Five- and Six-Coordinate Ruthenium(II) Complexes Containing the Bidentate Phosphane (−)-*N*,*N*-Bis(diphenylphosphanyl)-(*S*)-1-phenylethylamine [(*S*)-peap]: X-ray Crystal Structure of the First 16-Electron Ruthenium Complex Bearing a Four-Membered Ring $[RuCl\{\kappa^2\text{-}P,P\text{-}(S)\text{-peap}\}_2][SbF_6]\cdot C_2H_4Cl_2$

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Dedicated to Professor José Vicente Soler on the occasion of his 60th birthday

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The complex *trans*-$[RuCl_2\{\kappa^2\text{-}P,P\text{-}(S)\text{-peap}\}_2]$ (**1**) has been stereoselectively prepared by the treatment of a stoichiometric mixture of complex $[RuCl_2(DMSO)_4]$ (DMSO = dimethyl sulfoxide) and (*S*)-peap [(*S*)-peap = (–)-*N*,*N*-bis(diphenylphosphanyl)-(*S*)-1-phenylethylamine] in refluxing toluene. Irradiation of a dichloromethane solution of **1** with a UV lamp (400 W) at –15 °C affords the complex *cis*-$[RuCl_2\{\kappa^2\text{-}P,P\text{-}(S)\text{-peap}\}_2]$ (**2**). The thermodynamically stable *trans* isomer **1** has also been obtained by heating complex **2** in toluene. The reaction of **1** with $AgSbF_6$ in dichloromethane yields the complex $[RuCl\{\kappa^2\text{-}P,P\text{-}(S)\text{-peap}\}_2][SbF_6]$ (**3**), the first 16-electron cationic ruthenium complex bearing a four-membered chelate diphosphane ligand which has been fully characterized including its X-ray crystal structure. The reaction of unsaturated derivative **3** with CO gives the six-coordinate complex *cis*-$[RuCl(CO)\{\kappa^2\text{-}P,P\text{-}(S)\text{-peap}\}_2][SbF_6]$ (**4**) in a stereoselective manner, which slowly transforms into *trans*-$[RuCl(CO)\{\kappa^2\text{-}P,P\text{-}(S)\text{-peap}\}_2][SbF_6]$ (**5**) in a dichloromethane solution. The reaction of $[RuCl\{\kappa^2\text{-}P,P\text{-}(S)\text{-peap}\}_2][BF_4]$ with 1-phenyl-2-propyn-1-ol in 1,2-dichloroethane (60 °C) affords the allenylidene derivative *trans*-$[RuCl(=C=C=CHPh)\{\kappa^2\text{-}P,P\text{-}(S)\text{-peap}\}_2][BF_4]$ (**6**). The *cis*-$[Ru(acac)\{\kappa^2\text{-}P,P\text{-}(S)\text{-peap}\}_2][SbF_6]$ (**7**) is prepared by reaction of **3** and Na[acac].

Introduction

Six-coordinate ruthenium(II)diphosphane complexes $[RuX_2(P{-}P)_2]$ (X = halide), and especially the unsaturated five-coordinate derivatives $[RuX(P{-}P)_2]^+$, have attracted increasing attention in recent years, due in part to their potential interest involving homogeneous catalysis.[1] The 18-e six-coordinate diphosphane complexes, containing five- and six-membered chelate rings, can dissociate one of the halide ligands to give the unsaturated systems $[RuX(P{-}P)_2]^+$. Only a few of them have been characterized by X-ray crystallography i.e., $[RuCl(dppe)_2]^+$ [dppe = 1,2-bis(diphenylphosphanyl)ethane],[2] $[RuCl(dcpe)_2]^+$ [dcpe = 1,2-bis(dicyclohexylphosphanyl)ethane],[3] $[RuCl(bnpe)_2]^+$ [bnpe = 1,2-bis(1-naphthylphenylphosphanyl)ethane],[1e] $[RuX(dppp)_2]^+$ [dppp = 1,3-bis(diphenylphosphanyl)propane] (X = Cl,[4] F[5]). Apparently, the tendency to dissociate increases as the ring size of the chelate increases in the order six- > five- >> four-membered. So, diphosphane ligands, Ph_2PYPPh_2 [Y = CH_2, $C{=}CH_2$, CMe_2, N(R)], which form four-membered chelate rings, exclusively give six-coordinate *cis*- or *trans*-mononuclear complexes[6,7] and no examples of 16-electron five-coordinate cationic complexes have been reported to date.[8]

Continuing our interest in the chemistry of ruthenium complexes containing enantiopure bis(diphenylphosphanyl)amine ligands,[9] we report in this paper the synthesis of the first 16-electron cationic ruthenium complex bearing a four-membered chelate diphosphane ligand namely $[RuCl\{\kappa^2\text{-}P,P\text{-}(S)\text{-peap}\}_2][SbF_6]$ (**3**), which has been fully characterized including its X-ray crystal structure. The precursor six-coordinate complex *trans*-$[RuCl_2\{\kappa^2\text{-}P,P\text{-}(S)\text{-peap}\}_2]$ (**1**), its *cis* isomer (**2**) and analogous cationic derivatives, *cis*-$[RuCl(CO)\{\kappa^2\text{-}P,P\text{-}(S)\text{-peap}\}_2][SbF_6]$ (**4**), *trans*-

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[RuCl(CO){κ^2-*P*,*P*-(*S*)-peap}$_2$][SbF$_6$] (**5**), *trans*-[RuCl(=C=C=CHPh){κ^2-*P*,*P*-(*S*)-peap}$_2$][BF$_4$] (**6**) and [Ru(acac){κ^2-*P*,*P*-(*S*)-peap}$_2$][SbF$_6$] (**7**) have also been prepared.

Results and Discussion

Synthesis of *trans*-[RuCl$_2${κ^2-*P*,*P*-(*S*)-peap}$_2$] (1) and *cis*-[RuCl$_2${κ^2-*P*,*P*-(*S*)-peap}$_2$] (2)

The complex *trans*-[RuCl$_2${κ^2-*P*,*P*-(*S*)-peap}$_2$] (**1**) is stereoselectively prepared by the treatment of a stoichiometric mixture of complex [RuCl$_2$(DMSO)$_4$] (DMSO = dimethyl sulfoxide) and (*S*)-peap [(−)-*N*,*N*-bis(diphenylphosphanyl)-(*S*)-1-phenylethylamine] in refluxing toluene. The complex **1** has been isolated as an air stable yellow solid (78%) (Scheme 1).

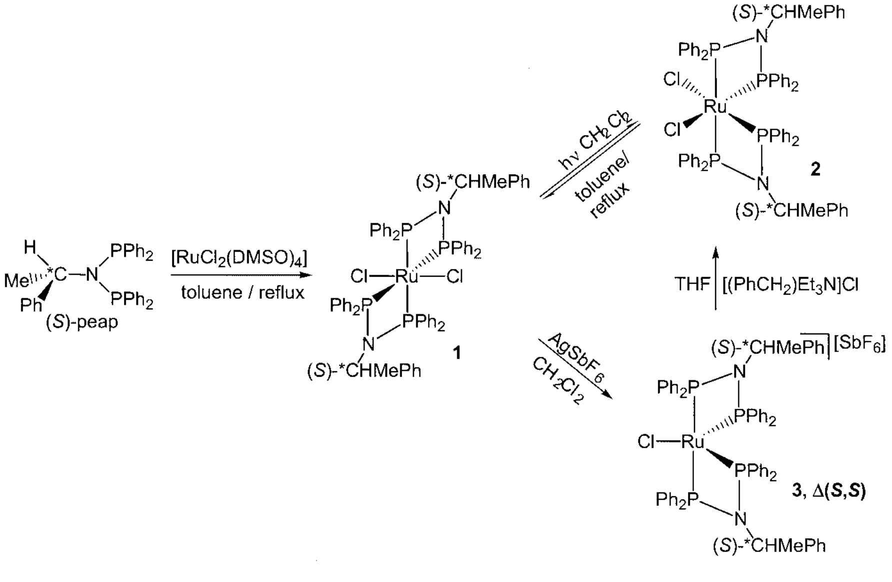
Irradiation with a UV lamp (400 W) of a dichloromethane solution of complex **1** at −15 °C for 1 h leads to an orange solution from which complex *cis*-[RuCl$_2${k^2-*P*,*P*-(*S*)-peap}$_2$] (**2**) can be isolated as an air stable orange solid (92%) (Scheme 1).

The complexes **1**−**2** are soluble in chlorinated solvents and insoluble in hexane and have been characterized by IR and NMR (^{1}H, ^{31}P{^{1}H} and ^{13}C{^{1}H}) spectroscopy (details are given in the Exp. Sect.). A sharp absorption band, assignable to the symmetrical vibration of the P-*N*−P group, is observed at ca. 850−870 cm^{-1} in the IR spectra.[10]

The ^{31}P{^{1}H} NMR spectrum of **1** shows a singlet signal at δ = 78.5, which is clearly downfield with respect to that of the free ligand (δ = 55.3 ppm, br), the deshielding ($\Delta\delta = \delta_{\text{complex}} - \delta_{\text{ligand}} = +23.2$) being intermediate to those found in the analogous *trans*-[RuCl$_2${κ^2-*P*,*P*−Ph$_2$PN(R)PPh$_2$}$_2$] [R = *i*Pr ($\Delta\delta$ = +27.1); H ($\Delta\delta$ = +18.0)].[7b] The ^{31}P{^{1}H} NMR spectrum of **2** shows two triplets (A_2X_2 spin system) at 72.57 and 87.73 ppm ($^2J_{\text{P,P}'}$ = 31.1 Hz) indicating that a single diastereoisomer, Δ(*S*,*S*) or Λ(*S*,*S*), is formed.[11] These signals can be assigned to the axial (P *trans* to P) and equatorial (P *trans* to Cl) phosphorus nuclei, respectively. Only one of the two diastereoisomers, Δ(*S*,*S*), is drawn in Scheme 1. Completion of the *trans*- to *cis*-isomerization is determined by the disappearance of the singlet resonance of complex **1** and the simultaneous appearance of two new signals assigned to complex **2**.

cis- to *trans*-Rearrangements

Complexes **1** and **2** undergo either *trans*/*cis* isomerization under thermal or photochemical conditions. The *cis* isomer **2** can be quantitatively converted into the thermodynamically stable *trans* isomer by heating in toluene (5 h) (Scheme 1).[12] The *cis*- to *trans*-isomerization does not take place at room temperature. It is interesting to note that the formation of the kinetically controlled *cis* isomer was not observed during the thermal synthesis of **1** starting from [RuCl$_2$(DMSO)$_4$] and (*S*)-peap. It can be suggested that if the *cis* isomer is actually formed in solution during the process, it immediately isomerizes to the thermodynamically more stable *trans* isomer **1**. On the other hand, the *trans*- to *cis*-rearrangement takes place by irradiation with a UV lamp as has been seen above. On the contrary, complexes [RuX$_2${κ^2-*P*,*P*−Ph$_2$PYPPh$_2$}$_2$] (X = halide; Y = CH$_2$,[13] C=CH$_2$ [14] or NH[8a]) undergo *trans*- to *cis*-isomerization by heating the *trans* isomers in refluxing chlorobenzene or 1,2-dichloroethane, and the reverse *cis*- to *trans* photochemical rearrangement has also been described for *cis*-[RuCl$_2$(dppm)$_2$].[13b] The factors responsible for determining the thermodynamically preferred forms of the *trans*/*cis* isomers are not entirely clear. Sullivan and Meyer argued, in the case of *cis*/*trans*-[RuCl$_2$(dppm)$_2$][13b] that the *cis* isomer is thermodynamically stable since it is stabilized by π-donation from the Cl atom through the Ru center to a *trans*-P atom, whereas this favorable interaction is not possible in the *trans* isomer. At present, we have no explanation



Scheme 1

for the different results obtained in our case, with the auxiliary ligand (*S*)-peap.

Electrochemical Behavior of Complexes 1 and 2

In order to compare the electrochemical properties of *trans*/*cis* isomers with those of the [RuX$_2$(P−P)$_2$] analogues, the electrochemical behavior of *trans*- and *cis*-[RuCl$_2${κ^2-*P*,*P*-(*S*)-peap}$_2$] complexes has been studied by cyclic voltammetry in CH$_2$Cl$_2$ solutions. All potentials are referenced to a silver-wire electrode. It was found that the *trans* isomer **1** undergoes one-electron oxidation [a chemically and electrochemically reversible process under the experimental conditions ($E_{1/2} = 1/2(E_\mathrm{p}^\mathrm{ox} + E_\mathrm{p}^\mathrm{red}) = 0.61$ V)], while the $E_{1/2}$ values for the analogous *trans* derivatives with dppm and Ph$_2$N(R)PPh$_2$ (R = H, Me) are 0.42 [13b] and 0.175−0.240 V,[7b] respectively. This means that the (*S*)-peap ligand is a much better stabilizing ligand for +2 oxidation state than dppm and the other bis(diphenylphosphanyl)amines. A second, chemically irreversible wave, corresponding to the Ru^{IV}/Ru^{III} couple, appears for all of the *trans*-ruthenium(III) complexes [for Ru^{III} complex containing the (*S*)-peap ligand at 1.25 V]. On the other hand, the *cis* isomer **2** only exhibits an irreversible anodic wave (E_p^ox = 1.19 V), while two waves are observed for *cis*-[RuCl$_2$(dppm)$_2$] and *cis*-[RuCl$_2$({κ^2-*P*,*P*−Ph$_2$N(Me)PPh$_2$)], the first one being chemically reversible, ($E_{1/2}$ = 0. 79 and 0. 35 V, respectively) and the second one chemically irreversible.

The oxidation wave from the *cis* isomer **2** is at a higher potential than the corresponding *trans* isomer **1**. This increasing potential in going from the *trans* to the *cis* isomer is well established in ruthenium(II) chemistry.[7b,13b]

Synthesis of Five-Coordinate Complex [RuCl{k^2-*P*,*P*-(*S*)-peap}$_2$][SbF$_6$] (3)

Complex **1** reacts with AgSbF$_6$ in dichloromethane at room temperature to give, after filtration of AgCl, the cationic complex [RuCl{κ^2-*P*,*P*-(*S*)-peap}$_2$][SbF$_6$] (**3**) isolated as an air stable red solid (93%) (Scheme 1). Analogous tetrafluoroborate (BF$_4$) and triflate (OSO$_2$CF$_3$) salts can be obtained similarly. Conversely, Higgins has recently reported that the treatment of *trans*-[RuCl$_2${κ^2-*P*,*P*-Ph$_2$PYPPh$_2$}$_2$] (Y = C=CH$_2$, NH) in 1,2-dichloroethane at room temperature with AgBF$_4$ or AgOSO$_2$CF$_3$ gives the *trans*-[RuCl{κ^2-*P*,*P*-Ph$_2$PYPPh$_2$}$_2$(μ-Cl)Ag]X (X = BF$_4$, OSO$_2$CF$_3$) and no AgCl precipitate is formed.[14b]

Complex **3** has been fully characterized by elemental analyses, IR and NMR (^{1}H, ^{31}P{^{1}H} and ^{13}C{^{1}H}) spectroscopy (details are given in the Exp. Sect.) as well as an X-ray diffraction study (see below). All the data suggest the formation of only one diastereoisomer. In particular, the ^{31}P{^{1}H} NMR spectrum shows two pseudotriplets (A$_2$X$_2$ spin system) at δ = 69.63 (P$_\mathrm{ax}$) and 101.67 (P$_\mathrm{eq}$) (t, $^2J_{\mathrm{P,P'}}$ = 42.3 Hz)[15] which are consistent with the formation of a sole diastereoisomer with a stereochemically rigid trigonal-bipyramidal structure (TBP). This pattern remains unchanged over a wide temperature range (193 to 353 K) in dichloromethane or 1,2-dichloroethane solution, indicating that a dynamic process involving an equilibrium between the two diastereoisomers Δ(*S*,*S*) and Λ(*S*,*S*) is unlikely.

The five-coordinate species seems to remain unchanged in more concentrated solutions since no change in the chemical shifts is observed. Therefore, an equilibrium between the monomer and the chloride-bridged dimer, as observed for the complex [RuCl(κ^2-*P*,*N*−Ph$_2$PCH$_2$CH$_2$-2-py)$_2$]$^+$ can be discarded.[16] In addition, the solutions maintain the typical red colour due to pentacoordinate species.[17]

To the best of our knowledge, **3** is the first example of a five-coordinate ruthenium(II) complex with four-membered chelate ligands that could be isolated and characterized by an X-ray diffraction analysis. Several attempts to prepare analogous complexes having diphosphane ligands Ph$_2$YPPh$_2$ (Y = CH$_2$, C=CH$_2$; NH) have been reported in the literature, but they did not lead to pure products.[8a] Steric and electronic effects apparently cooperate in stabilizing the Lewis-acidic 16-electron complex **3** containing the bulkier phosphane (*S*)-peap.

Structure of Complex [RuCl{κ^2-*P*,*P*-(*S*)-peap}$_2$][SbF$_6$]·C$_2$H$_4$Cl$_2$ (3)

The structure of the pentacoordinate complex [RuCl{κ^2-*P*,*P*-(*S*)-peap}$_2$][SbF$_6$] has been determined by a single X-ray analysis. Suitable crystals have been obtained by slow diffusion of pentane into a solution of complex **3** in 1,2-dichloroethane. ORTEP type views of the cation of complex **3** are shown in Figure 1 and selected bond lengths and angles are collected in Table 1.

The five coordinate cation [RuCl{κ^2-*P*,*P*-(*S*)-peap}$_2$]$^+$ displays a distorted trigonal-bipyramidal structure (Y-shaped)[18] with the bidentate (*S*)-peap ligands spanning axial and equatorial positions and the chloride atom occupying the remaining equatorial position as expected for π-stabilized 16-electron complexes.[1e,11] The P(4)−Ru−P(2) [167.87(3)°], Cl−Ru−P(4) [95.65(3)°] and Cl−Ru−P(2) [96.39(3)°] angles are indicative of a distorted TBP geometry. The Y-equatorial plane is further distorted, with an angle P(3)−Ru−P(1) of 99.76(3)°, and two different P−Ru−Cl angles [P(1)−Ru−Cl [136.61(4)°] and P(3)−Ru−Cl [123.53(4)°], as already observed in pentacoordinate ruthenium systems with other diphosphanes.[1e,2,3] The angle between the planes defined by [P(1), P(3), Ru] and [Cl, P(1), P(3)] is 1.55(2)°, indicating that the ruthenium atom is slightly displaced towards P(2) from the equatorial plane. The bite angles P(1)−Ru−P(2) [69.32(3)°] and P(3)−Ru−P(4) [69.61(3)°] of the chelate (*S*)-peap ligands show values similar to those found in the complex [RuH(η^5-C$_9$H$_7$){κ^2-*P*,*P*-(*S*)-peap}] [70.44(12)°].[9]

The distance Ru−Cl [2.3722(9) Å] lies in the range found for analogous five coordinate diphosphane complexes, like [RuCl(dppe)$_2$]$^+$,[2] and [RuCl(dcpe)$_2$]$^+$,[3] and is ca. 0.05 Å shorter than those observed in *trans*-[RuCl$_2${κ^2-*P*,*P*−Ph$_2$PN(R)PPh$_2$}$_2$] (R = Me, *i*Pr),[7b] a feature that supports the chloride ligand-to-metal π-donation. Other typical features are the shorter Ru−P$_\mathrm{eq}$ distances, [Ru−P(1) 2.2425(8) and Ru−P(3) 2.2265(9) Å], compared with the

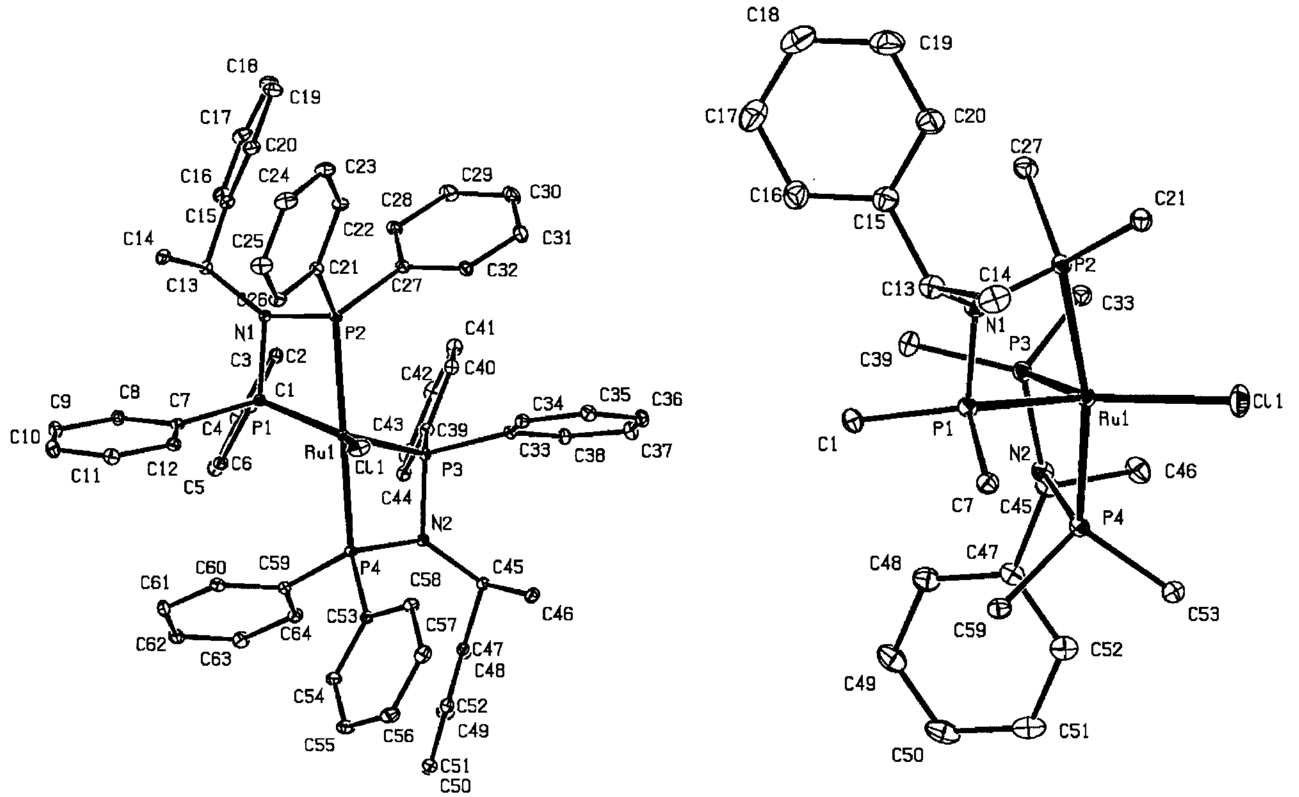


Figure 1. ORTEP type views of the molecular structure of the [RuCl{κ^2-*P,P*-(*S*)-peap}$_2$][SbF$_6$]·C$_2$H$_4$Cl$_2$ (**3**); hexafluoroantimoniate anion and C$_2$H$_4$Cl$_2$ molecule have been omitted for clarity; (left) view of cation complex projected along the Ru−Cl vector, drawn at 10% probability level; (right) view of cation complex projected perpendicular to the Ru−Cl vector, drawn at 30% probability level; for clarity, only the C *ipso* of the aryl groups of PPh$_2$ are depicted

Ru−P$_{ax}$ ones [Ru−P(2) 2.3768(8) and Ru−P(4) 2.3726(8) Å], thus suggesting that the former form strong phosphorous metal-dative bonds.[5,11] Usual Ru^{II}−P distances for phosphane ligands are in the range of 2.35−2.40 Å. Therefore it appears that these P$_{eq}$ atoms as well as the chloride ligand make up for the electron deficiency of the ruthenium(II).

The configuration at the ruthenium atom is Δ [diastereoisomer Δ(*S,S*)]. Analogously, only one diastereoisomer, Λ(*S,S*), was found for complex [RuCl(bnpe)$_2$][PF$_6$] [bnpe = (*S,S*)-1,2-bis(1-naphthylphenylphosphanyl)ethane] whose structure was determined by an X-ray study.[1e] So, complex [RuCl{κ^2-*P,P*-(*S*)-peap}$_2$][SbF$_6$] (**3**) is a five-coordinate system both, in the solid state and in solution (in ^{31}P NMR) and only one diastereoisomer has been found.

The catalytic activity of unsaturated complex **3** in the hydrogen transfer reaction of acetophenone has been investigated. The reaction has been performed in 2-propanol at 82 °C, in the presence of NaOH (acetophenone/cat/NaOH, 500:1:24) and monitored by gas chromatography. The ketone is rapidly reduced with 91% conversion in 1 h. Unfortunately, the enantioselective process fails because the (*S*)-peap ligand does not promote, in this case, any chiral induction. The remote location of the chiral centers from the reaction site might explain the lack of enantioselectivity.[19]

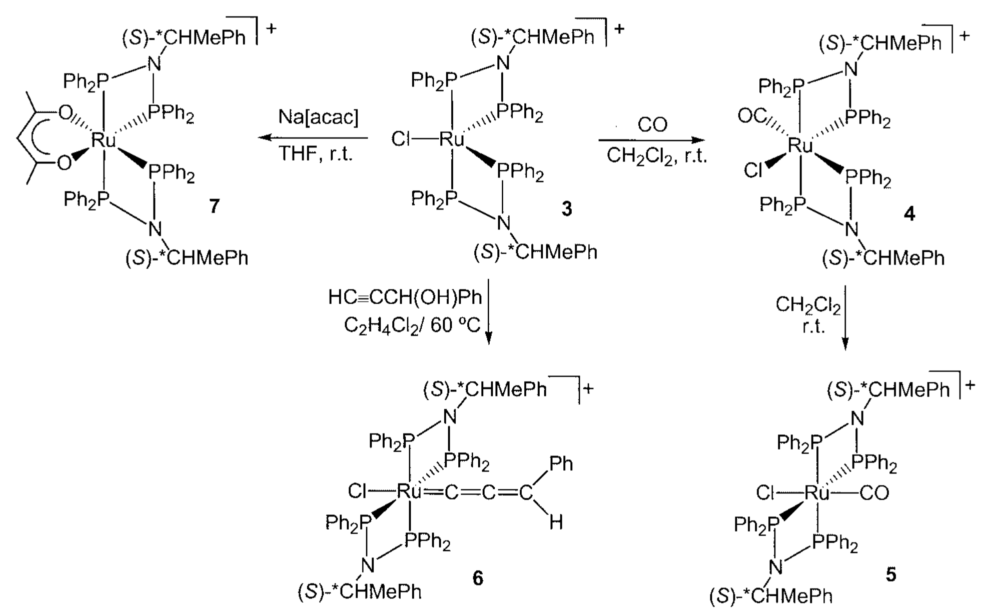
Synthesis of Cationic Complexes *cis*-[RuCl(CO){κ^2-*P,P*-(*S*)-peap}$_2$][SbF$_6$] (4), *trans*-[RuCl(CO){κ^2-*P,P*-(*S*)-peap}$_2$][SbF$_6$] (5), *trans*-[RuCl(=C=C=CHPh){κ^2-*P,P*-(*S*)-peap}$_2$][BF$_4$] (6) and *cis*-[Ru(acac){κ^2-*P,P*-(*S*)-peap}$_2$][SbF$_6$] (7)

As expected, the unsaturated complex **3** reacts with carbon monoxide at 1 atm to stereoselectively form the corresponding six-coordinate complex *cis*-[RuCl(CO){κ^2-*P,P*-(*S*)-peap}$_2$][SbF$_6$] (**4**) (93%). Complex **4** slowly isomerizes in CH$_2$Cl$_2$ solution to give, quantitatively, the isomer *trans*-[RuCl(CO){κ^2-*P,P*-(*S*)-peap}$_2$][SbF$_6$] (**5**) (Scheme 2).

These complexes are air stable pale yellow solids. Spectroscopic data (IR, ^{1}H, ^{31}P{^{1}H} and ^{13}C{^{1}H} NMR) support the proposed formulation. In particular, the IR spectra of complexes **4** and **5** show a strong ν(CO) absorption at 1997 and 1982 cm^{-1}, respectively. The ^{31}P{^{1}H} NMR spectra exhibit the expected pattern ABMX system for **4** (see Exp. Sect.) and a multiplet centered at δ = 72.83 ppm, typical of a closely spaced A$_2$B$_2$ system, occurs for **5**.

Similar *cis*- to *trans*-isomerization has been observed in analogous diphosphane complexes, i.e. [RuCl(CO)(dcpe)$_2$]$^+$,[20] and [RuCl(CO)(dppm)$_2$]$^+$.[8a]

Complex [RuCl{κ^2-*P,P*-(*S*)-peap}$_2$][BF$_4$] has also proven to be an excellent precursor for stabilized unsaturated car-



Scheme 2

bene complexes. Thus, the treatment of 1-phenyl-2-propyn-1-ol with [RuCl{κ^2-*P*,*P*-(*S*)-peap}$_2$][BF$_4$] in 1,2-dichloroethane (60 °C) affords the allenylidene derivative *trans*-[RuCl(=C=C=CHPh){κ^2-*P*,*P*-(*S*)-peap}$_2$][BF$_4$] (**6**) (76%) (Scheme 2). The formation of the allenylidene complex **6** requires heating the reaction at 60 °C for four hours in a minimum amount of solvent (around 0.5 mL for a 0.1 mmol scale) and an excess of alkynol (complex **3**/alkynol, 1:5). The synthesis of **6**, under more dilute conditions, does not go to completion but formation of decomposition products is observed. Probably, the higher steric requirement of the allenylidene fragment leads directly to the thermodynamically stable *trans* complex **6** and the *cis* isomer is not observed.

Analytical and spectroscopic data (IR, ^{1}H, ^{31}P{^{1}H} and ^{13}C{^{1}H} NMR) support the proposed formulation. Significantly, the ^{13}C{^{1}H} NMR spectrum of **6** is in agreement with the presence of the cumulene moiety, showing the expected resonances for C$_\alpha$ (δ = 322.32 ppm, pseudo triplet, $^2J_{C,P}$ = 14.8 Hz), C$_\beta$ (δ = 218.14 ppm, s) and C$_\gamma$ (δ = 150.11 ppm, s).[21] In addition the IR spectrum shows a strong absorption at 1939 cm^{-1} assigned to the ν(C=C=C) vibration.

The reaction of complex **3** with Na[acac] gives the complex [Ru(acac){κ^2-*P*,*P*-(*S*)-peap}$_2$][SbF$_6$] (**7**) wherein the [acac]$^-$ acts as an anionic bidentate chelate ligand (see Scheme 2). Complex **7** is isolated as an air stable yellow solid in 81% yield. Spectroscopic data (IR, ^{1}H, ^{31}P{^{1}H} and ^{13}C{^{1}H} NMR) are in accordance with the proposed formulation. The ^{31}P{^{1}H} NMR spectrum of **7** shows two triplets (A$_2$X$_2$ spin system) at 68.50 and 83.11 ppm ($^2J_{P,P}$ = 34.9 Hz) and suggest the formation of the *cis* product. Complex **3** also reacts with an excess of [(PhCH$_2$)Et$_3$N]Cl to yield the 18-electron *cis* isomer **2**, the preparation of which has been described above (Scheme 1).

Experimental Section

General Conditions: The reactions were carried out under dry nitrogen using standard Schlenk techniques. Solvents were dried by standard methods and distilled under nitrogen before use. The complex [RuCl$_2$(DMSO)$_4$][22] and (Ph$_2$P)$_2$N[(*S*)-*CHMePh] [(*S*)-peap][23] were prepared by literature methods. Infrared spectra were recorded with a Perkin−Elmer FT-1720-Y spectrometer using KBr disks. The conductivities were measured at room temperature, in *ca* 5 × 10^{-4} mol·L^{-1} acetone solutions, with a Jenway PCM3 conductimeter. C, H and N analyses were carried out with a Perkin−Elmer 240-B microanalyzer (inconsistent analyses are found for complexes **2**, **4**−**6** due to incomplete combustion). Mass spectra (FAB) were recorded using a VG-Autospec spectrometer, operating in the positive mode; 3-nitrobenzyl alcohol (NBA) was used as the matrix. NMR spectra were recorded with a Bruker AC300 (DPX-300 or AV-300) instrument at 300 MHz (^{1}H), 121.5 MHz (^{31}P) or 75.4 MHz (^{13}C) or a Bruker AC200 instrument at 200 MHz (^{1}H), 81.01 MHz (^{31}P) or 50.32 MHz (^{13}C), using SiMe$_4$ or 85% H$_3$PO$_4$ as standards.

Synthesis

Synthesis of *trans*-[RuCl$_2${κ^2-*P*,*P*-(*S*)-peap)}$_2$] (1): A mixture of [RuCl$_2$(DMSO)$_4$] (0.98 g, 2 mmol) and (*S*)-peap (1.958 g, 4 mmol) in 60 mL of toluene was heated under reflux for 3 h. The solvent was removed under reduced pressure and the yellow precipitate was washed with toluene and diethyl ether. The crude solid was recrystallized from dichloromethane/pentane, yielding 1.80 g of the solid **1** (78%). MS (FAB): *m*/*z* = 1150 [M$^+$ − 1], 1115 [M$^+$ − Cl − 1], 1079 [M$^+$ − 2 Cl − 1] (correct isotope patterns observed for each fragment). IR (KBr): ṽ = 853 cm^{-1} (s, PNP). ^{31}P{^{1}H} NMR

(CD$_2$Cl$_2$): δ = 78.5 (s) ppm. ^{1}H NMR (CDCl$_3$): δ = 1.45 (d, $J_{H,H}$ = 7.1 Hz, 6 H, *CCH$_3$), 5.14 (m, 2 H, *CH), 6.72−7.76 (m, 50 H, PPh$_2$, *CPh) ppm. ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): δ = 23.44 (s, *CCH$_3$), 62.45 (s, *C), 126.37−136.77 (PPh$_2$, *CPh), 142.08 (s, *CC$_{ipso}$) ppm. $C_{64}H_{58}Cl_2N_2P_4Ru\cdot CH_2Cl_2$ (**1**·CH$_2$Cl$_2$) (1150.99·CH$_2$Cl$_2$): calcd. C 63.17, H 4.89, N 2.27; found C 63.76, H 4.88, N 2.05.

Synthesis of *cis*-[RuCl$_2${κ^2-*P,P*-(*S*)-peap}$_2$] (2): A solution of complex **1** (0.345 g, 0.5 mmol) in 80 mL of dichloromethane was irradiated at −15 °C with a UV lamp (400 W) for 1 h. The solvent was removed to dryness and the product recrystallized from dichloromethane/diethyl ether yielding 0.317 g of **2** (92%). IR (KBr): ṽ = 849 cm^{-1} (s, PNP). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): δ = 72.57 (t, $^2J_{P,P'}$ = 31.1 Hz, 2 P$_{ax}$), 87.73 (t, $^2J_{P,P'}$ = 31.1 Hz, 2 P$_{eq}$) ppm. ^{1}H NMR (CD$_2$Cl$_2$): δ = 1.33 (d, $J_{H,H}$ = 7.2 Hz, 6 H, *CCH$_3$), 4.75 (m, 2 H, *CH), 6.38−8.26 (m, 50 H, PPh$_2$, *CPh) ppm. ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): δ = 23.26 (s, *CCH$_3$), 61.87 (s, *C), 125.15−139.07 (PPh$_2$, *CPh), 140.69 (s, *CC$_{ipso}$) ppm.

Synthesis of [RuCl{κ^2-*P,P*-(*S*)-peap}$_2$][SbF$_6$] (3): A mixture of complex **1** (1.15 g, 1 mmol) and AgSbF$_6$ (0.344 *g*, 1.1 mmol) was stirred at room temperature in 50 mL of dichloromethane for 1 h in the absence of light. The solution, whose color changed from yellow to red, was filtered through celite and the solvent removed to dryness. The oil obtained was recrystallized from diethyl ether to yield 1.26 g of complex **3** as a red solid (93%). The corresponding tetrafluoroborate (BF$_4$) or triflate (OSO$_2$CF$_3$) salts could be similarly prepared. MS (FAB): *m*/*z* = 1116 [M $^+$], 1080 [M$^+$ − Cl] (correct isotope patterns observed for each fragment). IR (KBr): ṽ = 849 (s, PNP), 658 cm^{-1} (s, SbF$_6^-$). Conductivity (acetone, 20 °C): 148 Ω^{-1} cm^2 mol^{-1}. ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): δ = 69.63 (t, $^2J_{P,P'}$ = 42.3 Hz, 2 P$_{ax}$), 101.67 (t, $^2J_{P,P'}$ = 42.3 Hz, 2 P$_{eq}$) ppm. ^{1}H NMR (CD$_2$Cl$_2$): δ = −0.06 ppm (d, $J_{H,H}$ = 7.2 Hz, 6 H, *CCH$_3$), 3.90 (m, 2 H, *CH), 6.49−7.70 (m, 50 H, PPh$_2$, *CPh) ppm. ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): δ = 21.25 (s, *CCH$_3$), 64.42 (s, *C), 124.88−136.55 (PPh$_2$, *CPh), 140.36 (s, *CC$_{ipso}$) ppm. $C_{64}H_{58}ClF_6N_2P_4RuSb\cdot 0.5CH_2Cl_2$ (**3**·0.5CH$_2$Cl$_2$) (1351.27·0.5CH$_2$Cl$_2$): calcd. C 55.58, H 4.27, N 2.01; found C 55.52, H 4.68, N 1.73.

Synthesis of *cis*-[RuCl(CO){κ^2-*P,P*-(*S*)-peap}$_2$][SbF$_6$] (4): Complex **3** (0.676 g, 0.5 mmol) was dissolved in 20 mL of dichloromethane, and CO gas was bubbled though the solution for 5 minutes. The solution immediately changed from red to colorless. The solvent was removed to dryness and the crude product recrystallized from dichloromethane/diethyl ether to yield 0.641 g of the pale yellow solid **4** (93%). IR (KBr): ṽ = 1997 (s, CO), 876 (m, PNP), 658 cm^{-1} (s, SbF$_6^-$). Conductivity (acetone, 20 °C): 126 Ω^{-1}·cm^2·mol^{-1}. ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): ABMX system, δ = 55.79 [P$_{eq}$ (P$_M$)], 63.63 [P$_{ax}$ (P$_A$)], 68.26 [P$_{ax}$ (P$_B$)], 76.79 [P$_{eq}$ (P$_X$)] (J_{AB} = 270.2, J_{BM} = 54.4, J_{AX} = 51.3, J_{AM} = 28.0, J_{MX} = 21.7, J_{BX} = 18.6) ppm. ^{1}H NMR (CD$_2$Cl$_2$): δ = 0.73 (d, $J_{H,H}$ = 6.8 Hz, 3 H, *CCH$_3$), 0.83 (d, $J_{H,H}$ = 7.1 Hz, 3 H, *CCH$_3$), 4.44 (m, 2 H, *CH), 6.28−7.99 (m, 50 H, PPh$_2$, *CPh) ppm.

Synthesis of *trans*-[RuCl(CO){κ^2-*P,P*-(*S*)-peap}$_2$][SbF$_6$] (5): Complex **4** (0.414 g, 0.3 mmol) was dissolved in 40 mL of dichloromethane and the solution was stirring at room temp. for 5 days until its complete conversion into the *trans* isomer. The solvent was removed to dryness and the crude product recrystallized from dichloromethane/diethyl ether yielding 0.393 g of **5** (95%). MS (FAB): *m*/*z* = 1144 [M $^+$], 1116 [M$^+$ − CO], 1080 [M$^+$ − CO − Cl] (correct isotope patterns observed for each fragment). IR (KBr): ṽ = 1982 (s, CO), 877 (m, PNP), 658 cm^{-1} (s, SbF$_6^-$). Conductivity (acetone, 20 °C): 126 Ω^{-1}·cm^2·mol^{-1}. ^{31}P{^{1}H} NMR (CDCl$_3$): δ = 72.83 (m) ppm. ^{1}H NMR (CD$_2$Cl$_2$): δ = 1.18 (d, $J_{H,H}$ = 6.8 Hz, 6 H, *CCH$_3$), 4.84 (m, 2 H, *CH), 6.90−7.65 (m, 50 H, PPh$_2$, *CPh) ppm. ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): δ = 23.52 (s, *CCH$_3$), 65.24 (s, *C), 128.19−135.52 (PPh$_2$, *CPh), 140.03 (s, *CC$_{ipso}$), 198.09 (t, $^2J_{C,P}$ = 11.8 Hz, CO) ppm.

Synthesis of *trans*-[RuCl(=C=C=CHPh){κ^2-*P,P*-(*S*)-peap}$_2$][BF$_4$] (6): To a mixture of complex [RuCl{κ^2-*P,P*-(*S*)-peap}$_2$][BF$_4$] (0.120 g, 0.1 mmol) in 0.5 mL of 1,2-dichloroethane, the alkynol HC≡CCH(OH)Ph (0.66 g, 0.5 mmol) was added. The reaction mixture was heated at 60 °C for 4 h and the solution color changed from red to scarlet. The addition of 30 mL of diethyl ether lead to the precipitation of a scarlet solid which was washed with diethyl ether (3 × 10 mL) and vacuum-dried to yield 0.1 g of complex **6** (76%). IR (KBr): ṽ = 1939 (s, C=C=C), 1059 (br. s, BF$_4^-$), 864 cm^{-1} (m, PNP). Conductivity (acetone, 20 °C): 125 Ω^{-1}·cm^2·mol^{-1}. ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): δ = 70.30 (m), 73.36 (m) ppm. ^{1}H NMR (CD$_2$Cl$_2$): δ = 1.36 (d, $J_{H,H}$ = 7.2 Hz, 6 H, *CCH$_3$), 5.10 (m, 2 H, *CH), 6.97−7.73 (m, 55 H, PPh$_2$, *CPh, C$_γ$Ph), 8.38 (s, 1 H, C$_γ$H) ppm. ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): δ = 23.75 (s, *CCH$_3$), 64.53 (s, *C), 127.88−135.80 (PPh$_2$, *CPh, C$_γ$Ph), 140.54 (s, *CC$_{ipso}$), 142.49 (s, C$_γ$C$_{ipso}$), 150.11 (s, C$_γ$), 218.14 (s, C$_β$), 322.32 (t, $^2J_{C,P}$ = 14.8 Hz, Ru=C$_α$) ppm. $C_{73}H_{64}BClF_4N_2P_4Ru$ (1316.44): calcd. C 66.60, H 4.90, N 2.13; found C 65.85, H 4.83, N 1.63.

Synthesis of [Ru(acac){κ^2-*P,P*-(*S*)-peap}$_2$][SbF$_6$] (7): A mixture of complex **3** (0.676 g, 0.5 mmol) and Na[acac] (0.122 g, 1 mmol) in 10 mL of tetrahydrofuran was stirred at room temp. for 1 h. The solution was then evaporated to dryness and the residue obtained was extracted with CH$_2$Cl$_2$ and filtered through celite. The concentration of the resulting solution to ca. 2 mL followed by the addition of 20 mL of hexane precipitated a pale yellow solid, which was washed with hexane (2 × 20 mL) and dried in vacuo, yielding 0.573 g of **7** (81%). MS (FAB): *m*/*z* = 1179 [M $^+$], 1080 [M$^+$ − acac] (correct isotope patterns observed for each fragment). IR (KBr): ṽ = 1580, 1518 (s, acac), 872 cm^{-1} (m, PNP), 658 (s, SbF$_6^-$). Conductivity (acetone, 20 °C): 117 Ω^{-1}·cm^2·mol^{-1}. ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): δ = 68.50 (t, $^2J_{P,P'}$ = 34.9 Hz, 2 P$_{ax}$), 83.11 (t, $^2J_{P,P'}$ = 34.9 Hz, 2 P$_{eq}$) ppm. ^{1}H NMR (CD$_2$Cl$_2$): δ = 0.73 (d, $J_{H,H}$ = 6.7 Hz, 6 H, *CCH$_3$), 1.69 (s, 6 H, 2COCH$_3$), 4.32 (m, 2 H, *CH), 4.38 (s, 1 H, CH), 6.49−7.87 (m, 50 H, PPh$_2$, *CPh) ppm. ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): δ = 23.64 (s, *CCH$_3$), 27.98 (s, 2COCH$_3$), 63.00 (s, *C), 99.34 (s, CH), 127.55−137.06 (PPh$_2$, *CPh), 140.12 (s, *CC$_{ipso}$), 186.61 (s, 2CO) ppm.

Electrochemical Measurements: The electrochemical experiments were performed with an EG&G PAR potentiostat/galvanostat model 273. Cyclic voltammetry measurements were carried out in a two-compartment three-electrode cell. The working electrode was a platinum disc electrode probed by a Luggin capillary connected to a silver-wire pseudo-reference electrode, a platinum auxiliary electrode was employed. Electrochemical solutions contained 0.1 M [NBu$_4$][PF$_6$] and 10^{-3} M complex in dichloromethane. Solutions were purged and maintained under nitrogen. The scan rate was 100 mV·s^{-1}. All values are referenced to an internal [Fe(η^5-C$_5$H$_5$)$_2$]$^{+/0}$ couple ($E°$ = 0.59 V).

General Procedure for Hydrogen Transfer Reaction: Acetophenone (5 mmol) and complex **3** (0.01 mmol) were placed in a three-bottomed Schlenk flask under dry nitrogen and 2-propanol (50 mL) was added. The solution was heated at 82 °C and the corresponding amount of base from a 0.080 M solution in 2-propanol was added after 15 min. The reaction was monitored by gas chromatography. 1-phenylethanol, acetophenone and acetone were the only products detected.

X-ray Structure Determination of 3·$C_2H_4Cl_2$: X-ray suitable single crystals were obtained by slow diffusion of pentane into a solution of complex **3** in 1,2-dichloroethane. Diffraction data were recorded with a Nonius Kappa CCD single-crystal diffractometer. The crystal distance was fixed at 29 mm, and 1100 frames were collected using the oscillation method, φ and ω−scans with 2° oscillation and 40 s exposure time per frame. Data collection strategy was calculated with the program Collect.[24] Data reduction and cell refinement were performed with the programs HKL Denzo and Scalepack.[25] Unit cell dimensions were determined from 11743 reflections. All data completeness was 99.4%. Data collection, crystal, and refinement parameters are collected in Table 1. The structure was solved by DIRDIF-96.[26] An empirical absorption correction was applied using XABS2.[27] Anisotropic least-squares refinement was carried out with SHELXL-97.[28] All non-hydrogen atoms, were anisotropically refined. H atoms were geometrically placed and their coordinates were refined riding on their parent atoms with isotropic displacement parameters set to 1.2 times the U_{eq} of the atoms to which they are attached (1.5 for methyl groups). The final cycle of full-matrix least-squares refinement based on 11860 reflections and 742 parameters converged to final values of R_1 [$F^2 > 2\sigma(F^2)$] = 0.0324. Atomic scattering factors were taken from International Tables for X-ray Crystallography.[29] The function minimized was $([\Sigma w F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$ where $w = 1/[\sigma^2(F_o^2) + (00498P)^2 + 2.3959P]$ where $P = (\text{Max.}\ (F_o^2 + 2F_c^2)/3$ with $\sigma^2(F_o^2)$ from counting statistics. Geometrical calculations were made with PARST.[30] The crystallographic plots were made with PLATON.[31] CCDC-216434 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44−1223/336−033; E-mail: deposit@ccdc.cam.ac.uk].

Table 1. Crystal data and structure refinement for **3**·$C_2H_4Cl_2$

Empirical formula	$C_{66}H_{62}Cl_3F_6N_2P_4RuSb$
Formula mass	1450.23
Temperature (K)	200(2)
Wavelength (Å)	1.54180
Crystal system	monoclinic
Space group	$P2_1$
a (Å)	11.8362(2)
b (Å)	17.8946(4)
c (Å)	15.1354(2)
α (deg)	90
β (deg)	94.697(1)
γ (deg)	90
V (Å^3)	3195.0(1)
Z	2
$D_{calcd.}$ (g cm^{-3})	1.507
Abs. coeff. (mm^{-1})	7.859
F(000)	1464
Crystal size (mm)	0.25 × 0.15 × 0.12
Radiation	Cu-K_α
Monochromator	graphite
θ range for data collecn (deg)	2.93 to 69.93
Index ranges	$-14 \le h \le 14$, $-20 \le k \le 21$, $-18 \le l \le 18$
Number of rflns. collected	131810
Number of independent rflns.	11860 [R(int) = 0.076]
Completeness to 2θ = 69.93 θ	99.4%
Refinement method	full-matrix least-squares on F^2
Number of data/restraints/params	11860/1/748
Goodness-of-fit on F^2	1.044
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0321$, $wR_2 = 0.0824$
R Indices (all data)	$R_1 = 0.0341$, $wR_2 = 0.0837$
Absolute structure parameter	0.008(4)
Largest diff. peak and hole	0.949 and −0.973 e·Å^{-3}

Table 2. Selected bond lengths (Å) and angles (°) for complex **3**·$C_2H_4Cl_2$

Distances	
Ru−Cl	2.3722(9)
Ru−P(1)	2.2425(8)
Ru−P(2)	2.3768(8)
Ru−P(3)	2.2265(9)
Ru−P(4)	2.3726(8)
Angles	
P(1)−Ru−Cl	136.61(4)
P(3)−Ru−Cl	123.53(4)
P(2)−Ru−Cl	96.39(3)
P(4)−Ru−Cl	95.65(3)
P(3)−Ru−P(1)	99.76(3)
P(4)−Ru−P(2)	167.87(3)
P(1)−Ru−P(2)	69.32(3)
P(3)−Ru−P(4)	69.61(3)
P(1)−Ru−P(4)	102.59(3)
P(3)−Ru−P(2)	102.19(3)

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