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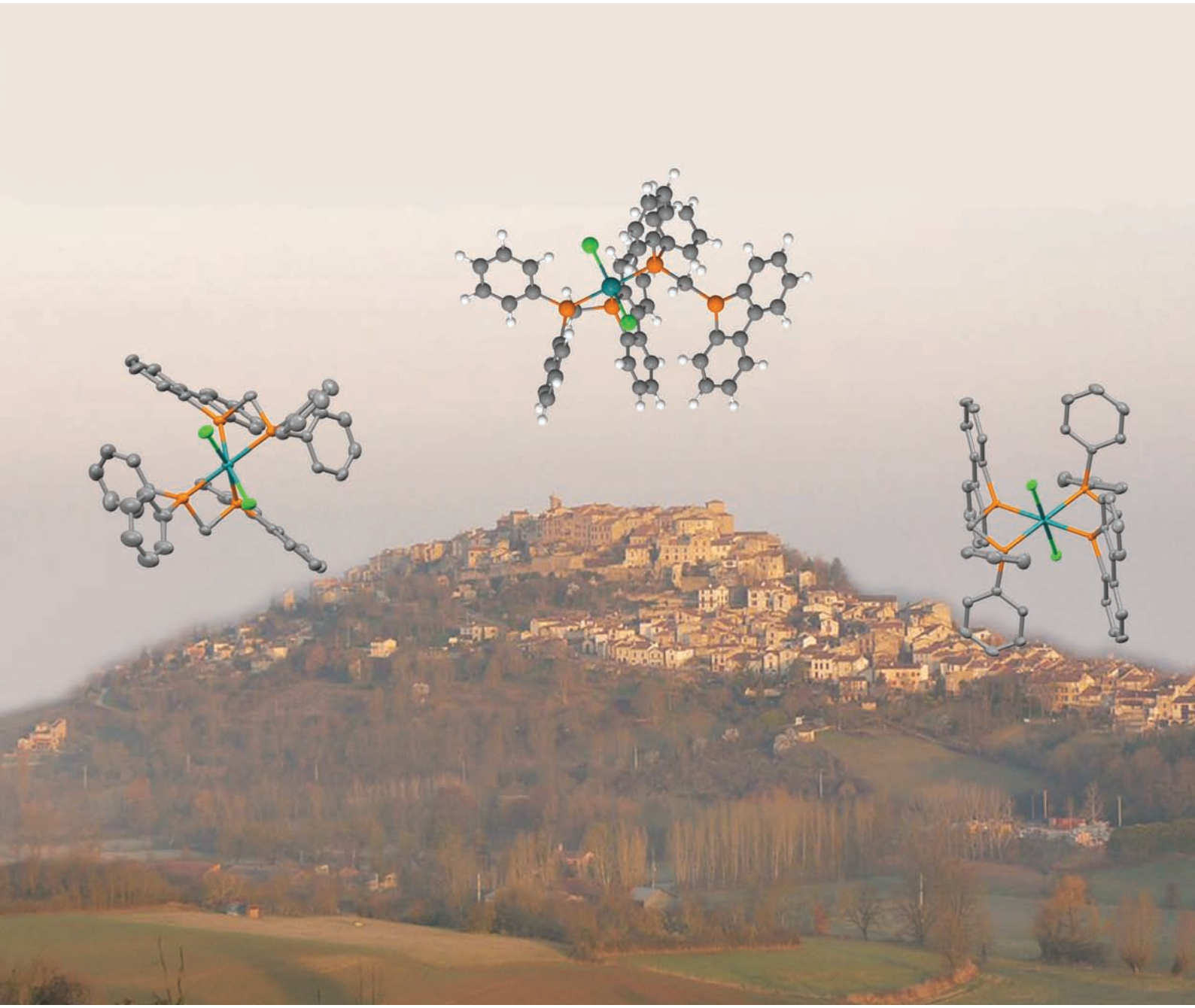

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Novel phospholyl(diphenylphosphino)methane-ruthenium complexes: unexpected non-assisted *cis* to *trans* isomerization of $[RuCl_2(\kappa^2\text{-P–P}')_2]$†‡

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Using the unsymmetrical P–P′ phospholyl(phosphino)methane ligand, complex *cis*-$[RuCl_2(\kappa^2\text{-P–P}')_2]$ is easily prepared from $[RuCl_2(DMSO)_4]$. The two phosphole-phosphorus atoms lie in the *trans* position to the two *cis*-chloro ligands. This complex slowly isomerizes spontaneously at 20 °C to the *trans*-$[RuCl_2(\kappa^2\text{-P–P}')_2]$ diastereoisomer where the two phosphole moieties are mutually *trans*, as well as the two chloro ligands and the two Ph_2P moieties. DFT calculations show that this non-classical *cis–trans* isomerisation process requires a 3 kcal mol^{-1} energy and involves the decoordination of a phosphole arm.

Introduction

Small-bite angle diphosphines in which the two phosphorus centers are separated only by a single atom linker unit, such as 1,1-bis(diphenylphosphino)methane (dppm),[1] give various coordination modes being monodentate, or bi-coordinated in either chelating- (resulting in highly strained 4-membered metallocycles) or bridging-geometries (including A-frame complexes).

In the coordination sphere of ruthenium(II), dppm can act as a chelating ligand leading to *cis*- and/or *trans*-isomers of $[RuX_2(P\text{–}P)_2]$.[2,3] The *trans*-$[RuCl_2(\kappa^2\text{-}Ph_2PCH_2PPh_2)_2]$ complex containing the dppm constrained ligand was prepared very early on by Chatt and Hayter.[2]

Two X-ray crystal structures of the methanol solvate or the dichloromethane disolvate have been solved and show a distorted octahedral geometry.[4] The *cis*-isomer has been prepared from $[RuCl_2(PPh_3)_4]$ by reaction of the $Ph_2PCH_2PPh_2$ ligand at 150–200 °C in the absence of solvent.[3] Thermal conversion of *trans*-$[RuCl_2(\kappa^2\text{-}Ph_2PCH_2PPh_2)_2]$ into the *cis*-isomer was shown to be quantitative in refluxing dichloroethane (83.3 °C).[3] In addition, the presence of catalytic amounts of CuCl or CuI allows the *trans–cis* isomerization at room temperature, in the absence of light.[5] This catalysis is supposed to involve two Ru(μ-Cl)Cu and $Ru(\mu\text{-Cl})_2Cu$ containing-intermediates and thus to labilize the ruthenium–chloro bond(s). Inversely, photolysis or oxidative isomerization can convert the *cis* to the *trans*-isomer through a ruthenium(III) intermediate.[3] Cyclic voltammetry of the *cis*-$[RuCl_2(\kappa^2\text{-}Ph_2PCH_2PPh_2)_2]$ showed the presence of a free Cl^- ion in nonaqueous solvents providing for instance in acetonitrile the *cis*-$[RuCl(CH_3CN)(\kappa^2\text{-}Ph_2PCH_2PPh_2)_2]Cl$ species.[3] Thus, the *cis–trans* isomerization can be promoted by photo- or electro-chemical activation.

Unsymmetrical diphosphinomethane ligands, $R^1{}_2PCH_2PR^2{}_2$, which are appropriate ligands for geometrical isomerism studies in six-coordinate complexes, have attracted less attention and to the best of our knowledge no ruthenium complexes have been reported. As part of our continuing interest in the design and coordination chemistry of hybrid phospholyl(phosphino)methane ligands,[6] we were interested in introducing the unsymmetric dibenzophospholyl(diphenylphosphino)methane ligand in the coordination sphere of ruthenium(II). In the present study, we report the selective synthesis of the *cis*-$[RuCl_2(\kappa^2\text{-P–P}')_2]$ complex and its unexpected isomerisation into the *trans*-$[RuCl_2(\kappa^2\text{-P–P}')_2]$ complex. The structures of both complexes were determined by single crystal X-ray diffraction analyses. DFT calculations have been carried out to study the *cis–trans* isomerisation mechanism.

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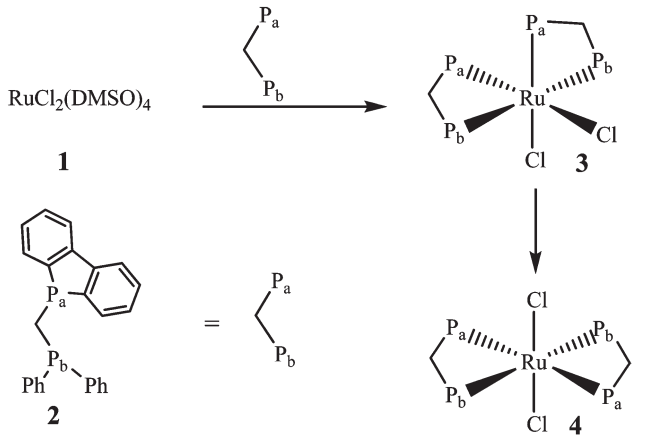
†This paper is dedicated to our colleague Professor David J. Cole-Hamilton, on the occasion of his 65th birthday. David, an outstanding scientist, was very creative in coordination catalysis to develop new concepts, to expand them to industrial catalysis and to analyze in depth how the catalyst is working under operating conditions.

‡Electronic supplementary information (ESI) available. CCDC 899803 and 899804. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2dt32032k



Scheme 1

Results and discussion

$[RuCl_2(DMSO)_4]$ (**1**) is a versatile starting precursor for the preparation of numerous $[RuCl_2(L\text{–}L')_2]$ complexes such as dichlorobis(diphosphine)ruthenium(II) complexes.[7] The reaction of 2 molar equiv. of dibenzophospholyl(diphenylphosphino)methane ligand **2**, prepared according to the previously described method,[6a] with 1 equiv. of complex **1** in dichloromethane at room temperature selectively leads to the formation of a bis(phosphole–phosphine)ruthenium complex **3** (Scheme 1), as supported by elemental analysis, mass spectrometry and NMR spectroscopy.

In addition, crystals of complex **3**, suitable for X-ray analysis, were obtained by slow diffusion of diethyl ether into a concentrated dichloromethane solution at −20 °C. X-ray structural analysis confirms the formation of the dichlorobis{dibenzophospholyl(diphenylphosphino)methane}ruthenium complex **3**. The molecular structure determined represented in Fig. 1 shows a near octahedral geometry for ruthenium. Indeed, this complex is deformed in the equatorial plane of the octahedron as shown by the Cl1–Ru1–P1 and the Cl2–Ru1–P3 angles (165.80 (5)°, 164.47 (5)° respectively) whereas the P2–Ru1–P4 angle in the axial position is 179.63 (5)°. Thus P1, P3, Cl1 and Cl2 are not rigorously in the same plane, since by considering the average plane passing by Cl1, Cl2 and Ru1, the two P3 and P1 atoms lie 0.588 Å above the plane for P3 and 0.550 Å below the plane for P1. In addition, the crystal structure reveals the arrangement around the Ru centre. The two Cl atoms are in *cis* configuration, the two phosphorus atoms P_a of the phosphole ring are *trans* to the chloro ligands whereas the two phosphorus atoms of the phosphino groups P_b are in the *trans* position (Fig. 1).

The two Ru–P bond lengths corresponding to the P_b atoms *trans* to each other, Ru(1)–P(2) 2.3573(14) Å, Ru(1)–P(4) 2.3491(14) Å, are significantly longer than those for the two P_a atoms *trans* to the chloro atoms, Ru(1)–P(3) 2.2690(13) Å and Ru(1)–P(1) 2.2924(13) Å. This difference could be the consequence of the *trans* influence of the chloro ligands due to the π-donation from the Cl through the Ru to the *trans* P1 and P3 as also

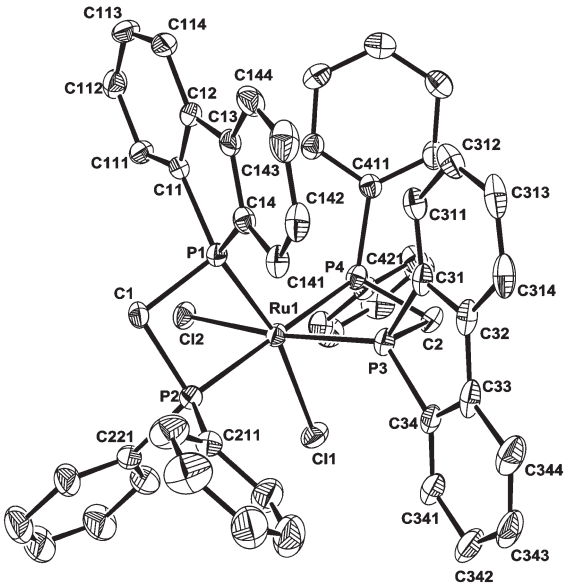


Fig. 1 Molecular view of complex **3** with the atom-labelling scheme. Ellipsoids are drawn at the 30% probability level. H atoms as well as the labels for the phenyl groups have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ru(1)–P(1) 2.2924(13), Ru(1)–P(3) 2.2690(13), Ru(1)–P(2) 2.3573(14), Ru(1)–P(4) 2.3491(14), Ru(1)–Cl(1) 2.4502(13), Ru(1)–Cl(2) 2.4671(12), P(1)–Ru(1)–P(2) 70.53(4), P(1)–Ru1–P(3) 101.43(5), P(1)–Ru(1)–P(4) 109.63(5), P(1)–Ru(1)–Cl(1) 165.80(5), P(1)–Ru(1)–Cl(2) 85.79(4)(5), P(2)–Ru(1)–P(3) 108.54(5), P(2)–Ru(1)–P(4) 179.63 (5), P(2)–Ru(1)–Cl(1) 95.46(5), P(2)–Ru(1)–Cl2) 86.78(5), P(3)–Ru(1)–P(4) 71.12(5), P(3)–Ru(1)–Cl(1) 84.88(5), P(3)–Ru(1)–Cl(2) 164.47(5), P(4)–Ru(1)–Cl(1) 84.39(5), P(4)–Ru(1)–Cl(2) 93.55(5), Cl(1)–Ru(1)–Cl(2) 91.30(4), P(1)–C(1)–P(2) 93.7(2), P(3)–C(2)–P(4) 93.5(2).

observed in related complexes.[8] We analyzed the possibilities of some interactions within the complex which could explain the relative stability of this configuration; however, although the 3.652 Å distance between the two centroids of two phenyl rings could be favourable to a π–π stacking, the 3.21 Å distance of the normal vector to the plane leads to a 2.25 Å slippage between the two planes, which prevents any interaction. Moreover, a 10° dihedral angle between the two ligands is consistent with the absence of any interaction.

For such a *cis*-complex containing an unsymmetric ligand, three diastereoisomers could be formed: two C_2 complexes corresponding to P_a *trans* and P_b *trans* to the chloro ligands (**A** and **B** forms) and one C_1 complex in which P_a and P_b are *trans* to the chloro ligands (**C** form) as represented in Fig. 2.

^1H and ^{31}P NMR data are consistent with the **A** or **B** forms of complex **3**. Indeed, the two doublets of doublets observed in ^{31}P NMR at 3.39 (dd, P_b, J_{PbPa} = 40.5, $J_{PbPa'}$ = 41.2 Hz) and at −16.36 (dd, P_a, J_{PaPb} = 40.5, $J_{PaPb'}$ = 41.2 Hz) can be interpreted as an AA′XX′ spin system. The higher field doublet of doublets pattern is assigned to the P_a atom of the phospholyl group and the lower field signal to the P_b atom of the diphenylphosphino group *via* ^1H–$^{31}P\{^1H\}$ HMQC experiments. This spin system is inconsistent with the **C** form which could display an ABCD spin system corresponding to the four nonequivalent phosphorus nuclei.

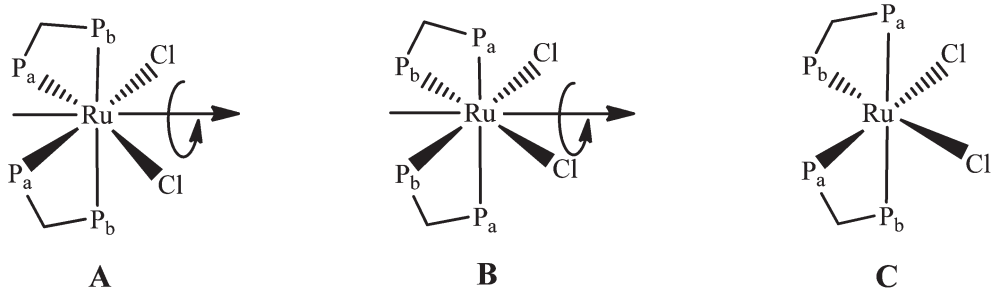


Fig. 2 The 3 possible diastereoisomers for complex **3**.

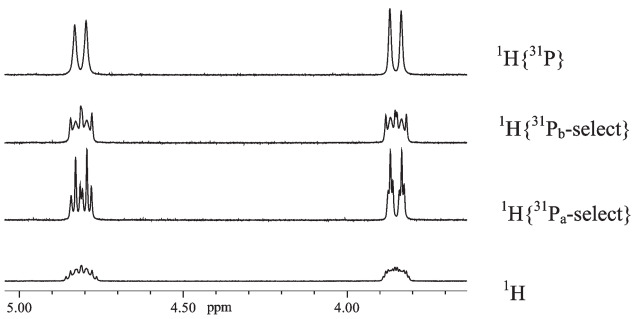


Fig. 3 ^1H NMR spectra of complex **3** in CD_2Cl_2.

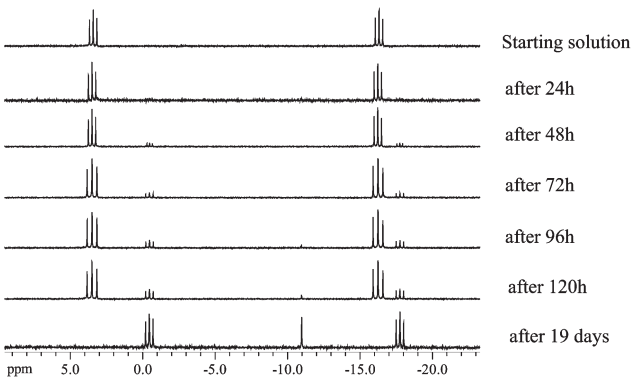


Fig. 4 $^{31}P\{^1H\}$ NMR isomerisation monitoring in CD_2Cl_2 at RT.

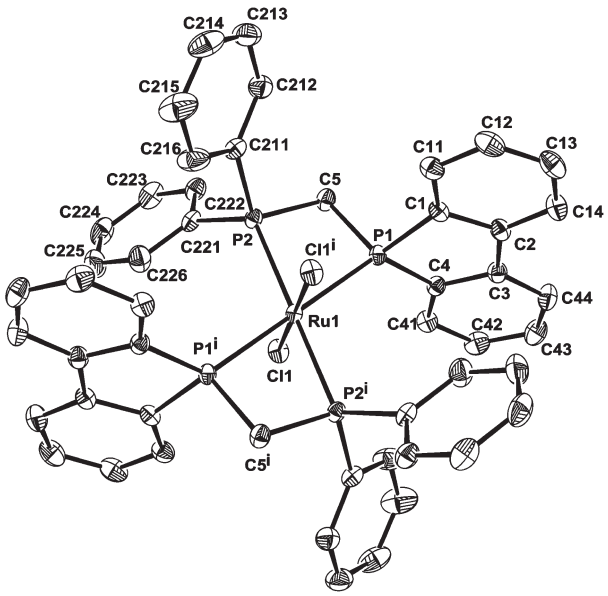


Fig. 5 Molecular view of complex **4** with the atom-labelling scheme. Ellipsoids are drawn at the 30% probability level. H atoms have been omitted for clarity. Selected bond lengths (Å) and bond angles (°): Ru(1)–P(1) 2.3282(4), Ru(1)–P(2) 2.3339(4), Ru(1)–Cl(1) 2.4149(4), P(1)–Ru(1)–P(2) 71.613(14), P(1)–Ru(1)–P(2)^i 108.387(13), P(1)–Ru(1)–Cl(1) 85.753(14), P(1)–Ru(1)–Cl(1)^i 94.247(13), P(2)–Ru(1)–Cl(1) 84.131(14), P(2)–Ru(1)–Cl(1)^i 95.869(14), P(1)–C(5)–P(2) 94.69(7) [symmetry code (i) $-x + 1, -y + 1, -z + 1$].

In ^1H NMR, the spin system observed for the methylene bridging protons also indicates the formation of the **A** or **B** forms. The two CH_2 groups are equivalent and resonate as two sets of broad multiplets centered at δ 4.81 and 3.85 ppm in a 1 : 1 ratio, which indicates that two protons of CH_2 are diastereotopic (AB spin system), as confirmed by deeper NMR ^1H- selective decoupling ^{31}P measurements (Fig. 3).

In addition, the ^1H NMR spectrum at room temperature indicates the hindrance to rotation of the dibenzophospholyl ring since the eight protons are inequivalent. Consequently, we assume that the privileged formation of the C_2-complex **3** (**A** form) is probably controlled by steric factors.

The *cis*-complex **3** slowly evolves in dichloromethane solution at room temperature since its complete transformation after 19 days was observed leading to the formation of a new complex **4** (Scheme 1). Monitoring the course of this conversion by ^{31}P NMR spectroscopy (Fig. 4), we observed the disappearance of the AA′XX′ system of the complex **3** concomitant with the appearance of a new AA′XX′ system at higher field relative to **3** (δ −0.49 (dd, P_b, J_{PaPb} = 27.0, 30.4 Hz) and −17.82 ppm (dd, P_a, J_{PaPb} = 27.0, 30.4 Hz).

Complex **4** is obtained as a pure isomer which could be isolated in good yield (60%). Elemental analysis, mass spectrometry, and ^1H NMR spectroscopy confirmed the formation of a bis(diphosphine)ruthenium complex **4**. The molecular structure, determined by X-ray analysis and represented in Fig. 5, shows the *trans* positions for the two chloro, the two P1 and the two P2 atoms. The four Ru–P bond distances lie in the range 2.3282–2.3338 Å as observed for related ruthenium(II) bisphosphine *trans*-disubstituted complexes.[9,10]

We observed again the formation of only one diastereoisomer among the two possible for complex **4** (Fig. 6).

^{31}P NMR supports the formation of the **D** form. The AA′XX′ spin system observed in ^{31}P NMR exhibits low J_{PP} coupling constants consistent with the **D** form but not with the **E** form which could display a higher J_{PP} coupling constant for the two P_a and P_b phosphorus atoms in the *trans*-position. Interestingly, the ^{31}P chemical shifts of **4** lie systematically upfield relative to **3**: 3.88 and 1.46 ppm away for phospholyl-P_a and phosphino-P_b, respectively. In contrast to complex **3**, the two equivalent methylene bridging protons resonate in ^{1}H NMR as only one set of multiplets centered at 4.93 ppm leading to a single signal by ^{31}P broadband decoupling which indicates that two protons of the CH_2 are equivalent. In addition, the four distinct protons observed for the dibenzophospholyl ring indicate the free rotation of this group in this case.

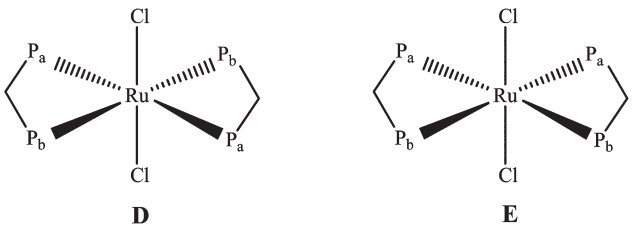


Fig. 6 The two possible diastereoisomers for complex **4**.

To explain the isomerization of the *cis*-**3** into the thermodynamic product *trans*-**4**, we have examined the possible intramolecular rearrangement of the ligands in six-coordinate complexes which can occur by twisting or dissociative processes (Fig. 7).

According to this analysis, an intramolecular twist mechanism can only lead to a new *cis*-complex. In addition, the isomerization of the *cis*-**3** into the thermodynamic product *trans*-**4** is inconsistent with a P_b bond-breaking/bond-making mechanism as the two P_b atoms stay in the *trans* position in complex **4**. According to these considerations, the isomerization *cis*-**3** → *trans*-**4** could occur either *via* a Cl^- decoordination or *via* a P_a-decoordination.

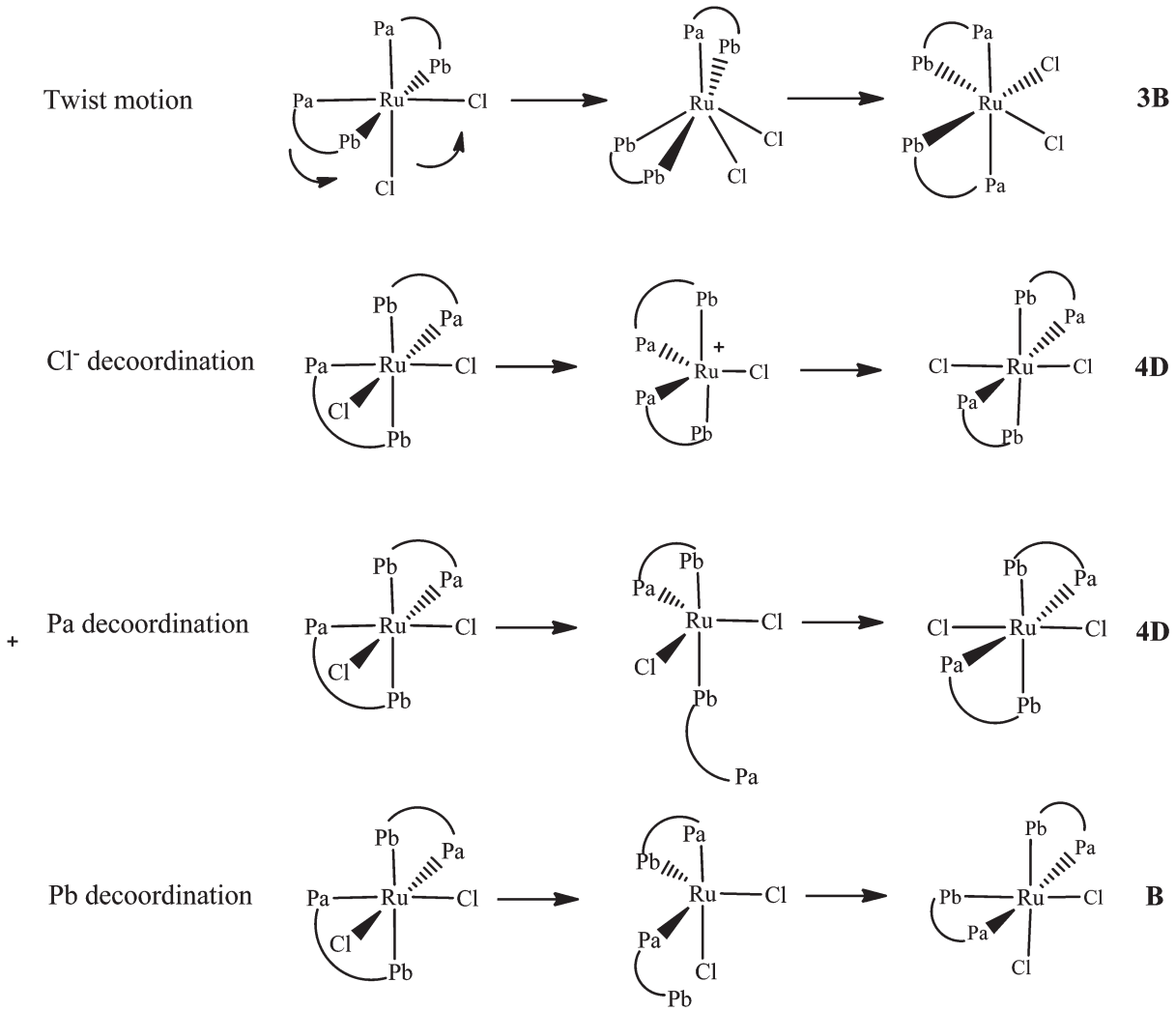


Fig. 7 Possible intramolecular rearrangements of complex **3** by twisting or dissociative processes.

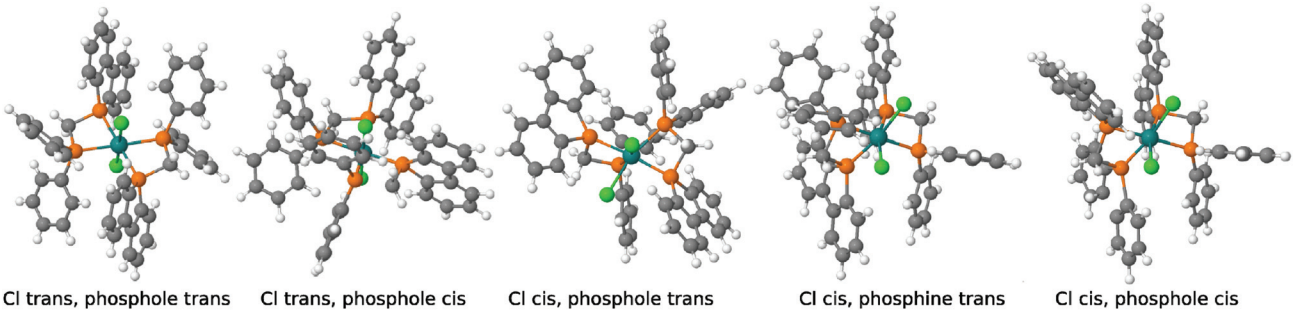


Fig. 8 Structures of the five possible isomers for the Ru complex (**4-D**, **4-E**, **3-B**, **3-A**, **3-C**).

In order to gain more insights into the relative stability of the *cis*- and *trans*-Ru complexes and on the isomerisation process, DFT calculations have been carried out. The five isomers are depicted in Fig. 8 (Cl in *trans*, phosphole in *trans*, complex **4**-form **D**; Cl in *trans*, phosphole in *cis*, complex **4**-form **E**; Cl in *cis*, phosphole in *trans*, complex **3**-form **B**; Cl in *cis*, phosphine in *trans*, complex **3**-form **A**; Cl in *cis*, phosphole in *cis*, complex **3**-form **C**).

The five isomers were optimized and their relative stability can be compared. The complex **4-D** is the most stable, followed by the complex **3-A** (less stable by 2.13 kcal mol^{-1}), then the complex **4-E** (with a difference of 2.95 compared to the complex **4-D**), then the complex **3-B** (with a difference of 8.91 kcal mol^{-1}). Finally, the complex **3-C** is the least stable, with a difference of 10.54 kcal mol^{-1} compared to the complex **4-D**.

To further understand the stability of the complex, NMR parameters of the two most stable complexes **4-D** and **3-A** have been computed. Comparing the shielding for the P atoms of the phospholes of the two complexes, we observe that the screening is bigger for **4-D** than for **3-A** ($\Delta\delta$ = +26 ppm). This trend is in agreement with what has been obtained experimentally through phosphorus NMR analysis. This indicates an increase of the electron density on the P atom of the phosphole in **4-D** and thus in the vicinity of the Ru atom. This will strengthen the Ru–P bonds thus leading to the stabilization of **4-D**. This bond strengthening is confirmed by the Wiberg bond indexes obtained through the use of the Natural Bond Orbital study (Ru–$P_{(phosphole)}$ bond indexes: 0.69 for **4-D** and 0.78 for **3-A**). The result shows stronger bond indexes for the Ru–$P_{(phosphole)}$ of **4-D** than those of **3-A**.

Finally, the *cis*–*trans* isomerization process has been investigated. Despite our effort, it has not been possible to locate any transition state for this isomerization. This might be explained by the fact that the decoordination of one phosphole arm from Ru in **3-A** leads to the rearrangement of the Cl atom from the *cis*- to *trans*-position (see Fig. 9). This complex has been optimized and is found to be a minimum on the Potential Energy Surface that is less stable than **3-A** by 16 kcal mol^{-1}. This complex is thus an intermediate in the reaction process and gives a rough estimate of the activation barrier of isomerization from complex **3-A** into the complex **4-D**. Isomerization involving the decoordination of a chloride rather than a phosphole arm has been computed to be much higher in energy (roughly 53.0 kcal mol^{-1}).

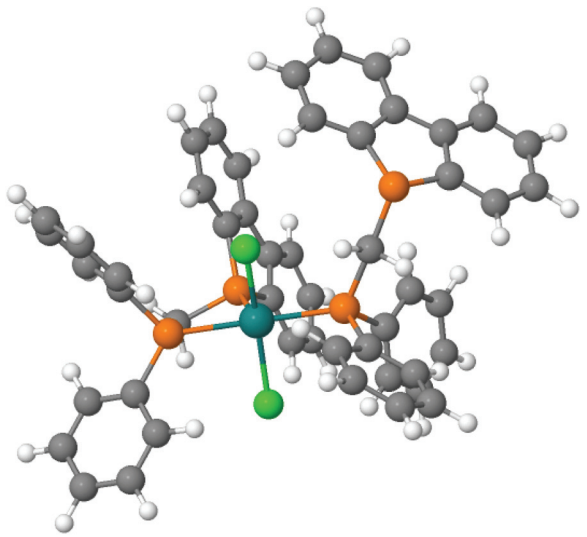


Fig. 9 Optimized structure of the complex with Cl in *cis* and a decoordinated phosphole arm.

In conclusion, addition of two equivalents of the unsymmetric phosphole–phosphine ligand to the ruthenium(II) $[RuCl_2(DMSO)_4]$ precursor leads to *cis*-$[RuCl_2(P_a–P_b)_2]$. A slow isomerization process has been analyzed by NMR experiments showing the exclusive formation of *trans*-$[RuCl_2(P_a–P_b)_2]$. DFT calculations are consistent with a slightly lower (3 kcal mol^{-1}) energy for the *trans*-isomer and with a *cis*-/*trans*-isomerization mechanism involving the decoordination of a phosphole arm. Further studies will be dedicated to the reactivity of these complexes and more particularly to explore their potential in catalysis.

Experimental section

General procedures

All reactions were carried out under an argon atmosphere in dried glassware. Solvents were dried and freshly distilled under an argon atmosphere over sodium–benzophenone for diethyl ether and P_2O_5 for CH_2Cl_2. Thin-layer chromatography

was performed on alumina. All NMR spectra data were recorded on Bruker DRX 300 or Advance 300–500 spectrometers with TMS as an internal reference for ^{1}H and ^{13}C, 85% phosphoric acid as an external reference for ^{31}P. Spectral assignments were made by means of routine one and two dimensional NMR experiments where appropriate. Mass spectral analyses were performed on a TSQ 7000 Thermoquest instrument (DCI). The major peak *m*/*z* was mentioned with the intensity as a percentage of the base peak in brackets. Elemental analyses were measured with a precision superior to 0.3% at the Microanalysis Laboratory of the LCC at Toulouse. Commercially available $[RuCl_2(DMSO)_4]$ was used as received and ligand **1** was prepared according to the literature.[5]

Synthesis of *cis*-[dichlorobis{dibenzophospholyl(diphenylphosphino)methane}-ruthenium(II)], 3. To a solution of $[RuCl_2(DMSO)_4]$ (0.043 g, 0.087 mmol) in CH_2Cl_2 (20 mL) was added a solution of dibenzophospholyl(diphenylphosphino)methane **2** (0.068 g, 0.178 mmol) in CH_2Cl_2 (20 mL) at −60 °C. The reaction mixture was allowed to warm to RT and stirred further for 20 h. The resulting orange solution was evaporated to dryness. Purification by alumina column chromatography (eluent: CH_2Cl_2 and CH_2Cl_2–MeOH (95 : 5)) yielded 0.055 g (67%) of the *cis*-complex as a yellow solid and <5% of the *trans*-isomer as an off-white solid. ^{1}H NMR (298 K, CD_2Cl_2, 400.13 MHz, ppm): δ 9.33 (m, 2H,=CH–, J_{HH} = 7.6 Hz, phosphole), 8.06 (m, 4H,=CH–, J_{HH} = 2.8, 7.6 Hz, PPh_2), 7.71 (d, 2H,=CH–, J_{HH} = 7.6 Hz, phosphole), 7.62 (dt, 2H,=CH–, J_{HH} = 1.2, 7.2 Hz, phosphole), 7.53 (t, 2H,=CH–, J_{HH} = 7.2 Hz, phosphole), 7.52 (d, 2H,=CH–, J_{HH} = 8.0 Hz, phosphole), 7.32 (m, 10H,=CH–, J_{HH} = 1.6, 4.8 Hz, PPh_2), 7.02 (t, 2H,=CH–, J_{HH} = 7.6 Hz, PPh_2), 6.97 (t, 2H,=CH–, J_{HH} = 7.6 Hz, phosphole), 6.71 (t, 4H,=CH–, J_{HH} = 7.6 Hz, PPh_2), 5.87 (td, 2H,=CH–, J_{HH} = 1.6, 7.2 Hz, phosphole), 5.17 (m, 2H,=CH–, J_{HH} = 7.6 Hz, phosphole), 4.81 (m, 2H, >CH_2, J_{HH} = 13.6 Hz, P_aCHHP_b), 3.85 (m, 2H, >CH_2, J_{HH} = 14.0 Hz, P_aCHHP_b). $^{31}P\{^{1}H\}$ NMR (298 K, CD_2Cl_2, 161.976 MHz, ppm): δ 3.39 (t, P_a, J_{PaPb} = 40.5, 41.2 Hz), −16.36 (t, P2, J_{PaPb} = 40.5, 41.2 Hz). $^{13}C\{^{1}H\}$ NMR (298 K, CD_2Cl_2, 75.468 MHz, ppm): δ 142.78 (t, >C=, J_{CP} = 4.91 Hz), 141.74 (t, >C=, J_{CP} = 5.1 Hz), 135.84 (t, >C=, J_{CP} = 18.4 Hz), 134.45 (t,=CH–, J_{CP} = 5.6 Hz), 132.95 (t,=CH–, J_{CPb} = 5.8 Hz, PPh_2), 131.72 (t,=CH–, J_{CPb} = 7.0 Hz, PPh_2), 131.35 (=CH–, phosphole), 130.02 (t,=CH–, J_{CPb} = 6.4 Hz, PPh_2), 129.64 (d,=CH–, J_{CPa} = 3.40 Hz, phosphole), 129.40 (=CH–, phosphole), 128.79 (t,=CH–, J_{CPa} = 4.8 Hz, phosphole), 127.85 (*t*,=CH–, J_{CPb} = 5.1 Hz, PPh_2), 127.68 (t,=CH–, J_{CPb} = 5.0 Hz, PPh_2), 126.78 (t,=CH–, J_{CPa} = 5.0 Hz, phosphole), 120.80 (t,=CH–, J_{CPa} = 2.8 Hz, phosphole), 120.55 (t,=CH–, J_{CPa} = 2.87 Hz, phosphole), 44.53 (t, >CH_2, J_{CP} = 9.9 Hz, $P_aCH_2P_b$). MS (DCI, CH_4) *m*/*z*: (%) = 936.05 (50%) $[M]^+$, 901.09 (50%) $[M - Cl]^+$. Anal. calcd for: $C_{50}H_{40}Cl_2P_4Ru$: C 64.11; H 4.30. Found: C 64.06; H 4.42.

Synthesis of *trans*-[dichlorobis{dibenzophospholyl(diphenylphosphino)methane}-ruthenium(II)], 4. The *trans*-isomer complex has been formed by slow isomerization of the corresponding *cis*-isomer in CH_2Cl_2 at 20 °C. After 19 days, complex **4** was isolated by alumina column chromatography (eluent: CH_2Cl_2 and CH_2Cl_2–MeOH (95 : 5)). Yield (60%). ^{1}H NMR (298 K, CD_2Cl_2, 300.13 MHz, ppm): δ 8.34 (dt, 4H,=CH–, J_{HH} = 7.8 Hz, J_{HP} = 3.3 Hz, phosphole), 8.07 (d, 4H,=CH–, J_{HH} = 7.5 Hz, phosphole), 7.65 (t, 4H,=CH–, J_{HH} = 7.5 Hz, phosphole), 7.38 (t, 6H,=CH–, J_{HH} = 7.2 Hz), 7.23 (m, 10H,=CH–, J_{HH} = 7.2 Hz, PPh_2), 7.08 (t, 8H,=CH–, J_{HH} = 7.5 Hz), 4.93 (qt, 4H, >CH_2, J_{HP} = 4.5 Hz, $P_aCH_2P_b$). $^{31}P\{^{1}H\}$ NMR (298 K, CD_2Cl_2, 121.495 MHz, ppm): δ −0.49 (t, P_a, J_{PaPb} = 27.0, 30.4 Hz), −17.82 (t, P_b, J_{PaPb} = 27.0, 30.4 Hz). $^{13}C\{^{1}H\}$ NMR data were not recorded due to the slow solubility of this compound in the usual organic solvents. MS (DCI, CH_4) *m*/*z*: (%) = 936.05 (50%) $[M]^+$, 901.09 (50%) $[M - Cl]^+$. Anal. calcd for $C_{50}H_{40}Cl_2P_4Ru$: C 64.11; H 4.30. Found: C 64.04; H 4.25.

X-ray structure determinations

A single crystal of each compound was mounted under inert perfluoropolyether at the tip of a glass fiber and cooled in the cryostream of either a Bruker APEX2 diffractometer for **3** or an Agilent Technologies GEMINI EOS diffractometer for **4**. The structures were solved by direct methods (SIR97)[11] and refined by least-squares procedures on F^2 using SHELXL-97.[12] All H atoms attached to carbon atoms were introduced in the calculation at idealised positions and treated as riding models. One of the phenyls attached to P(2) in compound **3** is disordered over two positions with a ratio of 3 to 1. The refinement of this disordered phenyl group has been carried out using restraints available in SHELXL-97.[13] Moreover, in compound **3**, there are some solvents included but only the dichloromethane could be located and treated as a disordered molecule. However, owing to the poor quality of the data, some residual electron density was difficult to model. Therefore, the SQUEEZE function of PLATON[13] was used to eliminate the contribution of the electron density in the solvent region from the intensity data, and the solvent-free model was employed for the final refinement. The drawing of the molecules was realised with the help of ORTEP32.[14] Crystal data and refinement parameters are shown in Table S1.‡ Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-899803 and 899804.

Computational details

Ruthenium and chlorine were treated with a Stuttgart–Dresden pseudopotential in combination with the appropriate basis sets.[15,16] The basis sets were augmented by a set of polarization functions (f for Ru and d for Cl).[17] Carbon, phosphorus and hydrogen atoms were described with a 6-31G(d) polarized double-ζ basis set.[18] Calculations were carried out at the DFT level of theory using the hybrid functional B3PW91.[19,20] Geometry optimizations were carried out without any symmetry restrictions and the nature of the extremer (minima) was verified with analytical frequency calculations. For all transition states, the intrinsic reaction coordinate was followed to verify the direct connection between the transition state and the adducts. All these computations were performed with the

Gaussian 03[21] [7] suite of programs. Gibbs free energies were obtained at 298.15 K within the harmonic approximation.

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