10 instrument.

X-Ray structure determinations were performed at room temperature for **3a** and at 160 K for **2a** on a Stoe IPDS diffractometer equipped with a graphite oriented monochromator utilising MoKα radiation (λ=0.71073). Structures were solved by direct methods (SIR92)[18] and refined by least-squares procedures on Fobs. H atoms could be located on difference Fourier syntheses, but they were introduced into the calculation in the idealised position (d(CH)= 0.96 Å) and their atomic coordinates were recalculated after each cycle. They were given isotropic thermal parameters 20% higher than those of the carbon to which they are attached. Least-squares refinements were carried out by minimising the function $w(F_o-F_c)^2$, where F_o and F_c are the observed and calculated structure factors. The calculations were carried out with the CRYSTALS package programs.[19] Molecular views were drawn using ORTEP 3.[20] Crystal and data collection parameters, the final residual values, the relevant structure refinement parameters, the atomic coordinates for the non-hydrogen atoms, the positional and isotropic displacement coefficients for hydrogen atoms, a list of anisotropic displacement coefficients for the non-hydrogen atoms and a full list of bond distances and bond angles have been deposited with the Cambridge Crystallographic Data Base.

The starting materials 2,2′-biphosphole compound **1**[8] and complexes **5**,[11] **7**,[11] **8**[11] and **10**[15] were prepared as previously described in the literature.

1,1′-Dicyano-3,3′,4,4′-tetramethyl-2,2′-biphosphole (2). A solution of 1,1′-diphenyl-3,3′,4,4′-tetramethyl-2,2′-biphosphole **1** (0.160 g, 0.43 mmol) in 5 ml of THF was added to a suspension of lithium (10-fold excess) in THF. After 3 h, the excess lithium was removed from the crude mixture. This solution was then added to a solution of cyanogen bromide (0.405 g, 3.85 mmol) in 5 ml of THF and 10 ml of toluene at −60 °C. The mixture was then allowed to warm at room temperature for 1 h. The mixture was concentrated under vacuum and filtrated over silica gel to give 0.083 g of a yellow solid (71%). ^{31}P-NMR ($CDCl_3$): δ −37.34 (83%, **2a**) and −41.88 (17%, **2b**).

2a: ^{1}H NMR ($CDCl_3$): δ 1.99 (s, 6H, Me31, 31′), 2.18 (s, 6H, Me21, 21′), 6.32 (m, 2H, =C*H*–P); ^{13}C NMR ($CDCl_3$): δ 157.9 (t, J_{CP} 7 Hz, C2), 151.0 (t, J_{CP} 20 Hz, C3), 131.5 (t, J_{CP} 25 Hz, C1), 119.5 (s, CH, C4), 115.9 (d, J_{CP} 82 Hz, CN), 18.8 (t, J_{CP} 2.2 Hz, C31,131), 15.7 (s, C21,121). MS (DCI, CH_4), *m/z*: 290 (M^++18, 100%), 272 (M^+, 2%). Anal. Found (Calcd.) for $C_{14}H_{14}N_2P_2$: C, 61.59 (61.76); H, 5.20 (5.15); N, 10.15 (10.29). Single crystals of **2a** were isolated by slow evaporation in dichloromethane.

1,1′-Diphenyl-3,3′,4,4′-tetramethyl-2,2′-biphosphole dioxide (3). To a solution of biphosphole **1** (310 mg, 0.082 mmol) in dichloromethane (6 ml) cooled at −15°C, was slowly added a solution of 3-chloroperoxybenzoic acid (290 mg, 1.67 mmol, 2.02 equiv.) in dichloromethane (2.5 ml). During the addition the temperature was kept between −15°C and −10°C. After stirring for 3.5 h at −10°C, the mixture was washed at room temperature twice with a saturated solution of $NaHCO_3$. The two phases were separated on a phase separator filter and the organic phase was evaporated to give 310 mg (92%) of compound **3** (**3a**+**3b**) as a pale yellow powder. The major product **3a** was obtained in a pure form as colourless crystals from a dichloromethane solution by slow diffusion with pentane.

3a: ^{1}H NMR: δ 2.08 (s, 6H, Me31,131), 2.15 (t, $^{3+4}J_{HP}$ 2.2 Hz, 6H, Me21,121), 5.86 (d, $^{2}J_{HP}$ 27.8 Hz, 2H, =CH–P), 6.97–7.02 (m, 4H, Ph), 7.14–7.19 (m, 2H, Ph), 7.29–7.34 (m, 4H, Ph); $^{31}P\{^{1}H\}$ NMR: δ 42.20; $^{13}C\{^{1}H\}$ NMR: δ 154.14 (dd, $^{2}J_{CP}$ 19.9 Hz, $^{4}J_{CP}$ 2.8 Hz, C2,12), 153.69 (dd, $^{2}J_{CP}$ 29.1 Hz, $^{4}J_{CP}$ 5.5 Hz, C3,13), 131.46 (s, C114,214), 130.15 (d, $^{2}J_{CP}$ 10.8 Hz, C112,116,212,216), 128.53 (d, $^{3}J_{CP}$ 12.6 Hz, C113,115,213,215), 128.48 (dd, $^{1}J_{CP}$ 99.0 Hz, $^{2}J_{CP}$ 8.8 Hz, C1,11), 126.27 (d, $^{1}J_{CP}$ 97.2 Hz, C111,112), 122.43 (dd, $^{1}J_{CP}$ 98.3 Hz, $^{4}J_{CP}$ 2.2 Hz, C4,14), 17.91 (d, $^{3}J_{CP}$ 18.6 Hz, C31,131), 15.27 (dd, $^{3}J_{CP}$ 15.0 Hz, $^{4}J_{CP}$ 2.7 Hz, C21,121). MS (DCI/NH_3): 407 (M+1, 100%). Anal. Found (Calcd.) for $C_{24}H_{24}P_2O_2$: C, 70.21 (70.93); H, 5.96 (5.95).

3b: ^{1}H NMR: δ 1.72 (s, 6H, Me31,131), 2.07 (s, 6H, Me21,121), 5.95 (d, $^{2}J_{HP}$ 25.0 Hz, 2H, =CH–P), 7.21–7.71 (m, 10H, Ph); $^{31}P\{^{1}H\}$ NMR: δ 41.00.

1,1′-Diphenyl-3,3′,4,4′-tetramethyl-2,2′-biphosphole disulfide (4). To a solution of biphosphole **1** (270 mg, 0.72 mmol) in dichloromethane (8 ml) was added 104 mg (3.24 mmol, 4.5 equiv.) of sulfur. After 2 h of reflux, the solvent was evaporated to give 299 mg (95%) of compound

4 (**4a**+**4b**) as yellow powder. **4a** and **4b** were separated by chromatography on silica gel with dichloromethane as eluant.

4a: ^{1}H NMR: δ 2.11 (t, $^4J_{HP}$ 2.63 Hz, 6H, Me21,121), 2.14 (s, 6H, Me31,131), 6.03 (d, $^2J_{HP}$ 31.49 Hz, 2H, ═C*H*–P), 7.03 (m, 4H, Ph), 7.19 (m, 2H, Ph), 7.35 (m, 4H, Ph); ^{31}P{^{1}H} NMR: δ 50.75; ^{13}C{^{1}H} NMR: δ 153.32 (dd, $^2J_{CP}$ 25.6 Hz, $^3J_{CP}$ 7.6 Hz, C2,12), 152.32 (dd, $^2J_{CP}$ 15.0 Hz, $^4J_{CP}$ 2.1 Hz, C3,13), 131.17 (d, $^4J_{CP}$ 3.1 Hz, C114,214), 131.10 (dd, $^1J_{CP}$ 82.9 Hz, $^2J_{CP}$ 11.5 Hz, C1,11), 130.31 (d, $^2J_{CP}$ 12.0 Hz, C112,116,212,216), 128.42 (d, $^3J_{CP}$ 12.9 Hz, C113,115,213,215), 127.08 (dd, $^1J_{CP}$ 82.1 Hz, $^4J_{CP}$ 2.7 Hz, C4,14,), 124.02 (d, $^1J_{CP}$ 76.5 Hz, C111,211), 17.91 (d, $^3J_{CP}$ 16.6 Hz, C31,131), 15.42 (dd, $^3J_{CP}$ 13.3 Hz, $^4J_{CP}$ 1.9 Hz, C21,121). MS (DCI/NH_3): 439 (M+1, 100%). Anal. Found (Calcd.) for $C_{24}H_{24}P_2S_2$: C, 65.63 (65.73); H, 5.36 (5.51); S, 14.68 (14.62). Single crystals of **4a** were obtained by slow evaporation in dichloromethane.

4b: ^{1}H NMR: δ 1.66 (t, $^4J_{HP}$ 2.33 Hz, 6H, Me21,121), 2.09 (s, 6H, Me31,131), 6.09 (d, $^2J_{HP}$ 30,9 Hz, 2H, ═CH–P), 7.37 (m, 4H, Ph), 7.49 (m, 2H, Ph), 7.62 (m, 4H, Ph); ^{31}P{^{1}H} NMR: δ 51.37; ^{13}C{^{1}H} NMR: δ 153.49 (dd, $^2J_{CP}$ 15.0 Hz, $^4J_{CP}$ 2.0 Hz, C3,13), 150.56 (dd, $^2J_{CP}$ 25.8 Hz, $^3J_{CP}$ 7.7 Hz, C2,12), 133.05 (dd, $^1J_{CP}$ 81.7 Hz, $^2J_{CP}$ 11.2 Hz, C1,11), 131.89 (d, $^4J_{CP}$ 3.0 Hz, C114,214), 131.08 (d, $^2J_{CP}$ 11.7 Hz, C112,116,212,216), 128.44 (d, $^3J_{CP}$ 12.8 Hz, C113,115,213,215), 127.13 (d, $^1J_{CP}$ 77.8 Hz, C111,211), 125.59 (dd, $^1J_{CP}$ 82.7 Hz, $^4J_{CP}$ 2.1 Hz, C4,14), 18.03 (d, $^3J_{CP}$ 16.6 Hz, C31,131), 15.01 (dd, $^3J_{CP}$ 13.4 Hz, $^4J_{CP}$ 1.8 Hz, C21,121). MS (DCI/NH_3): 439 (M+1, 95%). Anal. Found (Calcd.) for $C_{24}H_{24}P_2S_2$: C, 65.75 (65.73); H, 5.40 (5.51); S, 14.36 (14.62). Single crystals of **4b** were obtained by slow evaporation in dichloromethane.

[Ru(η^3-2-methylallyl)$_2$(1,1′-diphenyl-3,3′,4,4′-tetramethyl-2,2′-biphosphole)] (6). To a solution of [Ru(η^3-allyl)$_2$(η^4-cycloocta-1,5-diene)] (50 mg, 0.16 mmol) in dichloromethane (2 ml) was added a solution of biphosphole **1** (59 mg, 0.16 mmol) in dichloromethane (2 ml). After stirring for 8 d at room temperature, the resulting red solution was evaporated to dryness. The complex **6** thus obtained was a deep red oil extremely air, moisture and light sensitive.

6: ^{1}H NMR: δ 1.17 (s, 2H, allyl), 1.36 (s, 2H, allyl), 1.69 (s, 2H, allyl), 1.77 (s, 2H, allyl), 1.92 (s, 6H, Me_{allyl}), 1.95 (s, 6H, Me21,121), 2.08 (d, $^4J_{H-H}$ 1.9 Hz,6H, Me31,131), 6.07 (dd, $^2J_{H-P}$ 30.4 Hz, $^4J_{H-H}$ 1.9 Hz, 2H, ═C*H*–P), 7.22 (m, 6H, Ph), 7.43 (m, 4H, Ph); ^{31}P{^{1}H} NMR: δ 73.00. MS (DCI/NH_3): 587 (M+1, 100%)

[Ru(acetate)$_2$(1,1′-diphenyl-3,3′,4,4′-tetramethyl-2,2′-biphosphole)$_2$] (9, 11). To a solution of [Ru(η^2-acetate)$_2$-(η^4-cycloocta-1,5-diene)] (100 mg, 0.3 mmol) in methyl alcohol (5 ml) was added a solution of biphosphole **1** (220 mg, 0.6 mmol, 2 equiv.) in methyl alcohol (10 ml). The mixture was stirred for 30 min at room temperature. After removal of the solvent, the *trans–meso* complex **9** was obtained as an orange-yellow powder. Yield: 135 mg (50%).

9: ^{1}H NMR: δ 1.67 (s, 6H, CO_2CH_3), 1.92 (s, 12H, Me121,221, 421,521), 2.04 (d, $^4J_{H-H}$ 1.0 Hz, 12H, Me131,331,431,531), 6.78 (m, 4H, ═CH–P), 6.86 (m, 12H, Ph), 6.96 (m, 8H, Ph); ^{31}P{^{1}H} NMR: δ 58.18. MS (FAB, MNBA matrix); *m*/*z*: 968 (M^+, 45%), 909 ($[M-(CO_2CH_3)]^+$, 100%), 849 ($[M-2(CO_2CH_3)]^+$, 66%).

The *cis*-(±)-complex **11** was quantitatively obtained from the *trans–meso* **9** in 6 h in a dichloromethane solution.

11: ^{31}P{^{1}H} NMR: δ 34.17–34.41 (m), 38.65–39.69 (m), 50.17–50.76 (m), 61.20–62.27 (m), 62.75–63.47 (m). MS (FAB, MNBA matrix); *m*/*z*: 909 ($[M-(CO_2CH_3)]^+$, 100%), 849 ($[M-2(CO_2CH_3)]^+$, 42%).

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