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Pentamethylcyclopentadienyl ruthenium(II) complexes containing chiral diphosphines: synthesis, characterisation and electrochemical behaviour. X-ray structure of $(\eta^5\text{-}C_5Me_5)Ru\{(S,S)\text{-}Ph_2PCH(CH_3)CH(CH_3)PPh_2\}Cl$

Franco Morandini [a,*], Anna Dondana [a], Ingrid Munari [a], Giuseppe Pilloni [a], Giambattista Consiglio [b], Angelo Sironi [c], Massimo Moret [c]

[a] *Dipartimento di Chimica Inorganica, Metallorganica e Analitica and Centro CNR, Via F. Marzolo 1, I-35131 Padua, Italy*

[b] *Technisch-Chemisches Laboratorium, ETH Zentrum, Universitätstrasse 6, CH-8092, Zürich, Switzerland*

[c] *Dipartimento di Chimica Strutturale e Stereochimica Inorganica, Via Venezian 21, I-20133 Milan, Italy*

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Abstract

Some pentamethylcyclopentadienyl ruthenium(II) diphosphine chloride complexes have been prepared by ligand exchange starting with the parent triphenylphosphine derivatives and their reactivities compared with those of the corresponding cyclopentadienyl compounds. The pentamethyl ligand causes a greater extent of asymmetric induction when the (*R*)-prophos and (*R*)-phenphos ligands are used as well as a higher lability of the stereochemistry at the stereogenic ruthenium centre. A shift of about 200 mV in the oxidation potential is caused by the substitution at the penta-hapto ligand. The order of basicity of the diphosphine ligands was also evaluated and was found to be consistent with previous determinations. The crystal structure of $(\eta^5\text{-}C_5Me_5)Ru\{(S,S)\text{-}$chiraphos$\}Cl$ shows a coordination around the ruthenium atom similar to that found for the $(\eta^5\text{-}C_5H_5)Ru\{(S,S)\text{-}$chiraphos$\}Cl$ complex.

Keywords: Crystal structures; Electrochemistry; Ruthenium complexes; Chiral diphosphine complexes; Pentamethylcyclopentadienyl complexes

1. Introduction

In recent years we have prepared a series of cyclopentadienyl (C_5H_5) complexes of ruthenium(II) containing chiral diphosphines homologues of the 1,2-bis(diphenylphosphine)ethane with C1 and C2 symmetry [1]. The ruthenium centre is stereogenic for compounds of the former type [2]; consequently they gave the opportunity to study the stereochemistry of simple metallorganic reactions which are fundamental steps in catalytic processes [1]. Compounds of the latter type were used as templates for asymmetric stoichiometric [3,4] and catalytic reactions [5].

Modification of the basicity at the metal atom in organotransition metal complexes can be a way to alter their reactivity. In fact, it is well known that the reactivity at the metal centre is influenced by the type of ancillary ligands. Strong electron-donating ligands can increase the electron density at the metal centre [6,7], thus favouring, for example, oxidative addition reactions [8].

The strong donor ligand pentamethylcyclopentadienyl (C_5Me_5) is able to stabilize metal complexes from both an electronic and a steric point of view [9]. Angelici has recently proposed a scale for the determination of the basicity of organotransition metal complexes based on the enthalpies of protonation with a strong acid such as CF_3SO_3H in a non-coordinating solvent as 1,2-dichloroethane [10]. He observed an increase of basicity when diphosphines are used instead of phosphines, when hydride complexes are compared with halogeno derivatives, for which the order of basicity decreases from chlorine to bromine to iodine, and when C_5Me_5 is substituted for C_5H_5. Moreover, Lindner, Vrieze and co-workers showed that the cationic complexes $[(\eta^5\text{-}C_5H_5)Ru(P\text{^}O)(P\text{–}O)]SbF_6$ and $[(\eta^5\text{-}C_5Me_5)Ru(P\text{^}O)(P\text{–}O)]SbF_6$ exhibit a very different reactivity toward CO. The latter complex coordinates CO instantaneously, while the cyclopentadienyl compounds needs more than 12 h [11].

Recently various ruthenium(II) complexes containing the C_5Me_5 ligand and phosphines or diphosphines have been investigated [9,12–25]. In the present work we report on the synthesis and characterisation of new complexes of the type $(\eta^5\text{-}C_5Me_5)Ru(L\text{^}L')Cl$ in which L^L' are chiral diphos-

* Corresponding author. Tel.: +39-49-827 5198; fax: +39-49-827 5161; e-mail: morandini@chim02.unipd.it

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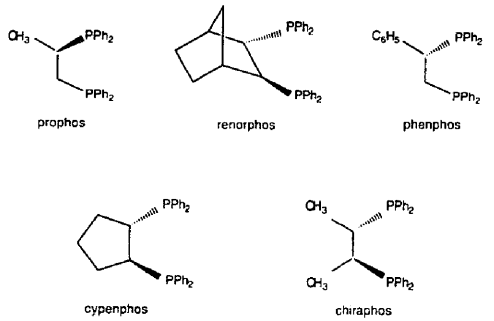
phines having C1 or C2 symmetry and on some acetonitrile derivatives thereof. The crystal structure of $(\eta^5\text{-}C_5Me_5)$-Ru{(*S,S*)-$Ph_2PCH(CH_3)CH(CH_3)PPh_2$}Cl has been determined and compared with that of the corresponding cyclopentadienyl derivative. The electrochemical behaviour of the complexes has confirmed the order of basicity of the diphosphines already observed for the iridium complexes $[Ir(L\hat{}L)_2]^+$ containing the same ligands [26].

2. Results and discussion

2.1. Synthesis and spectroscopic properties

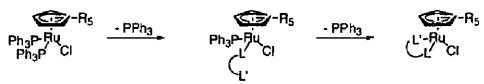
The complexes of general formula $(\eta^5\text{-}C_5Me_5)$-Ru(L^L')Cl (L^L' = chiral diphosphines) were prepared



by substitution of the triphenylphosphine ligand from $(\eta^5\text{-}C_5Me_5)Ru(PPh_3)_2Cl$ (Scheme 1) [9,27]. For preparative purposes the exchange reactions were carried out by treating the starting ruthenium compound with the appropriate diphosphine in a 1:1 molar ratio in boiling toluene for about 6 h. The expected complexes were obtained as microcrystalline orange compounds. They are soluble in toluene and dichloromethane and insoluble in n-hexane. The complexes were purified by recrystallisation from dichloromethane/n-hexane.

The formation of the chelate complexes was monitored by $^{31}P\{^1H\}$ NMR spectroscopy at room temperature in toluene-d_8 as the solvent to possibly identify differences in reactivity with respect to the parent cyclopentadienyl compound $(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2Cl$ [28].

The $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture with dppe registered after 5 min shows the presence of the chelate complex at δ 74.64 ppm, of free triphenylphosphine at δ −5.85 ppm and of unreacted dppe. Resonances between δ 45.50 and 38.50 ppm as well as a doublet centred at δ −13.99 ppm are consistent with the formation of intermediates, in which dppe acts as a monodentate ligand (Scheme 1). The reactions with the C_2 diphosphines (*S,S*)-chiraphos and (*rac*)-cypenphos (L=L') show a pattern similar to that of dppe. Also for these ligands the chelate complexes form



Scheme 1.

within a few minutes. Small amounts of reaction intermediates with resonances in the range δ 40–50 ppm are also visible.

For (*R*)-prophos, (*rac*)-renorphos and (*R*)-phenphos, two diastereomers are expected to form owing to the stereogenicity of the ruthenium atom (Scheme 1, L≠L'). After 5 min of reaction, the renorphos derivatives form in a diastereomeric ratio of 85/15. This ratio does not change during the progress of the reaction and is equal to that observed when the reaction is carried out in boiling toluene. In contrast, the two diastereomers are obtained in a 1:1 ratio for the (*R*)-prophos ligand, instead of 95/5 observed in boiling toluene. For both ligands, resonances due to reaction intermediates are present at δ 40–50 ppm. A diastereomeric ratio of 75/25 is observed in the formation of the (*R*)-phenphos derivatives.

In the cases examined the displacement reactions at room temperature go to completion in about 20 h. They are thus much faster than for the parent cyclopentadienyl compounds; in the latter case, for instance, more than 1 month is needed for the prophos ligand [28]. As for the cyclopentadienyl complex [28], the displacement occurs stepwise through the formation of stereoisomeric intermediates, in which the diphosphines act as a monodentate ligand (Scheme 1). However, the relative stability of the intermediate appears different. In fact, in the exchange reaction with the chiraphos ligand no intermediate was identified for the parent cyclopentadienyl complex, implying a more rapid chelate closing with respect to the rate of the first substitution. The different reactivity could be ascribed to an enhanced basicity on the metal centre when C_5Me_5 ligand is substituted for C_5H_5, thus favouring dissociation of a triphenylphosphine. However, steric factors are expected to act in the same direction.

The diastereomeric ratio for the (*R*)-prophos complexes formed at room temperature (1:1) does not correspond to the thermodynamic equilibrium. In fact, after heating the equimolar mixture at 343 K for 24 h in chlorobenzene, the diastereomeric ratio becomes 95/5 [29]. In contrast, epimerisation does not take place in toluene. Probably a lack of enantiosite selection in the displacement reaction of the two enantiotopic triphenylphosphine molecules and of regioselectivity in the coordination of the bidentate ligand in a monodentate fashion are responsible for the 1:1 ratio at room temperature. The 95/5 ratio observed at higher temperature might therefore arise from a relatively long-lived 16-electron intermediate under those conditions [30]. Either regioselectivity or long life of the unsaturated intermediate could be responsible for the diastereoselectivity observed in the formation of the norphos complexes. The ΔG° values for the equilibrium between the two epimers at the metal are about 1.2 kcal mol^{-1} for $(\eta^5\text{-}C_5Me_5)Ru\{(R^*,R^*)\text{-norphos}\}Cl$

complex, about 2 kcal mol^{-1} for (η^5-C_5Me_5)Ru{(*R*)-prophos}Cl and about 0.8 kcal mol^{-1} for (η^5-C_5Me_5)Ru{(*R*)-phenphos}Cl. For these ligands the thermodynamically favoured diastereomer is that having the larger difference in the chemical shifts for the two phosphorus atoms in the $^{31}P\{^1H\}$ NMR spectrum. This situation most probably corresponds to the *ul*-diastereomer [1,31]. Furthermore, at least for the last two ligands, the extent of asymmetric induction at the metal is higher than for the compounds containing the unsubstituted cyclopentadienyl ligand [29].

The complexes show a dynamic process in solution in the temperature range 178–300 K when analysed by $^{31}P\{^1H\}$ NMR in CD_2Cl_2. At 178 K the process is frozen out giving rise to a well-defined singlet for (η^5-C_5Me_5)Ru(dppe)Cl and AX (or AB) spectrum for all the other complexes. When the temperature is raised, the $^{31}P\{^1H\}$ NMR spectra show a broadening of the resonances for all the complexes. The (*R*)-prophos and (*rac*)-renorphos derivatives show a diastereomer population corresponding to that also observed in $C_6D_5CD_3$ at room temperature. In fact, we have checked that the prophos-containing diastereomers do not undergo epimerisation under these conditions. However, the use of the mixed $CDCl_3/CD_2Cl_2$ caused complete epimerisation in less than 24 h.

The coalescence temperature is close to 300 K and the activation energies for the dynamic process are about 12–13 kcal mol^{-1}. The most probable explanation for the observed behaviour is to assume some ion separation involving the chlorine ligand (Eq. (1)) which, however, is not large enough to cause epimerisation at the metal.

$$(\eta^5\text{-}C_5Me_5)Ru(L\hat{}L')Cl \rightarrow [(\eta^5\text{-}C_5Me_5)Ru(L\hat{}L')]^+ + Cl^- \quad (1)$$

In fact, slowing down of the λ–δ equilibration of the chelate ring or of the rotation of the C_5Me_5 ligand are inconsistent with the observed solvent effect and appear less probable [32,33].

The compounds (η^5-C_5Me_5)Ru(L^L)Cl (L^L = dppe, (*rac*)-cypenphos, (*S,S*)-chiraphos and (*R*)-prophos) react rapidly in methanol with acetonitrile in the presence of NH_4PF_6 as the halogen scavenger to afford quantitatively the corresponding acetonitrile derivatives [1].

$$(\eta^5\text{-}C_5Me_5)Ru(L\hat{}L')Cl + NH_4PF_6 + CH_3CN \rightarrow [(\eta^5\text{-}C_5Me_5)Ru(L\hat{}L')(CH_3CN)]PF_6 \quad (2)$$

The complexes are formed as yellow microcrystalline compounds, soluble in dichloromethane. Their $^{31}P\{^1H\}$ NMR spectra in CD_2Cl_2 are temperature independent. This behaviour supports the above interpretation that the fluxional behaviour operating for the chloro derivatives in dichloromethane solution is due to a rapid dissociation–association process of the chlorine anion.

In contrast to the parent cyclopentadienyl compounds the reaction with acetonitrile (Eq. (2)) does not seem to be stereospecific [1]. Starting with the (*R*)-prophos complexes in a 54/46 or in a 95/5 diastereomeric ratio the acetonitrile derivatives are formed with ratios of 66/34 and 87/13, respectively. However, on allowing the solution to stand, epimerisation at the metal takes place and a thermodynamic ratio close to 95/5 is obtained. The (*rac*)-renorphos-containing compounds give rise to the two possible acetonitrile diastereomers in a 48/52 molar ratio. This relatively facile epimerisation probably results from the higher basicity at the metal caused by the pentamethyl ligand. This basicity should contribute to a stabilisation of the electronically unsaturated intermediate deriving from nitrile dissociation.

3. Electrochemistry

We have investigated the electrochemical behaviour of the aforementioned ruthenium complexes (and of the analogous complexes containing 1,1′-ferrocenylbis(diphenylphosphine)) to test the effects on the redox properties of the metal centre when systematic changes in the ligands, i.e. C_5H_5 versus C_5Me_5 and phosphorus ligands, are introduced. For all ruthenium complexes reported here the voltammetric profile at the platinum electrode in 1,2-dichloroethane/0.2 M [n-Bu_4N]ClO_4 is that anticipated for a one-electron, fully reversible oxidation by most of the criteria of stationary electrode polarography [34], i.e. the ratio of the cathodic to the anodic peak currents, i_p^c/i_p^a, is unity over the range of the experimental (20–200 mV s^{-1}) cyclic scan rate, and the peak-to-peak separation, ΔE_p, and the peak width, $E_p - E_{p/2}$, are invariably 59 and 57 mV, respectively. The cyclic voltammograms of the two complexes containing the ferrocenyldiphosphine (dppf) exhibit a second, ferrocene-centred, oxidation process with a potential value considerably more anodic than that displayed by the uncoordinated ligand [35]. Sizable anodic shifts of the redox potential of the ferrocene/ferrocinium couple upon phosphination of the C_5H_5 rings and complexation of the resulting dppf ligand as well as variations among the different known coordination modes of the ligands have already been observed in these and other laboratories [36,37]. Notably, these ferrocene redox couples, at variance with the relevant ruthenium-based ones, are centred at approximately the same $E_{1/2}$, in either the two neutral complexes (0.430 (C_5H_5) and 0.415 (C_5Me_5) V) or the two cationic derivatives (0.815 (C_5H_5) and 0.825 (C_5Me_5) V), thus revealing that the ruthenium–dppf bonding is not significantly affected by the substitution of Me for H in the auxiliary cyclopentadienyl ligand. The uncomplicated one-electron charge transfer reaction associated with ruthenium is confirmed by the course of controlled potential coulometry experiments. Thus, exhaustive electrolyses carried out at potentials past the anodic peak result in the removal of 1 mol of electrons per mole of depolarizer to give stable solutions with voltammetric reduction profiles almost complementary to the oxidation pattern of the precursor.

Figs. 1 and 2 show representative cyclic voltammograms of the ruthenium(II) complexes containing the dppf and the

Table 1
Electrochemical and ^{31}P NMR [a] parameters for some cyclopentadienyl ruthenium complexes

Complex	$Cp' = \eta^5$-C_5H_5			$Cp' = \eta^5$-C_5Me_5		
	$E_{1/2}$ (mV)	δ (ppm)	$\Delta\delta$ (ppm)	$E_{1/2}$ (mV)	δ (ppm)	$\Delta\delta$ (ppm)
(η^5-Cp')Ru(PPh_3)$_2$Cl	105	39.04	44.69	−90	40.4[c]	46.11
(η^5-Cp')Ru(dppe)Cl	−15	80.43	93.68	−190	74.53	87.88
(η^5-Cp')Ru{(*R*)-prophos}Cl [b]	−40	84.35	83.61	−220	79.85	79.11
(η^5-Cp')Ru{(*S,S*)-chiraphos}Cl [b]	−60	85.38	96.14	−245	80.39	91.15
(η^5-Cp')Ru(dppf)Cl	60	46.04	63.44	−125	41.60	59.00
[(η^5-Cp')Ru(dppf)(CH_3CN)]PF_6	345	45.83	63.23	275	44.43	61.83

[a] $\Delta\delta$ is the downfield shift of the $^{31}P\{^1H\}$ NMR resonance of the phosphorus ligand upon coordination at the metal centre (cf. Ref. [39]).
[b] Only the values of δ and $\Delta\delta$ that correspond to the P atom showing the larger difference are reported.

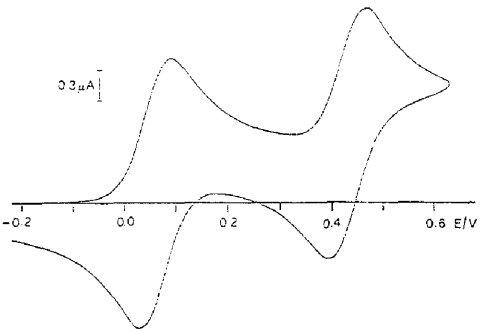


Fig. 1. Cyclic voltammogram for oxidation of 2.1 mmol dm^{-3} (η^5-C_5H_5)Ru(dppf)Cl in DCE, 0.2 mol dm^{-3} TBAP, at 25°C (scan rate 200 mV s^{-1}). Potentials are referred to ferrocenium/ferrocene couple: $E_{1/2}$ 0.420 V vs. aq. SCE.

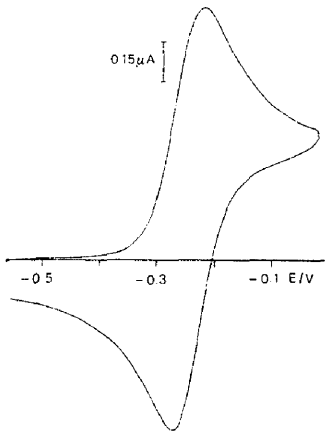


Fig. 2. Cyclic voltammogram for oxidation of 1.5 mmol dm^{-3} (η^5-C_5Me_5)Ru{(*S,S*)-chiraphos}Cl in DCE, 0.2 mol dm^{-3} TBAP, at 25°C (scan rate 200 mV s^{-1}). Potentials are referred to ferrocenium/ferrocene couple: $E_{1/2}$ = 0.420 V vs. aq. SCE.

(*S,S*)-chiraphos diphosphines, and Table 1 summarizes half-wave potentials, $E_{1/2}$, as the mean value of the potentials for anodic and cathodic peak currents.

From the figures of Table 1 it appears that substitution of C_5Me_5 for C_5H_5 shifts $E_{1/2}$ cathodically by about 200 mV. It is noteworthy that substitution of Me for H in ferrocene shifts $E_{1/2}$ by ca. 50 mV [38]. Moreover, the sequence of $E_{1/2}$ values upon changing the phosphorus ligand (the residual part and environment being kept constant) is in accordance with the expected donating abilities of the ligands. For instance, the difficulty of oxidation should increase (and does) in the order dppe > prophos > chiraphos, which is consistent with the trend of increasing ease to reduce already observed for [Ir(diphosphine)$_2$]$^+$ system [26].

Although we are aware that ^{31}P chemical shifts are notoriously difficult to rationalize [39], as electrochemical data do provide a useful insight into the relative basicity of phosphine ligands, we speculated on a relationship between $E_{1/2}$ and $^{31}P\{^1H\}$ NMR data for the two series of isostructural and isoelectronic ruthenium complexes. In Fig. 3 $E_{1/2}$ values are plotted versus $\Delta\delta$ (Table 1). A satisfactory linearity with approximately identical slope for C_5H_5 and C_5Me_5 derivatives is obtained. It appears that the ease of oxidation of the ruthenium centre, which is influenced by the basicity of the phosphine, runs parallel to the downfield shift of the $^{31}P\{^1H\}$ NMR signal of the ligand over a wide range of values.

4. Crystal structure of (η^5-C_5Me_5)Ru{(*S,S*)-chiraphos}Cl (1)

The crystal structure of (η^5-C_5Me_5)Ru{(*S,S*)-chiraphos}Cl (**1**) consists of a packing of discrete molecules separated by normal contacts. Fig. 4 reports an ORTEP drawing of the molecule in its absolute (*S,S*) configuration. Relevant bond parameters are reported in Table 2. The coordination around the Ru atom may be regarded as octahedral, with one face of the octahedron occupied by the chlorine and the diphosphine ligands and the opposite one by the permethylated cyclopentadienyl ligand, similar to that found in the (η^5-C_5H_5)Ru{(*S,S*)-chiraphos}Cl (**2**) species which has a similar geometry [40].

The Ru–Cl bond distance (2.447(2) Å) in **1** is intermediate (but substantially equal to) between those in **2** and its indenyl analogue (η^5-C_9H_7)Ru{(*S,S*)-chiraphos}Cl (**3**),

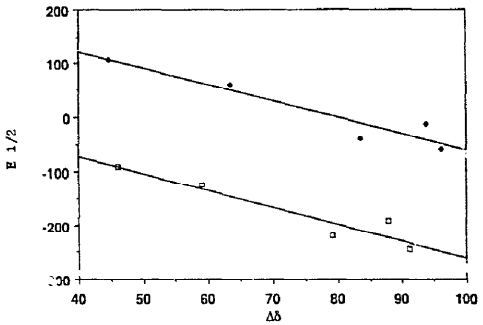


Fig. 3. Dependence of $E_{1/2}$ from $\Delta\delta$. Upper: $(\eta^5\text{-}C_5H_5)Ru(L\hat{}L)Cl$ complexes. Lower: $(\eta^5\text{-}C_5Me_5)Ru(L\hat{}L)Cl$ complexes.

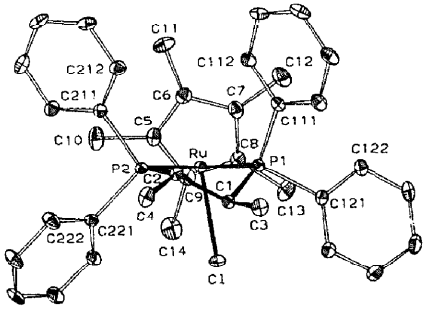


Fig. 4. ORTEP view of the partial labelling scheme along the bisector of the P–Ru–P angle. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for sake of clarity.

2.453(2) and 2.441(2) Å, respectively [40]. The two Ru–P bond lengths (2.286(2) and 2.308(1) Å), one slightly shorter than the other, show the same behaviour as found in **2** (2.270(2) and 2.297(1) Å) and **3** (2.239(2) and 2.312(1) Å).

The permethylated cyclopentadienyl ligand (C_5Me_5) is η^5 coordinated to the Ru atom, and the Ru–C interactions range from 2.198(2) to 2.258(2) Å (av. 2.231). Such an average Ru–C bond distance is larger than that in the related C_5H_5 derivative **2** (2.208 Å) but smaller than that found in the C_9H_7 derivative **3** (2.254 Å). According to the number of ring substituents, the (expected) relative order of steric hindrance should be $C_5H_5 < C_9H_7 < C_5Me_5$, and the 'anomalous' behaviour of **3** is due to the presence of two 'long' Ru–C interactions, i.e. to the common $\eta^5 \rightarrow \eta^3$ distortion of indenyl derivatives which, even if sterically assisted, is normally attributed to electronic factors.

Inspection of the Cp–Ru–P bond angles, which are much larger in **1** (average, 133.3°) than in **2** and **3** (averages, 129.1 and 128.8°, respectively), substantially confirms the above analysis. However, the Cp–Ru–Cl bond angle displays the opposite behaviour (116.5(5) versus 120.6 and 119.9 in **1**, **2** and **3**, respectively), while the P–Ru–P and P–Ru–Cl angles are substantially similar in the three derivatives.

The Ru–P–C_{ipso}–C_{ortho} angles (addressing the face/edge exposure), the P–Ru–P–C_{ipso} angles (describing the axial/equatorial character of the phenyl groups) and other pertinent dihedral angles (addressing the metallacycle conformation) are reported in Table 2. The metallacycle has a δ (absolute) conformation since the avoidance of the two methyls for the crowded axial positions binds the (*S,S*)/(*R,R*) chiraphos absolute configuration to the δ/λ metallacycle conformation. While the δ/λ choice is determined by the equatorial/axial preference of the methyl groups, the observed flap conformation can be accounted for by the pseudo octahedral coordination about the Ru atom. Indeed, an ideally skewed δ conformation of the metallacycle would require a C2 symmetric chiraphos conformation with a pseudo axial and a pseudo equatorial phenyl ring (with complementary face/edge exposure) on each phosphorus atom. However, the presence of the chloride ligand almost orthogonal to the P(1)–Ru–P(2) plane makes the whole $Ph_2CH(Me)P(2)$ moiety rotate around the P(2)–Ru bond in order to alleviate the steric strain. On the other hand, the chloride ligand bends towards P1 (Cl–Ru–P1 81.74(5)°) and away from P2 (Cl–Ru–P2 93.09(5)°) in order to avoid some short non-bonding interaction with one of the phenyl rings bound to P2 [Cl...H226 2.540(6) Å). The very same behaviour is present in **2** and **3** but, more importantly, is also common to the $(\eta^5\text{-}C_5H_5)Ru(dppe)Cl$ species [41] (**4**) which, lacking the methyl substituents on the metallacycle carbon atoms but sharing with **1** (**2** and **3**) the pseudo octahedral coordination at the Ru atom, confirms the above interpretation for the observed flap conformation of the pentaatomic metallacycle.

Further insight into the stereochemistry of 1,2-bis(diphenylphosphino)ethane derivatives can be obtained by comparing their structures with those of related derivatives with unbridged diphosphines such as $(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2Cl$ [42] (**5**) and $(\eta^5\text{-}C_5Me_5)Ru\{P(p\text{-}C_6H_4CF_3)_3\}_2Cl$ (**6**) [43]. In particular, the similarity of the Cl–Ru–P1 and Cl–Ru–P2 angles in these species clearly shows that the asymmetric bonding mode of chlorine in **1**, **2**, **3** and **4** is related to the presence of the metallacycle. In contrast, the presence of the bridging diphosphine has little influence on the stereochemical response upon the $C_5H_5 \rightarrow C_5Me_5$ substitution since in both cases (**2** versus **1** and **5** versus **6**) the Cp–Ru–P bond angles widen at the expense of the Cp–Ru–Cl angle, i.e. the chlorine atom can fit in the pocket between two methyls of the C_5Me_5 ligand while the phosphines cannot. However, while the P(1)–Ru–P(2) angle is similar in **1** and **2** (since it cannot be shrunk any more) it shrinks by about 10° on moving from **5** to **6**.

5. Experimental

5.1. Structure determination and refinements

A transparent orange crystal of dimensions 0.25×0.20×0.17 mm was mounted on an Enraf-Nonius

(*rac*)-1,2-Bis(diphenylphosphino)cyclopentane (cypenphos) [47], (2*S*,3*S*)-2,3-bis(diphenylphosphino)butane (chiraphos) [48], (*R*)-1,2-bis(diphenyl-phosphino)propane (prophos) [49], (*R*)-1-phenyl-1,2-bis(diphenylphosphino)ethane (phenphos) [50], (*R*,*R*)-2-*exo*-3-*endo*-bis-(diphenylphosphino)bicyclo[2.2.1]hep-tane (renorphos) [51], $[(\eta^5\text{-}C_5Me_5)RuCl_2]_n$ [27] and $(\eta^5\text{-}C_5H_5)Ru(L\hat{}L)Cl$ [28] were prepared according to published procedures.

5.4. $(\eta^5\text{-}C_5Me_5)Ru(PPh_3)_2Cl$

A suspension of 1.0 g (3.25 mmol) of $[(\eta^5\text{-}C_5Me_5)RuCl_2]_n$ was treated with 2.20 g (8.38 mmol) of triphenylphosphine under stirring at reflux temperature for 5 h in 40 ml of anhydrous ethanol. The suspension was left at room temperature for 12 h and the microcrystalline orange compounds was filtered off, washed with n-hexane and dried under vacuum. Recrystallisation was from dichloromethane/n-hexane. The yield is 90%. ^{1}H NMR(CD_2Cl_2): 7.46–7.12 (m, 30H, C_6H_5); 1.01 (t, 15H, J_{HH} = 1.46, C_5Me_5). ^{31}P NMR (CD_2Cl_2): 40.46(s). ^{1}H NMR($C_6D_5CD_3$): 7.45–6.45 (m, 30H, C_6H_5); 0.85 (t, 15H, J_{HH} = 1.46 Hz, C_5Me_5). *Anal.* Found: C, 69.41; H, 5.82. Calc. for $C_{46}H_{45}P_2ClRu$: C, 69.38; H, 5.70%.

5.5. General procedure for the preparation of $(\eta^5\text{-}C_5Me_5)Ru(diphos)Cl$ complexes

$(\eta^5\text{-}C_5Me_5)Ru(PPh_3)_2Cl$ (0.2 g, 0.25 mmol) was reacted at reflux temperature with an equimolecular amount of the appropriate diphosphine in 30 ml of toluene for 5 h. The solvent was then removed under reduced pressure and 20 ml of n-hexane was added to the residue. The orange microcrystalline compounds were filtered off, washed with n-hexane and dried in vacuo. Recrystallisation was from dichloromethane/n-hexane. Yields are in the range 70–80%.

Elemental analyses and NMR parameters for the complexes are as follows.

5.5.1. $(\eta^5\text{-}C_5Me_5)Ru(dppe)Cl$

^{1}H NMR (CD_2Cl_2): 7.66–7.20 (m, 20 H, C_6H_5); 2.58–2.13 (m, 4H, CH_2); 1.42 (s, 15H, C_5Me_5). ^{31}P{^{1}H} NMR (CD_2Cl_2): T=300 K: 75.52 ppm (s). T=178 K: 75.12 (s). ^{13}C{^{1}H} NMR (CD_2Cl_2): 134.33–127.66 (m, C_6H_5); 89.42 (s, C_5Me_5); 28.58 (t, CH_2, J_{PC} = 21.99 Hz; 9.87 (s, C_5Me_5). ^{1}H NMR($C_6D_5CD_3$): 7.40–6.67 (m, 20H, C_6H_5); 2.35–2.20 (m, 4H, CH_2); 1.10 (t, 15H, C_5Me_5, J_{PH} = 1.46 Hz). ^{31}P{^{1}H} NMR: 74.64(s). *Anal.* Found: C, 64.17; H, 5.73. Calc. for $C_{36}H_{39}P_2ClRu$: C, 64.52; H, 5.86%.

5.5.2. $(\eta^5\text{-}C_5Me_5)Ru\{(rac)\text{-}cypenphos\}Cl$

^{1}H NMR (CD_2Cl_2): 7.90–7.31 (m, 20H, C_6H_5); 3.48–1.71 (m, 8H, CH + CH_2); 1.31 (s, 15H, C_5Me_5). ^{31}P{^{1}H} NMR (CD_2Cl_2): (T=300 K) 51.50(bs). T=176 K: 58.90 (d, J_{PP} = 21.97 Hz); 44.84 (d, J_{PP} = 21.97 Hz). ^{13}C{^{1}H} NMR (CD_2Cl_2): 141.97–127.33 (m, C_6H_5); 88.13 (s, C_5Me_5); 40.56–22.56 (m, CH + CH_2); 9.55 (s, C_5Me_5). ^{1}H NMR ($C_6D_5CD_3$): 7.87–6.97 (m, 20H, C_6H_5); 3.40–2.20 (m, 8H, CH + CH_2); 1.16 (t, 15H, C_5Me_5). ^{31}P{^{1}H} NMR ($C_6D_5CD_3$): 58.59 (d, J_{PP} = 39.06 Hz); 43.05 (d, J_{PP} = 39.06 Hz). ^{13}C{^{1}H} NMR ($C_6D_5CD_3$): 133.27–124.16 (m, C_6H_5); 88.36 (s, C_5Me_5); 9.55 (s, C_5Me_5). *Anal.* Found: C, 66.57; H, 5.95. Calc. for $C_{39}H_{43}P_2ClRu$: C, 66.15; H, 6.10%.

5.5.3. $(\eta^5\text{-}C_5Me_5)Ru\{(S,S)\text{-}chiraphos\}Cl$

^{1}H NMR (CD_2Cl_2): 7.89–7.36 (m, 20H, C_6H_5); 2.92–1.92 (m, 2H, CH); 1.32 (s, 15 H, C_5Me_5); 1.12 (bs, 6H, CH_3). ^{31}P{^{1}H} NMR (CD_2Cl_2): T=300K, 72.76 (bs); T=178K, 80.90(m); 69.39(m). ^{1}H NMR ($C_6D_5CD_3$): 7.91–6.68 (m, 20H, C_6H_5); 3.03–1.60 (m, 2H, CH); 1.11 (t, 15H, C_5Me_5, J_{PH} = 1.46 Hz); 0.74 (dd, 6H, CH_3, J_{HH} = 3.41 Hz; J_{PH} = 7.32 Hz). ^{31}P{^{1}H} NMR ($C_6D_5CD_3$): 80.39 (d, J_{PP} = 26.85 Hz); 70.84 (d, 26.85 Hz). ^{13}C{^{1}H} NMR ($C_6D_5CD_3$): 130.02–124.17 (m, C_6H_5); 89.50 (s, C_5Me_5); 43.82–38.96 (m, CH); 9.80 (s, CH_3). *Anal.* Found: C, 65.60; H, 6.20. Calc. for $C_{38}H_{43}P_2ClRu$: C, 65.37; H, 6.21%.

5.5.4. $(\eta^5\text{-}C_5Me_5)Ru\{(R)\text{-}prophos\}Cl$

^{1}H NMR (CD_2Cl_2): 7.30–6.87 (m, 20H, C_6H_5); 3.15–2.52 (m, 3H, CH + CH_2); 1.26 (t, 15H, C_5Me_5); 0.94 (bs, 3H, CH_3). ^{31}P{^{1}H} NMR (CD_2Cl_2): T=300 K, 84.6 (bs); 58.22 (bs). T=178 K: major diastereomer (95%): 83.46 (d, J_{PP} = 29.21 Hz); 57.68 (d, J_{PP} = 29.21 Hz); minor diastereomer (5%): 73.34 (m); 63.88 (m). ^{1}H NMR ($C_6D_5CD_3$): 7.31–6.79 (m, 20H, C_6H_5); 2.85–1.84 (m, 3H, CH + CH_2); 1.16 (t, 15H, C_5Me_5, J_{PH} = 1.46 Hz); 0.62 (dd, 3H, CH_3, J_{HH} = 6.83 Hz, J_{PH} = 9.76 Hz). ^{31}P{^{1}H} NMR ($C_6D_5CD_3$): major diastereomer (95%): 83.96 (d, J_{PP} = 29.29 Hz); 57.62 (d, J_{PP} = 29.29 Hz); minor diastereomer (5%): 75.92 (d, J_{PP} = 19.53 Hz); 67.04 (d, J_{PP} = 19.53 Hz). ^{13}C{^{1}H} NMR ($C_6D_5CD_3$): 133.75–124.16 (m, C_6H_5); 89.18 (s, C_5Me_5); 34.35 (m, CH + CH_2); 9.80 (s, C_5Me_5). *Anal.* Found: C, 65.82; H, 6.20. Calc. for $C_{37}H_{41}P_2ClRu$: C, 65.37; H, 6.21%.

5.5.5. $(\eta^5\text{-}C_5Me_5)Ru\{(R,R)\text{-}renorphos\}Cl$

^{1}H NMR (CD_2Cl_2): 7.85–7.40 (m, 20H, C_6H_5); 2.80–1.68 (m, 10H, CH + CH_2); 1.36 (s, 15H, C_5Me_5). ^{31}P{^{1}H} NMR (CD_2Cl_2): T=300 K, 61.59 (bs); 38.84 (bs); T=175 K. major diastereomer (85%): 61.54 (d, J_{PP} = 43.94 Hz); 39.17 (d, J_{PP} = 43.94 Hz). Minor diastereomer (15%): 51.99 (d, J_{PP} = 46.38 Hz); 48.18 (d, J_{PP} = 46.38). ^{13}C{^{1}H} NMR: 138.50–127.50 (m, C_6H_5); 87.47 (s, C_5Me_5); 42.47–23.86 (m, CH + CH_2); 9.87 (s, C_5Me_5). ^{1}H NMR ($C_6D_5CD_3$): 7.40–6.90 (m, 20H, C_6H_5); 3.14–2.06 (m, 8H, CH + CH_2); 1.20 (t, 15H, C_5Me_5, J_{PH} = 1.46 Hz). ^{31}P{^{1}H} NMR ($C_5D_5CD_3$): major diastereomer (85%): 61.58 (d, J_{PP} = 43.94 Hz); 36.88 (d, J_{PP} = 43.94 Hz). Minor diastereomer (15%): 53.17 (d, J_{PP} = 46.38 Hz); 44.40 (d, J_{PP} = 46.38 Hz). ^{13}C{^{1}H} NMR

($C_6D_5CD_3$): 129.88–124.03 m, 65; 87.75 (s, C_5Me_5); 40.87–20.86 (m, $CH+CH_2$); 10.15 (s, C_5Me_5). *Anal.* Found: C, 66.35; H, 5.29. Calc. for $C_{41}H_{45}P_2ClRu$: C, 66.78; H, 5.16%

5.5.6. (η^5-C_5Me_5)Ru{(R)-phenphos}Cl

^1H NMR (CD_2CL_2): 7.42–6.73 (m, 25 H, C_6H_5); 2.67–2.50 (M, 3H, $CH+CH_2$); 1.38, 1.30 (s, 15H, C_5Me_5). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): $T=300$ K: 90.32(bs); 54.99(bs); $T=175$ K major diastereomer (75%): 89.58 (d, $J_{PP}=34.18$ Hz); 54.31 (d, $J_{PP}=34.18$ Hz). Minor diastereomer (25%): 79.82 (d, $J_{PP}=29.29$ Hz); 64.47 (d, $J_{PP}=29.29$ Hz). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): 138.07–126.19 (m, C_6H_5); 88.94 (s, C_5Me_5); 45.17 (m, $CH+CH_2$); 9.06 (s, C_5Me_5). ^1H NMR ($C_6D_5CD_3$): 7.57–6.51 (m, 25H, C_6H_5); 2.42–2.22 (m, 3H, $CH+CH_2$); 1.14, 1.19 (t, 15H, C_5Me_5, $J_{PH}=1.50$ Hz). $^{31}P\{^1H\}$ NMR ($C_6D_5CD_3$): major diastereomer (75%): 89.82 (d, $J_{PP}=31.73$ Hz); 54.75 (d, $J_{PP}=31.73$ Hz). Minor diastereomer (25%): 79.79 (d, $J_{PP}=26.85$ Hz); 70.06 (d, $J_{PP}=26.85$). *Anal.* Found: C, 67.15; H, 5.33. Calc. for $C_{42}H_{43}P_2ClRu$: C, 67.61; H, 5.60%.

5.5.7. (η^5-C_5Me_5)Ru(dppf)Cl

^1H NMR (CD_2Cl_2): 7.85–7.36 (m, 20H, C_6H_5); 5.07, 4.08, 4.05, 3.89 (s, 8H, C_5H_4); 1.01 (s, 15H, C_5Me_5). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): 41.60(s). *Anal.* Found: C, 64.47; H, 5.30. Calc. for $C_{44}H_{43}P_2ClFeRu$: C, 63.97; H, 5.24%.

5.5.8. (η^5-C_5H_5)Ru(dppf)Cl

^1H NMR (CD_2Cl_2): 7.40–7.36 (m, 20H, C_6H_5); 5.10, 4.31 (s, 8H, C_5H_4); 4.12 (s, 5H, C_5H_5). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): 46.04 (s). *Anal.* Found: C, 62.05; H, 4.51. Calc. for $C_{39}H_{33}P_2ClRuFe$: C, 61.96; H, 4.40%.

5.6. General procedure for the preparation of [(η^5-C_5Me_5)Ru(diphos)(CH_3CN)]PF_6 complexes

0.1 g (ca. 0.15 mmol) of (η^5-C_5Me_5)Ru(L^L)Cl complex was reacted with 1 ml of CH_3CN in the presence of an excess of NH_4PF_6 as halogen scavenger in 20 ml of anhydrous methanol. The yellow–orange suspension was stirred under nitrogen for 5 h until the colour of the suspension changed to pale yellow. The solvent was removed under reduced pressure and the residue treated with 10 ml of CH_2Cl_2 and filtered off. After adding 20 ml of n-hexane to the crude compounds and stirring for several hours, the complexes were filtered off, washed with n-hexane, dried in vacuo and recrystallised by CH_2Cl_2/n-hexane. The yields are in the range 70–80%.

Elemental analysis and NMR parameters for the complexes are as follows.

5.6.1. [(η^5-C_5Me_5)Ru(dppe)(CH_3CN)]PF_6

^1H NMR (CD_2Cl_2): 7.51–7.26 (m, 20H, C_6H_5); 2.43 (d, 4H, CH_2, $J_{PH}=16.1$ Hz); 1.53 (t, 3H, CH_3CN, $J_{PH}=1.46$ Hz); 1.44 (t, 15H, C_5Me_5, $J_{PH}=1.46$ Hz). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): 75.52 (s); −144.48 (st, PF_6, $J_{PF}=712.9$ Hz). *Anal.* Found: C, 55.71; H, 5.93; N, 1.68. Calc. for $C_{38}H_{42}P_3NF_6Ru$: C, 55.61; H, 5.16; N, 1.70%.

5.6.2. [(η^5-C_5Me_5)Ru{(rac)-cypenphos}(CH_3CN)]PF_6

^1H NMR (CD_2Cl_2): 7.70–7.21 (m, 20H, C_6H_5); 2.81–1.75 (m, 10H, $CH+CH_2$); 2.02 (t, 3H, CH_3CN, $J_{PH}=1.46$ Hz); 1.38 (t, 15H, C_5Me_5, $J_{PH}=1.46$ Hz). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): 45.56 (s) (d, $J_{PP}=36.62$ Hz); 32.56 (d, $J_{PP}=36.62$ Hz); −158.0 (st, PF_6, $J_{PF}=712.9$ Hz). *Anal.* Found: 56.71; H, 5.33; N, 1.60. Calc. for $C_{41}H_{46}P_3NF_6Ru$: C, 57.01; H, 5.38; N, 1.63%.

5.6.3. [(η^5-C_5Me_5)Ru{(S,S)-chiraphos}(CH_3CN)]PF_6

^1H NMR (CD_2Cl_2): 7.56–7.36 (m, 20H, C_6H_5); 2.62–2.11 (m, 2H, CH); 1.59 (t, 3H, CH_3CN, $J_{PH}=1.46$ Hz); 1.37 (t, 15H, C_5Me_5, $J_{PH}=1.46$ Hz); 1.17 (dd, 3H, CH_3, $J_{PH}=10.25$ Hz, $J_{HH}=3.41$ Hz); 1.00 (dd, 3H, CH_3, $J_{PH}=11.71$ Hz, $J_{HH}=6.43$ Hz). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): 82.51 (d, $J_{PP}=34.18$ Hz); 75.31 (d, $J_{PP}=34.18$ Hz); −143.45 (st, PF_6, $J_{PF}=708.0$ Hz). *Anal.* Found: C, 56.81; H, 5.28; N, 1.61. Calc. for $C_{40}H_{46}P_3NF_6Ru$: C, 56.60; H, 5.46; N, 1.65%.

5.6.4. [(η^5-C_5Me_5)Ru{(R)-prophos}(CH_3CN)]PF_6

^1H NMR (CD_2Cl_2): 7.53–7.27 (m, 20H, C_6H_5); 1.96–182 (m, 3H, $CH+CH_2$); 1.68 (t, 3H, CH_3CN, $J_{PH}=1.46$ Hz); 1.38 (t, 15H, C_5Me_5, $J_{PH}=1.46$ Hz); 1.10 (dd, 3H, CH_3, $J_{PH}=11.23$ Hz, $J_{HH}=6.34$ Hz). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): major diastereomer (95%): 83.80 (d, $J_{PP}=29.29$ Hz); 58.28 (d, $J_{PP}=29.29$ Hz). Minor diastereomer (5%): 88.40 (d, $J_{PP}=19.53$ Hz); 74.68 (d, $J_{PP}=19.53$ Hz). −144.45 (st, PF_6, $J_{PF}=712.9$ Hz). *Anal.* Found: C, 56.35; H, 5.12, N, 1.76. Calc. for $C_{39}H_{44}P_3NF_6Ru$: C, 56.11; H, 5.31; N, 1.68%.

5.6.5. [(C_5Me_5)Ru(dppf)(CH_3CN)]PF_6

^1H NMR (CD_2Cl_2): 7.46 (m, 20H, C_6H_5); 4.26, 4.14 (s, 8H, C_5H_4); 2.81 (t, $J_{PH}=1.46$ Hz, 3H, CH_3CN); 1.05 (t, $J_{PH}=1.46$ Hz, 15H, C_5Me_5). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): 44.43 (s). *Anal.* Found: C, 56.42; H, 4.63. Calc. for $C_{46}H_{46}P_3F_6NFeRu$: C, 56.56; H, 4.75%.

5.6.6. [(C_5H_5)Ru(dppf)(CH_3CN)]PF_6

^1H NMR(CD_2Cl_2): 7.46–7.25 (m, 20H, C_6H_5); 4.43, 4.41, 4.31 (s, 8H, C_5H_4); 4.37 (s, 5H, C_5H_5); 2.24 (t, $J_{PH}=1.46$ Hz, 3H, CH_3CN). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): 45.83 (s). *Anal.* Found: C, 54.03; H, 4.08. Calc. for $C_{41}H_{36}P_3F_6NFeRu$: C, 54.32; H, 4.00%.

6. Supplementary material

Supporting information includes a list of final atomic coordinates, anisotropic displacement parameters and bond distances and angles (5 pages).

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