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# A study of the coordination ability of 2,5-di(2-pyridyl)phospholes on Ru centres

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Dedicated to Professor P. Royo on the occasion of his 65th birthday and for his outstanding contribution to organometallic chemistry

**Abstract**

The coordination behaviour of the readily available 1-phenyl-2,5-di(2-pyridyl)phosphole (NPN) toward Ru centres was investigated. Neutral and ionic compounds of formula [RuCl(*p*-cymene)(NPN)]TfO (TfO = $CF_3SO_3$)... (**1**), [RuCl(*p*-cymene)(NPN)]$BF_4$ (**2**), [RuCl($C_6Me_6$)(NPN)]TfO (**3**), RuCp′Cl(NPN) [Cp′ = $C_5H_5$ (**4**), $C_5Me_5$ (**5**)], Ru($C_5Me_5$)($\sigma^1$-$C_8H_{13}$)(NPN) (**6**), $RuCl_2$(NPN)$_2$ (**7**) and RuClH(cod)(NPN) (cod = 1,5-cyclooctadiene) (**8**) were obtained. Two diastereomers were obtained for **1**, **2** and **4**, (**a**, **b**) while three were found in the case of **8** (**a**–**c**). According to NMR spectroscopy, the 2,5-bis(2-pyridyl)phosphole acts as a 1,4-*P*,*N* chelate ligand in all cases. This behaviour was confirmed by an X-ray diffraction study performed on complex **1a**. Proton transfer studies on complex **8** demonstrated the influence of the molecular structure on the ability to form dihydrogen bridges.
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*Keywords:* Ruthenium complexes; Phospholes; Hydrides

## 1. Introduction

Phospholes have been extensively used as ligands in coordination chemistry and homogeneous catalysis [1]. They act as classical two-electron donor tertiary phosphines towards transition metals due to the lack of endocyclic delocalization of the phosphorus lone pair [2]. Functionalisation of the heterocyclic phosphole ring in 2- or 2,5-positions by coordinative moieties offers the possibility to obtain polydentate ligands [3]. 1-Phenyl-2,5-di(2-pyridyl)phosphole (NPN, Scheme 1) is a stable derivative, readily available via the 'one pot' Fagan–Nugent route [4], which presents a versatile coordination behaviour. This compound can act as a monodentate *P*-donor toward $W(CO)_5$ [4a], as an *N*,*P*-chelate toward Pd(II) centres [5a] or as a tridentate *N*,*P*,*N*-ligand on a dicationic Pd(I)–Pd(I) fragment [5b] (Scheme 1). The chelate P,N-coordination offers a free basic pyridyl group close to the metal centre. This feature can allow performing ligand–metal hydrogen transfer or to force dihydrogen bridges through interaction between metal–hydride and pyridyl–proton moieties, processes that give rise to interesting reactivity properties [6]. Such phenomena have been observed with different transition metals including ruthenium [7]. Herein, we report a study on the coordination ability of 2,5-di(2-pyridyl)phosphole NPN with different Ru-containing fragments and protonation experiments of one of the resulting complexes.

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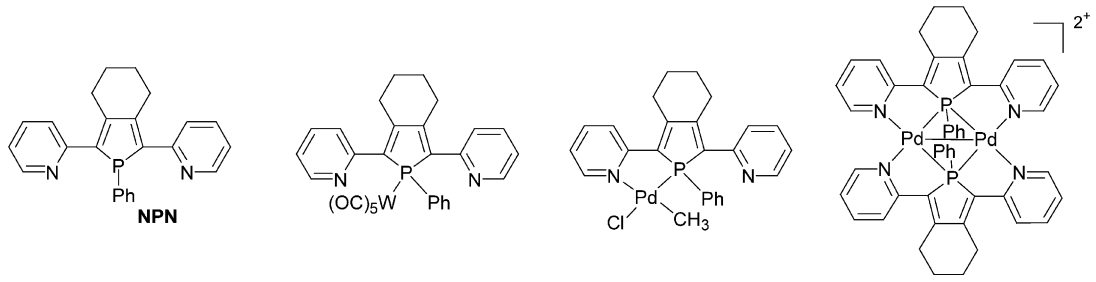


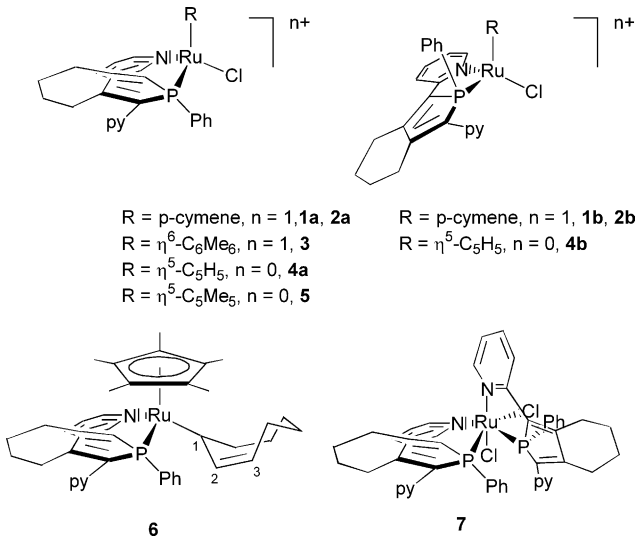

Scheme 1.

## 2. Results and discussion

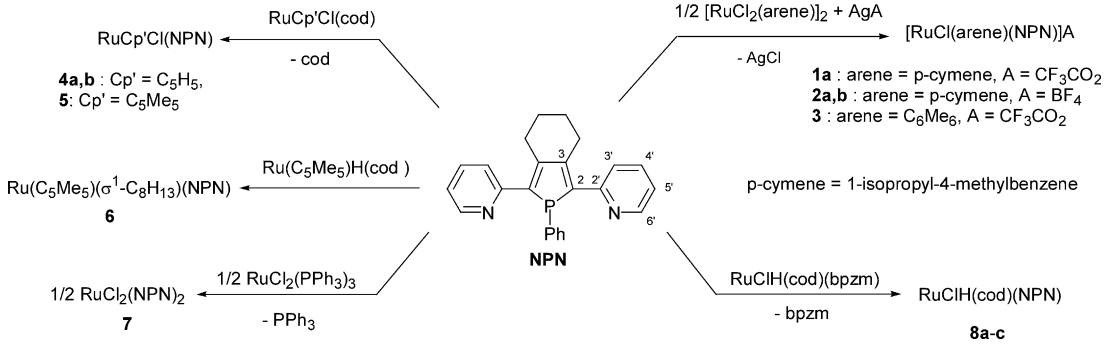
Complexes **1**–**8** (Scheme 2) were prepared using known Ru starting materials according to standard methods of fragmentation (**1**–**3**), ligand substitution (**4**,**5**,**7**,**8**, cod = 1,5-cyclooctadiene, bpzm = bis(pyrazol-1-yl)methane) or insertion reaction (**6**). In all cases, with the exception of **7**, the NPN/metal ratio was 1/1 and the corresponding stoichiometry was obtained for each of the reaction products. Complexes **1**–**8** were characterised by elemental microanalysis, IR-, $^{1}$H-, $^{31}$P{$^{1}$H}- and $^{13}$C{$^{1}$H}-NMR spectroscopy excepted derivative **7** which evolves in the time required to record a $^{13}$C{$^{1}$H}-NMR. In all cases, a large $^{31}$P-NMR coordination shift effect was observed ($\Delta\delta > 49$ ppm). This high shift effect is characteristic of P,N-chelating coordination of 2-pyridylphospholes on transition metal centres [5,8]. Two sets of signals are recorded for the pyridine moieties in the $^{1}$H- and $^{13}$C{$^{1}$H}-NMR spectra. The chemical shifts of the resonances for the protons $H^{6'}$ and $C^{6'}$ (see Scheme 2 for numbering) are particularly useful because they are usually markedly different for the coordinated and uncoordinated pyridine rings.

### 2.1. Complexes with a piano-stool structure

Coordination of 2-(2-pyridyl)phospholes to '(arene)RuCl' or 'Cp′RuCl' fragments can give rise to two diastereoisomeric complexes possessing a piano-stool structure. In the case of 2-(2-pyridyl)-5-(2-thienyl)phosphole, only one of the possible diastereoisomers was formed upon coordination on an '(arene)RuCl' moiety [8]. In marked contrast, according to the $^{1}$H- and $^{13}$C{$^{1}$H}-NMR data, complexes with 2,5-di(2-pyridyl)phosphole ligand are obtained as a mixture of two diastereoisomers noted **a** and **b** (Scheme 3: **1a**/**1b** and **2a**/**2b**, 5/1 ratio; **4a**/**4b**, 3/2 ratio). These isomers differ in the orientation of the phosphole Ph substituent with respect to the Ru-coordinated arene or Cp group and it is very likely that an *anti* orientation that diminishes the steric hindrance (isomers **a**, Scheme 3) is more favourable. The following experimental features support this hypothesis.




Scheme 3.




Scheme 2.

At room temperature, a 5/1 solution of diastereisomers **1a** and **1b** evolves to complex **1a** after several days. This observation clearly shows that complexes are in equilibrium and that derivative **1a** is thermodynamically more stable than its isomer **1b**. The molecular structure of complex **1a** was determined by an X-ray diffraction study (Fig. 1, Table 1). As anticipated, the *p*-cymene and the *P*-Ph substituent of the phosphole point in opposite direction (*anti* conformer). The bond lengths and angles around the Ru centre [Ru(1)–P(1), 2.315(2) Å; Ru(1)–N(1), 2.139(5) Å; P(1)–Ru(1)–N(1), 79.9(1)°] are consistent with known literature values [8] and reveal the absence of strain due to the formation of the five-membered metallacycle. The inter-ring twist angle between the phosphole ring and the coordinated pyridine (49.1°) is superior to that involving the free pyridine group (25.2°). It is noteworthy that the uncoordinated nitrogen atom points toward the Ru-centre. However, the distance between these two atoms reaches 4.09 Å revealing the absence of any interaction.

The steric hindrance around the ruthenium atom has a dramatic influence on the diastereoselectivity of 2,5-di(2-pyridyl)phosphole coordination. With Ru centres bearing bulky arene ligands such as $C_6Me_6$ or $C_5Me_5$, a diastereoselective coordination occurred and complexes **3**, **5** and **6** were isolated as single diastereomers.

The reaction leading to complex **6** warrants a separate discussion. In contrast to its precursor Ru($C_5Me_5$)H(cod) (Scheme 2), complex **6** does not show any hydride resonance in the $^1$H-NMR spectrum. Three resonances are observed between 3.2 and 5.3 ppm, each signal integrates for one proton and they are correlated by COSY (see Fig. 2). One of these protons ($H^1$) is coupled to phosphorus ($J_{HP} = 32.7$ Hz), which suggests a direct bonding of the corresponding CH group to the Ru centre. The chemical shift of this signal (4.22 ppm) is similar to that found in a cycloheptatrienyl ligand with a $\sigma^1$-allyl moiety bonded to Ru [9]. These data strongly suggest that the three aforementioned $^1$H resonances correspond to a $\sigma^1$-allyl moiety. The formation of **6** (Scheme 3) involves the insertion of one alkene function of the cod group into the Ru–H bond, induced by the coordination of the NPN ligand, followed by an internal isomerisation of the remaining C=C double bond of the cyclooctenyl fragment. The migration of a hydride group to cod has precedents for Ru [10] and even for CpRu derivatives [10e]. However, a $\eta^3$-allyl or a vinyl group were shown to be the final products depending on whether the incoming ligand was a monodentate or a bidentate donor. Consequently, carbene intermediates such as those considered responsible for the formation of vinyl products in the reaction of CpRuH(cod) with diphosphines [10e] seem to be of only minor importance in the reaction of Ru($C_5Me_5$)H(cod) with the hetero-ditopic 2-pyridylphosphole ligand.

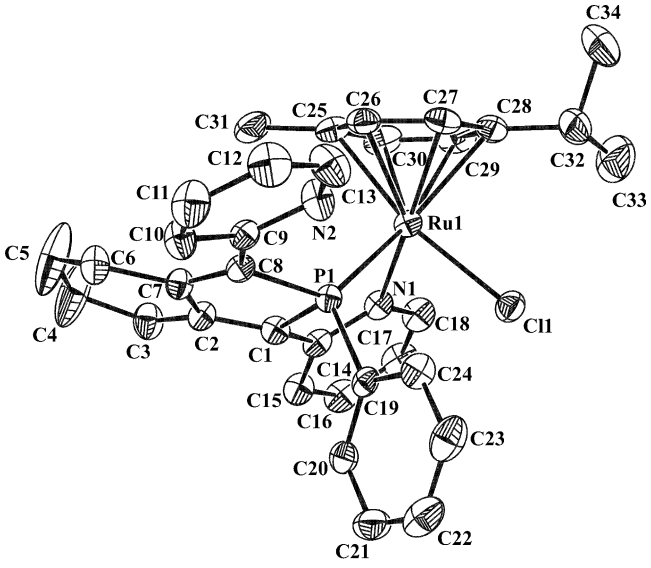



Fig. 1. ORTEP view of complex **1a** with atom-labeling. Thermal ellipsoids show 30% probability levels.

Table 1
Selected bond lengths (Å) and bond angles (°) for complex **1a**

| | | | |
|---|---|---|---|
| *Bond lengths* | | | |
| Ru(1)-P(1) | 2.315(2) | N(1)–C(14) | 1.351(7) |
| Ru(1)–N(1) | 2.139(5) | C(14)–C(1) | 1.470(7) |
| Ru(1)–Cl(1) | 2.389(2) | C(1)–P(1) | 1.780(5) |
| Ru(1)–C(25) | 2.227(6) | C(1)–C(2) | 1.355(7) |
| Ru(1)–C(26) | 2.161(6) | C(2)–C(7) | 1.479(7) |
| Ru(1)–C(27) | 2.181(5) | C(7)–C(8) | 1.363(7) |
| Ru(1)–C(28) | 2.264(6) | C(8)–P(1) | 1.816(5) |
| Ru(1)–C(29) | 2.238(6) | C(8)–C(9) | 1.457(7) |
| Ru(1)–C(30) | 2.185(6) | C(9)–N(2) | 1.345(7) |
| *Bond angles* | | | |
| Cl(1)–Ru(1)–P(1) | 88.9(1) | Ru(1)–P(1)–C(8) | 127.4(2) |
| Cl(1)–Ru(1)–N(1) | 84.5(1) | P(1)–C(8)–C(9) | 119.2(4) |
| P(1)–Ru(1)–N(1) | 79.9(1) | C(8)–C(9)–N(2) | 114.4(5) |
| Ru(1)–N(1)–C(14) | 120.8(3) | P(1)–C(8)–C(7) | 109.3(4) |
| N(1)–C(14)–C(1) | 113.3(5) | C(8)–C(7)–C(2) | 114.5(5) |
| C(14)–C(1)–P(1) | 115.6(4) | C(7)–C(2)–C(1) | 113.1(5) |
| C(1)–P(1)–Ru(1) | 96.3(2) | C(7)–C(8)–C(9) | 131.5(5) |

## 2.2. Octahedral complexes

Complexes **7** and **8** were obtained through ligand displacement ($PPh_3$, cod) from the corresponding Ru starting material by NPN (Scheme 2). Complex **7** was obtained by reacting $RuCl_2(PPh_3)_3$ with two equivalents of NPN at 40 °C. When the reaction was carried out with only one equivalent of NPN or at room temperature with two equivalents, the $^{31}P\{^1H\}$-NMR spectrum of the reaction mixture showed the presence of **7** and of an intermediate that was not isolated. This intermediate is very probably a $RuCl_2(PPh_3)$(NPN) complex since its $^{31}P\{^1H\}$-NMR spectrum exhibits two mutually coupled doublets ($J_{PP} = 34.9$ Hz) with chemical shifts typical of a coordinated $PPh_3$ (54.7 ppm) and an *N*,*P*-chelate 2-

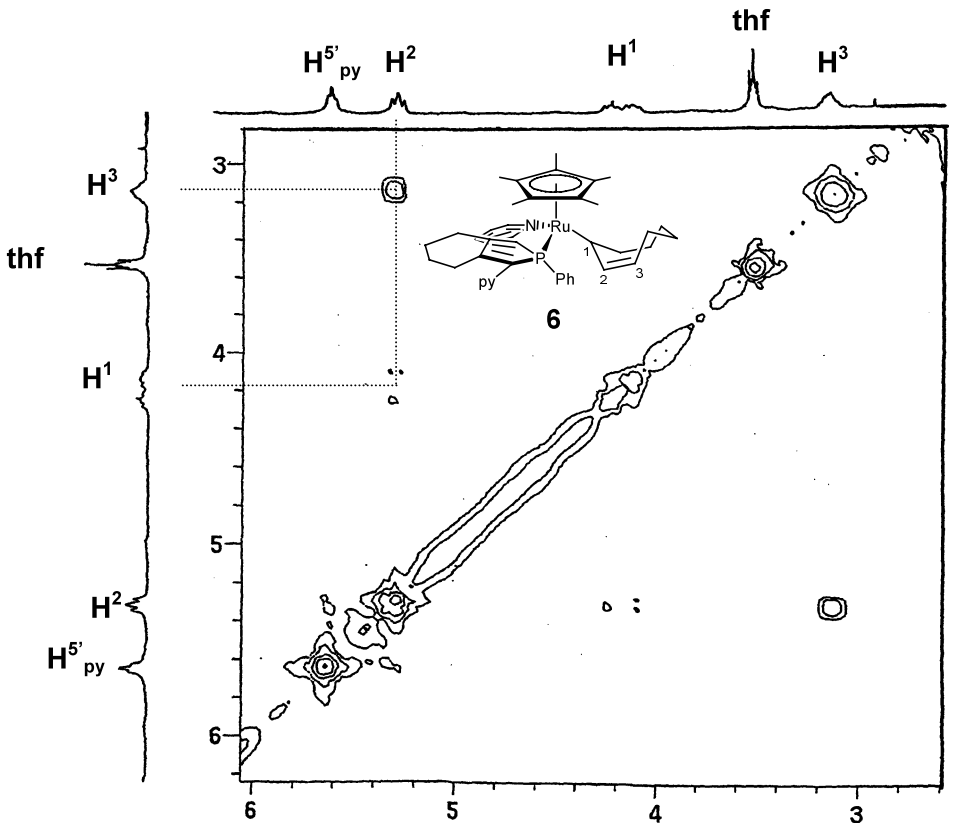
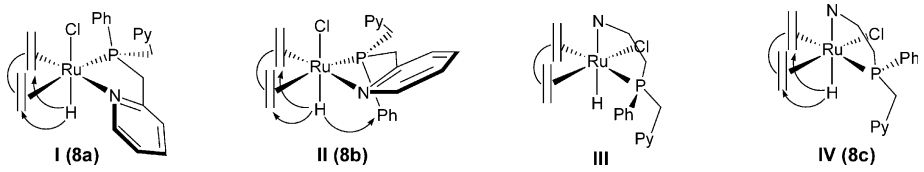



Fig. 2. $^{1}H-^{1}H$ COSY spectrum for complex **6** showing the correlations on the allyl group.

pyridylphosphole (74.3 ppm). The $^{31}P\{^{1}H\}$-NMR spectrum of compound **7** contains two doublets at low field ($\delta$: 75.6, 79.8) with a low coupling constant (33.6 Hz) characteristic of phosphorus atoms in a mutually *cis* disposition. In the $^{1}H$ spectra, a pair of $H^{6'}$ resonances are observed indicating the presence of two coordinated ($\delta$: 10.26, 1H; 9.92, 1H) and two free ($\delta$: 8.57, 2H) pyridyl groups. Taking into account these data, we propose that the most reasonable structure for complex **7** is that presented in Scheme 3. Only one diastereomer was observed, which indicates a high selectivity in the orientation of the Ph substituents of the two phosphole ligands. The orientation of the P-phenyl substituent towards the Cl ligand is probably the least sterically demanding.

The NMR spectra of complex **8** (Scheme 2) show the presence of three isomers (**a**–**c** in this discussion), as deduced from the observation of three different singlets in the $^{31}P\{^{1}H\}$-NMR spectrum and three doublets in the hydride region (1:2:1 ratio) of the $^{1}H$-NMR spectrum. The $H^{6'}$ pyridine resonances and several of the olefinic cod protons were assigned after COSY and NOE experiments. The rest of the resonances are obscured by the complexity of the $^{1}H$-NMR spectrum. The structures of the three isomers **8a**–**c** (Scheme 4) are proposed on the basis of the following points. NOE irradiation of each hydride signal leads to an effect on a specific pair of olefinic cod resonances (the observed NOE interactions are indicated with arrows in Scheme 4). This behaviour is characteristic of a *fac* disposition of the donor groups in the RuH(cod) moiety [11]. Furthermore, the doublets of the hydrides exhibit $^{2}J_{HP}$ values of ca. 20–30 Hz, which is typical of a mutually *cis* disposition of the coordinated P and H atoms. The doublet for **8c** shows a hyperfine coupling of 3.2 Hz and this does not disappear upon $^{31}P$ decoupling. This small splitting could be due to a coupling with one cod proton (olefinic) as a consequence of a possible distortion in the octahedral geometry of the complex. Such a distortion has been frequently observed in X-ray structures of Ru complexes bearing the RuH(cod) unit [10d,12]. Lastly, as observed for the precedent complexes, the $^{1}H$ and $^{13}C\{^{1}H\}$-NMR spectra of the different isomers of compound **8** contain the characteristic pair of resonances for the pyridine $CH^{6'}$ groups, indicating a *N*,*P*-chelate coordination. Note that the $^{31}P$-NMR chemical shifts of complexes **8a**–**c** ($\delta$, 38.9–52.14 ppm) are also consistent with *N*,*P*-coordination.

It can be seen that the structural difference between the pairs **I**–**II** and **III**–**IV** (Scheme 4) is the distribution of the coordinated pyridine and Cl groups, whereas the difference between the components of each pair is the relative orientation of the phosphole Ph substituent. The only hydride resonance that shows an NOE with an




Scheme 4.

*ortho* phenyl proton is that of **8b**, to which we assign structure **II** (Scheme 4). The electronic character of the ligand in the *trans* position determines mainly the chemical shift of a hydride. Thus, since similar chemical shifts are recorded for **8a** and **8b**, we propose structure **I** for **8a**. The assignment of structure **IV** for complex **8c** is based on steric considerations.

### 2.3. Protonation experiment on isomers *8a–c*

The three isomers of complex **8** bear an hydride ligand and, in order to study the influence of the structure on a proton transfer process, they were allowed to react with one equivalent of $CF_3CO_2H$ in acetone-$d_6$ solution. The addition of the acid was carried out in an NMR tube at −80 °C and the temperature was then slowly increased in the NMR probe in order to observe the different steps in the proton transfer. Comparison of the spectra at −80 °C before and after the addition shows a slight shift to lower field of the $H^{6'}$ resonance for the three isomers. For **8a** and **8b**, a shift to higher field of the hydride resonances was observed (Fig. 3). Although a general decrease in the resolution of these resonances was observed, hydride signals for **8a** and **8b** were still doublets whereas the corresponding resonance for **8c** became very broad (Fig. 3). This broadening becomes less marked as the temperature is increased and at room temperature the doublet pattern reappears. $T_{1\ min}$ values for the hydride resonances of **8a** and **8b** change only slightly after protonation (350 $ms^{-1}$ at 223 K in a 300 MHz for **8a–c** and 300 $ms^{-1}$ at 213 K after the protonation for **8a**,**b**). Unfortunately, the $T_{1\ min}$ value for **8c** after the protonation could not be accurately determined because of the broadening of this resonance, but a general inspection of the corresponding spectra indicates that it is not very different from those of the isomers **8a** and **8b**. On the basis of this information, we propose that the proton is directly transferred from the acid to the uncoordinated pyridine unit. The unsuitable orientation of this group rules out any other step in the proton transfer in **8a** and **8b** (Scheme 4) whereas in **8c** a proton–hydride interaction that leads to the broadening of the hydride signal is observed, probably as a result of the formation of a dihydrogen bridge. This interaction appears to be weak and is broken when the temperature is increased, in accordance with the low relaxation effect on the hydride and with the redefinition of the hydride as the temperature rises. Thus, we can conclude that the structures of the three isomers remain unaffected by the protonation reaction. Complex **8c** is the only one that is susceptible to undergo a second intramolecular proton transfer step due to the proximity of the uncoordinated pyridine group and of the Ru–H bond (Scheme 4). Note that we have recently demonstrated that the protonation of neutral Ru hydrides can lead to an isomerisation process that improves the formation of an intramolecular dihydrogen bridge [7d].

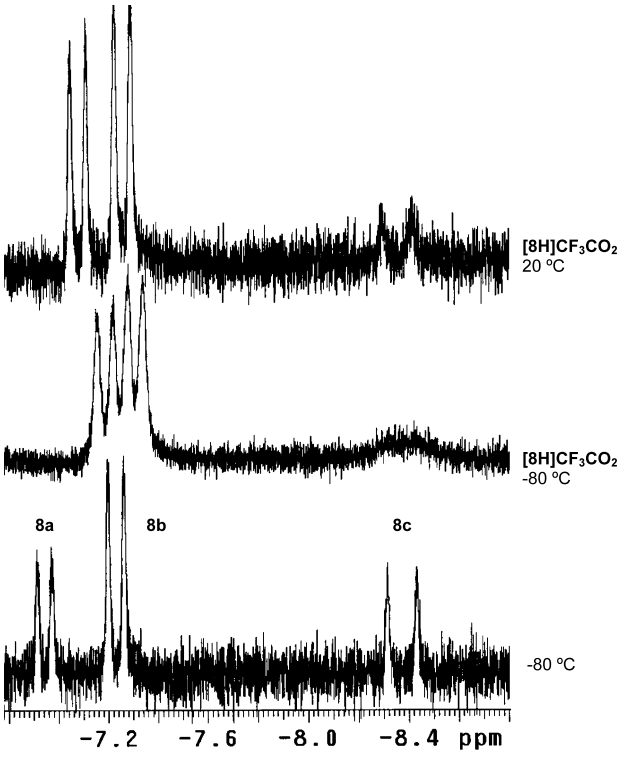



Fig. 3. High frequency region of the $^1$H-NMR spectra (hydride resonances) of **8a–c** and the respective protonated species.

## 3. Conclusions

We have prepared new families of [2,5-di(2-pyridyl)phosphole]Ru complexes with either a piano-stool or octahedral structure. In all cases, the heteroditopic N,P,N-ligand acts as an 1,4-chelate. A stereoselective coordination is observed when bulky ligands are present in the Ru-coordination sphere. Three isomers are formed in the case of the complex RuClH(cod)(NPN) and the structure of these isomers was elucidated by

NMR data. The first step in the reaction of these isomers with $CF_3CO_2H$ is the protonation of the uncoordinated pyridine group. A second step, involving the possible formation of a weak dihydrogen bridge, is also observed for only one of the isomeric forms, reflecting the influence of the structure on the formation of this type of interaction.

## 4. Experimental

### 4.1. Starting materials and general conditions

#### 4.1.1. General comments

All manipulations were carried out under an atmosphere of dry oxygen-free nitrogen using standard Schlenk techniques. Solvents were distilled from the appropriate drying agents and degassed before use. AgTfO and $AgBF_4$ were used as purchased from Aldrich. Ru starting materials were prepared as reported in the literature: $[RuCl_2(\eta^6\text{-}p\text{-cymene})]_2$ and $[RuCl_2(\eta^6\text{-}C_6Me_6)]_2$ [13], $Ru(\eta^5\text{-}C_5H_5)Cl(cod)$ and $Ru(\eta^5\text{-}C_5H_5)H(cod)$ [14] $Ru(\eta^5\text{-}C_5Me_5)Cl(cod)$ [15], $Ru(\eta^5\text{-}C_5Me_5)H(cod)$ [16], $RuCl_2(PPh_3)_3$ [17] RuClH(bpzm)(cod) [18]. 1-phenyl-2,5-di(2-pyridyl)phosphole (NPN) was prepared according with a previously reported method [4]. Elemental analyses were performed with a Thermo Quest FlashEA 1112 microanalyzer. IR spectra were recorded as KBr pellets with a Perkin–Elmer PE 883 IR spectrometer. $^1H$, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ spectra were recorded on a Varian Unity 300 spectrometer. Chemical shifts (ppm) are given relative to TMS ($^1H$ and $^{13}C$) or $H_3PO_4$ ($^{31}P$). The signals in the $^{13}C\{^1H\}$-NMR spectra are singlets unless specified. COSY spectra: standard pulse sequence with an acquisition time of 0.214 s, pulse width 10 ms, relaxation delay 1 s, number of scans 16, number of increments 512. The NOE difference spectra were recorded with the following acquisition parameters: spectral width 5000 Hz, acquisition time 3.27 s, pulse width 90°, relaxation delay 5 s, dpwr = 1, number of scans 240. For variable temperature spectra the probe temperature (±1 K) was controlled by a standard unit calibrated with a methanol reference.

#### 4.1.2. X-ray structural determination of *1a*

$C_{34}H_{35}N_2PRu$, $CF_3SO_3$, $CH_2Cl_2$, $M = 873.13$, monoclinic, $P2_1/c$, $a = 13.047(6)$, $b = 18.589(8)$, $c = 15.263(5)$ Å, $\beta = 90.69(3)°$, $V = 3701(3)$ Å$^{-3}$, $Z = 4$, $D_{calc} = 1.567$ Mg m$^{-3}$, $\lambda(Mo\text{–}K_\alpha) = 0.71073$ Å, $\mu = 7.94$ cm$^{-1}$, $F(000) = 1776$, $T = 293$ K. The sample ($0.35 \times 0.32 \times 0.28$ mm$^3$) was studied on an automatic diffractometer CAD4 NONIUS with graphite monochromatized Mo–$K_\alpha$ radiation. The cell parameters were obtained by fitting a set of 25 high-theta reflections. The data collection ($2\theta_{max} = 54°$, scan $\omega/2\theta = 1$, $t_{max} = 60$ s, range *hkl*: $h = 0/16$, $k = 0/23$, $l = -19/19$, (decay < 0.5%) gave 8400 unique reflection of which 4750 had $I > 2.0\sigma(I)$. After Lorentz and polarization corrections [19] the structure was solved with SIR-97 [20] which revealed the non hydrogen atoms of the structure (one cation, one anion and a dichloromethane molecule). After anisotropic refinement most hydrogen atoms were found in a difference map. The whole structure was refined with SHELXL-97 [21]: 437 variables, 4750 reflections with $I > 2.0\sigma(I)$, $w = 1/[\sigma^2(F_o^2) + (0.0705P)^2 + 4.19P]$ where $P = (F_o^2 + 2F_c^2)/3$ with the resulting $R_1 = 0.0567$, $wR_2 = 0.134$, $S = 1.022$, and residual $\Delta\rho < 0.089$ e A$^{-3}$. An ORTEP plot was generated with PLATON-98 [22].

### 4.2. Preparations

#### 4.2.1. *[RuCl(p-cymene)(NPN)]TfO (1)*

Phosphole NPN (0.150 g, 0.41 mmol) and AgTfO (0.105 g, 0.41 mmol) were added to a solution of [Ru(*p*-cymene)$Cl_2]_2$ (0.125 g, 0.20 mmol) in dichlorometane (20 ml). The reaction mixture was stirred at room temperature (r.t.) for 2 h. The precipitate of AgCl was filtered off and the solution obtained was evaporated to dryness. A brown solid of **1** was obtained after washing with pentane (10 ml). Yield, 252.1 mg (80%). Anal. Calc. for $C_{35}H_{35}ClF_3N_2O_3PRuS$ (787.87): C, 53.35; H, 4.48; N, 3.55. Found: C, 52.98; H, 4.48; N, 3.41%. IR (cm$^{-1}$): 1599, 1580 ($\nu CN_{phosphole}$); 1271 (TfO). **1a**: $^{31}P\{^1H\}$-NMR ($CDCl_3$): $\delta$ 65.9 (s). $^1H$-NMR ($CDCl_3$): 9.15 (d, 1H, $^3J_{HH} = 5.3$ Hz, H$^{6'}$); 8.70 (d, 1H, $^3J_{HH} = 4.7$ Hz, H$^{6'}$); 8.18–7.86 (m, Ph and pyridine); 6.00 (d, 1H, $^3J_{HH} = 6.6$ Hz, arom. C$H_{p\text{-cymene}}$); 5.90 (d, 1H, $^3J_{HH} = 6.1$ Hz, arom. C$H_{p\text{-cymene}}$); 5.81 (d, 1H, $^3J_{HH} = 5.4$ Hz, arom. C$H_{p\text{-cymene}}$); 5.41 (m, 1H, arom. C$H_{p\text{-cymene}}$); 3.21 (m, 2H, =C–C$H_2$); 2.70 (m, 2H, =C–C$H_2$); 2.10–1.81 (m, 4H, =C–C$H_2$–C$H_2$); 1.64 (3H, Me$_{p\text{-cymene}}$); 1.26 (d, $^3J_{HH} = 6.7$ Hz, 3H, CH$Me_{2,p\text{-cymene}}$); 1.21 (d, $^3J_{HH} = 7.1$ Hz, 3H, CH$Me_{2,p\text{-cymene}}$). $^{13}C\{^1H\}$-NMR ($CDCl_3$): 159.09 (s, C$^{6'}$); 149.57 (s, C$^{6'}$); 139.67 (s, C$^{4'}$); 137.75 (s, C$^{4'}$); 132.85 (d, $^2J_{CP} = 9.1$ Hz, C$_{ortho\text{-Ph}}$); 131.36 (d, $^4J_{CP} = 2.5$ Hz, C$_{para\text{-Ph}}$); 128.31 (d, $^3J_{CP} = 11.1$ Hz, C$_{meta\text{-Ph}}$); 124.76 (s, C$^{5'}$); 124.35 (d, $^3J_{CP} = 7.5$ Hz, C$^{3'}$); 124.0 (d, $^3J_{CP} = 7.5$ Hz, C$^{3'}$); 123.71 (s, C$^{5'}$); 110.11 (s, $C_{ipso}$–CH$_{3,p\text{-cymene}}$); 97.27 (s, $C_{ipso}$–$^iPr_{p\text{-cymene}}$); 94.08 (m, arom. C$H_{p\text{-cymene}}$); 93.63 (d, $^2J_{CP} = 7.5$ Hz, arom. C$H_{p\text{-cymene}}$); 88.24 (s, arom. C$H_{p\text{-cymene}}$); 84.12 (s, arom. C$H_{p\text{-cymene}}$); 31.08 (s, CHMe$_{2,p\text{-cymene}}$); 29.60 (d, $^3J_{CP} = 9.1$ Hz, =C–C$H_2$); 27.56 (d, $^3J_{CP} = 6.0$ Hz, =C–C$H_2$); 23.78 (s, CH$Me_{2,p\text{-cymene}}$); 22.68 (s, CH$Me_{2,p\text{-cymene}}$); 21.75 (s, =C–CH$_2$–C$H_2$); 20.54 (s, =C–CH$_2$–C$H_2$); 17.99 (Me$_{p\text{-cymene}}$). **1b**: $^{31}P\{^1H\}$-NMR ($CDCl_3$): $\delta$ 69.6 (s). $^1H$-NMR ($CDCl_3$, only assigned resonances): 9.61 (d, 1H, $^3J_{HH} = 5.1$ Hz, H$^{6'}$); 8.82 (d, 1H, $^3J_{HH} = 4.7$ Hz, H$^{6'}$); 6.25 (d, 1H, $^3J_{HH} = 6.3$ Hz, arom. C$H_{p\text{-cymene}}$); 6.10 (d, 1H, $^3J_{HH} =$

5.6 Hz, arom. C$H_{p\text{-cymene}}$); 1.87 (s, 3H, Me$_{p\text{-cymene}}$); 1.10 (d, $^3J_{HH}$ = 6.7 Hz, 3H, CH$Me_{2,p\text{-cymene}}$); 0.94 (d, $^3J_{HH}$ = 7.1 Hz, 3H, CH$Me_{2,p\text{-cymene}}$).

#### 4.2.2. [RuCl(p-cymene)(NPN)]$BF_4$ (2)

Phosphole NPN (0.150 g, 0.41 mmol) and $AgBF_4$ (0.079 g, 0.41 mmol) were added to a solution of [Ru(*p*-cymene)$Cl_2$]$_2$ (0.125 g, 0.20 mmol) in dichloromethane (20 ml). The reaction mixture was stirred at r.t. for 1 h. The precipitate of AgCl was filtered off and the obtained solution was evaporated to dryness. A brown solid of **2** was obtained after washing with pentane (2 × 10 ml). Yield, 238.0 mg (82%). Anal. Calc. for $C_{34}H_{35}BClF_4N_2PRu$ (725.67): C, 56.27; H, 4.82; N, 3.86. Found: C, 56.55; H, 4.76; N, 3.96%. IR (cm$^{-1}$): 1570 ($\nu$CN$_{phosphole}$); 1055 ($BF_4$). **2a**: $^{31}P\{^1H\}$-NMR ($CDCl_3$): $\delta$ 65.6 (s). $^1$H-NMR ($CDCl_3$): 9.16 (d, 1H, $^3J_{HH}$ = 5.2 Hz, H$^{6'}$); 8.70 (d, 1H, $^3J_{HH}$ = 4.2 Hz, H$^{6'}$); 7.95 –7.53 (m, Ph and pyridine); 5.97 (d, 1H, $^3J_{HH}$ = 6.1 Hz, arom. C$H_{p\text{-cymene}}$); 5.92 (d, 1H, $^3J_{HH}$ = 5.6 Hz, arom. C$H_{p\text{-cymene}}$); 5.78 (d, 1H, $^3J_{HH}$ = 5.6 Hz, arom. C$H_{p\text{-cymene}}$); 5.47 (m, 1H, arom. C$H_{p\text{-cymene}}$); 2.47 (sept., 1H, C$H$Me$_{2,p\text{-cymene}}$); 3.22–2.73 (m, 4H, =C–C$H_2$); 1.95–1.84 (m, 4H, =C–CH$_2$–C$H_2$); 1.61 (3H, Me$_{p\text{-cymene}}$); 1.22 (d, $^3J_{HH}$ = 7.1 Hz, 3H, CH$Me_{2,p\text{-cymene}}$); 1.27 (d, $^3J_{HH}$ = 6.8 Hz, 3H, CH$Me_{2,p\text{-cymene}}$). $^{13}C\{^1H\}$-NMR ($CDCl_3$): 159.54 (s, C$^{6'}$); 150.00 (s, C$^{6'}$); 140.00 (s, C$^{4'}$); 137.00 (s, C$^{4'}$); 133.10 (d, $^2J_{CP}$ = 8.1 Hz, C$_{ortho\text{-Ph}}$); 131.98 (d, $^4J_{CP}$ = 2 Hz, C$_{para\text{-Ph}}$); 128.12 (d, $^3J_{CP}$ = 10.0 Hz, C$_{meta\text{-Ph}}$); 125.15 (s, C$^{5'}$); 124.10 (s, C$^{5'}$); 123.80 (d, $^3J_{CP}$ = 7.5 Hz, C$^{3'}$); 123.44 (d, $^3J_{CP}$ = 7.5 Hz, C$^{3'}$); 110.85 (s, $C_{ipso}$–CH$_{3,p\text{-cymene}}$); 97.15 (s, $C_{ipso}$–$^i$Pr$_{p\text{-cymene}}$); 94.75 (m, C$H_{p\text{-cymene}}$); 94.15 (d, $^2J_{CP}$ = 7.5 Hz, C$H_{p\text{-cymene}}$); 87.81 (s, C$H_{p\text{-cymene}}$); 83.68 (s, C$H_{p\text{-cymene}}$); 31.5 (s, C$H$Me$_{2,p\text{-cymene}}$); 29.95 (d, $^3J_{CP}$ = 10.0 Hz, =C–C$H_2$); 27.84 (d, $^3J_{CP}$ = 7.5 Hz, =C–C$H_2$); 24.12 (s, CH$Me_{2,p\text{-cymene}}$); 23.00 (s, =C–CH$_2$–C$H_2$); 22.00 (s, =C–CH$_2$–C$H_2$); 21.22 (s, CH$Me_{2,p\text{-cymene}}$); 18.36 (s, Me$_{p\text{-cymene}}$). **2b**: $^{31}P\{^1H\}$-NMR ($CDCl_3$): $\delta$ 69.6 (s). $^1$H-NMR ($CDCl_3$, only assigned resonances): 9.59 (d, 1H, $^3J_{HH}$ = 5.1 Hz, H$^{6'}$); 8.70 (d, 1H, $^3J_{HH}$ = 4.3 Hz, H$^{6'}$); 6.27 (d, 1H, $^3J_{HH}$ = 6.8 Hz, C$H_{p\text{-cymene}}$); 6.05 (d, 1H, $^3J_{HH}$ = 6.3 Hz, C$H_{p\text{-cymene}}$); 5.85 (d, 1H, $^3J_{HH}$ = 6.3 Hz, C$H_{p\text{-cymene}}$); 1.86 (3H, Me$_{p\text{-cymene}}$); 1.07 (d, $^3J_{HH}$ = 6.8 Hz, 3H, CH$Me_{2,p\text{-cymene}}$); 0.96 (d, $^3J_{HH}$ = 7.1 Hz, 3H, CH$Me_{2,p\text{-cymene}}$).

#### 4.2.3. [RuCl($C_6Me_6$)(NPN)]TfO (3)

Phosphole NPN (0.165 g, 0.45 mmol) and AgTfO (0.116 g, 0.45 mmol) were added to a solution of [Ru($C_6Me_6$)$Cl_2$]$_2$ (0.150 g, 0.22 mmol) in dichlorometane (20 ml). The reaction mixture was stirred at r.t. for 2 h. The precipitate of AgCl was filtered off and the obtained solution was evaporated to dryness. A orange solid of **3** was obtained after washing with pentane (2 × 10 ml). Yield, 305.1 mg (85%). Anal. Calc. for $C_{37}H_{39}ClF_3N_2O_3PRuS$ (815.89): C, 54.46; H, 4.82; N, 3.43. Found: C, 54.64; H, 4.92; N, 3.23%. $^{31}P\{^1H\}$-NMR ($CDCl_3$): $\delta$ 61.2 (s). $^1$H-NMR ($CDCl_3$): 8.63 (d, 1H, $^3J_{HH}$ = 5.4 Hz, H$^{6'}$); 8.42 (d, 1H, $^3J_{HH}$ = 4.6 Hz, H$^{6'}$); 7.98–7.54 (m, Ph and pyridine); 3.32–2.81 (m, 4H, =C–C$H_2$); 1.85–2.20 (m, 4H, =C–CH$_2$–C$H_2$); 1.82 (d, $^4J_{HP}$ = 0.9 Hz, 18H, $C_6Me_6$). $^{13}C\{^1H\}$-NMR ($CDCl_3$): 155.00 (s, C$^{6'}$); 150.00 (s, C$^{6'}$); 140.85 (s, C$^{4'}$); 139.37 (s, C$^{4'}$); 133.52 (d, $^2J_{CP}$ = 9.0 Hz, C$_{ortho\text{-Ph}}$); 131.98 (d, $^4J_{CP}$ = 2.6 Hz, C$_{para\text{-Ph}}$); 127.35 (d, $^3J_{CP}$ = 10.6 Hz, C$_{meta\text{-Ph}}$); 125.71 (s, C$^{5'}$); 124.10 (s, C$^{5'}$); 123.80 (d, $^3J_{CP}$ = 7.4 Hz, C$^{3'}$); 123.44 (d, $^3J_{CP}$ = 7.4 Hz, C$^{3'}$); 98.74 (s, $C_6$Me$_6$); 29.95 (d, $^3J_{CP}$ = 6.5 Hz, =C–C$H_2$); 27.41 (d, $^3J_{CP}$ = 8.3 Hz, =C–C$H_2$); 22.21 (s, =C–CH$_2$–C$H_2$); 21.90 (s, =C–CH$_2$–C$H_2$); 15.42 (s, $C_6Me_6$).

#### 4.2.4. Ru($C_5H_5$)Cl(NPN) (4)

Phosphole NPN (0.149 g, 0.40 mmol) was added to a solution of Ru($C_5H_5$)Cl(cod) (0.125 g, 0.40 mmol) in THF (20 ml). The reaction mixture was stirred at 40 °C for 2 h. After evaporation to dryness and washing with pentane (10 ml), **4** was obtained as a brown solid. Yield, 182.3 mg (80%). Anal. Calc. for $C_{29}H_{26}ClN_2PRu$ (569.81): C, 61.12; H, 4.56; N, 4.91. Found: C, 61.07; H, 4.64; N, 4.86%. IR (cm$^{-1}$): 1560, 1525 ($\nu$CN$_{phosphole}$). $^{31}P\{^1H\}$-NMR ($(CD_3)_2CO$): $\delta$ 82.2 (s, **4b**); 68.6 (s, **4a**); $^1$H-NMR ($(CD_3)_2CO$): 9.53 (d, 1H, $^3J_{HH}$ = 5.6 Hz, H$^{6'}$, **4b**); 9.34 (d, 1H, $^3J_{HH}$ = 5.6 Hz, H$^{6'}$, **4b**); 8.65 (m, 2H, H$^{6'}$, **4a**); 7.9–6,8 (m, Ph and pyridine, **4a** and **4b**); 4.6 (s, $C_5H_5$, **4a**); 4.1 ($C_5H_5$, **4b**); 3.32–2.80 (m, 4H, =C–C$H_2$, **4a** and **4b**); 2.05–1.61 (m, 4H, =C–CH$_2$–C$H_2$, **4a** and **4b**). $^{13}C\{^1H\}$-NMR ($(CD_3)_2CO$): 159.29 (s, C$^{6'}$, **4b**); 159.27 (s, C$^{6'}$, **4a**); 150.31 (s, C$^{6'}$, **4b**); 150.30 (s, C$^{6'}$, **4a**); 137.20 (s, 2C), 135.36 (s) and 134.34 (s) (C$^{4'}$, **4a** and **4b**); 134.25 (d, $^2J_{CP}$ = 11.0 Hz, C$_{ortho\text{-Ph}}$, **4b**); 132.84 (d, $^2J_{CP}$ = 11.0 Hz, C$_{ortho\text{-Ph}}$, **4a**); 130.26 (d, $^4J_{CP}$ = 1.9 Hz, C$_{para\text{-Ph}}$, **4a** and **4b**); 129.02 (d, $^3J_{CP}$ = 10.0 Hz, C$_{meta\text{-Ph}}$, **4a**); 128.18 (d, $^3J_{CP}$ = 10.1 Hz, C$_{meta\text{-Ph}}$, **4b**); 125.04 (d, $^3J_{CP}$ = 7.0 Hz, C$^{3'}$, **4a**); 124.91 (d, $^3J_{CP}$ = 8.0 Hz, C$^{3'}$, **4a**); 124.87 (d, $^3J_{CP}$ = 7.0 Hz, C$^{3'}$, **4b**); 122.32 (d, $^3J_{CP}$ = 7.0 Hz, C$^{3'}$, **4b**); 122.17 (s), 122.12 (s), 121.85 (s) and 120.81 (s) (C$^{5'}$, **4a** and **4b**); 75.44 (s, $C_5H_5$, **4a**); 73.45 (s, $C_5H_5$, **4b**); signal of =C–C$H_2$ of **4a** must be overlapped with the solvent signal; 27.40 (2C, =C–C$H_2$, **4b**) 23.85 (2C, =C–CH$_2$–C$H_2$, **4a**); 23.12 (2C, =C–CH$_2$–C$H_2$, **4b**).

#### 4.2.5. Ru($C_5Me_5$)Cl(NPN) (5)

Phosphole NPN (0.208 g, 0.57 mmol) was added to a solution of Ru($C_5Me_5$)Cl(cod) (0.215 g, 0.57 mmol) in THF (20 ml). The reaction mixture was stirred at 40 °C for 3 h. After evaporation to dryness and washing with pentane (10 ml), **5** was obtained as a brown solid. Yield, 310.0 mg (85%). Anal. Calc. for $C_{34}H_{36}ClN_2PRu$ (639.86): C, 63.82; H, 5.62; N, 4.37. Found: C, 64.01; H, 5.64; N, 4.42%. IR (cm$^{-1}$): 1555, 1510

($\nu CN_{phosphole}$). $^{31}P\{^1H\}$-NMR ($CDCl_3$): $\delta$ 64.9 (s). $^1H$-NMR ($CDCl_3$): 8.87 (d, 1H, $^3J_{HH} = 4.8$ Hz, $H^{6'}$); 8.57 (d, 1H, $^3J_{HH} = 3.9$ Hz, $H^{6'}$); 7.65–6.98 (m, Ph and pyridine); 3.23 (m, 2H, =C–C$H_2$); 2.71 (m, 2H, =C–C$H_2$); 2.01–2.23 (m, 4H, =C–$CH_2$–C$H_2$); 1.30 (15H, $C_5Me_5$). $^{13}C\{^1H\}$-NMR ($CDCl_3$): 156.0 (s, $C^{6'}$); 149.27 (s, $C^{6'}$); 136.0 (s, $C^{4'}$); 135.0 (s, $C^{4'}$); 134.09 (bs, $C_{ortho\text{-}Ph}$); 129.56 (bs, $C_{para\text{-}Ph}$); 127.97 (bs, $C_{meta\text{-}Ph}$); 124.36 (s), 122.11 (bs); 121.35 (bs) and 120.91 (s) ($C^{5'}$ and $C^{3'}$); 83.19 (bs, $C_5Me_5$); 30.63 (bs, =C–$CH_2$); 27.57 (bs, =C–$CH_2$); 23.51 (s, =C–$CH_2$–$CH_2$); 22.93 (s, =C–$CH_2$–$CH_2$); 9.44 (s, $C_5Me_5$).

#### 4.2.6. *Ru($C_5Me_5$)($\sigma^1$-$C_8H_{13}$)(NPN) (**6**)*

Phosphole NPN (0.133 g, 0.36 mmol) was added to a solution of Ru($C_5Me_5$)H(cod) (0.125 g, 0.36 mmol) in thf (20 ml). The reaction mixture was stirred at r.t. for 3 h. After evaporation to dryness and washing with pentane (10 ml), **6** was obtained as a red solid. Yield, 167.0 mg (65%). Anal. Calc. for $C_{42}H_{49}N_2PRu$ (713.49): C, 70.70; H, 6.87; N, 3.92 Found: C, 70.27; H, 6.63; N, 4.01%. IR ($cm^{-1}$): 1563, 1599 ($\nu CN_{phosphole}$). $^{31}P\{^1H\}$-NMR ($(CD_3)_2CO$): $\delta$ 117.2 (s). $^1H$-NMR ($C_6D_6$): 8.63 (d, 1H, $^3J_{HH} = 6.2$ Hz, $H^{6'}$); 7.54 (d, 1H, $^3J_{HH} = 5.6$ Hz, $H^{6'}$); 8.0–7.5 (m, Ph and pyridine); 5.31 (m, 1H, –CH–C$H$=$CH_{cyclooct}$); 4.22 (1H, m, $^3J_{HP} = 32.7$ Hz, Ru–C$H$–CH=$_{cyclooct}$); 3.25 (m, 1H, –CH–CH=C$H_{cyclooct}$); 2.67 (m, 4H, =C–C$H_2$); 2.24–2.0 (m, 4H, =C–$CH_2$–C$H_2$); 2.32–1.22 ($CH_{2,cyclooct}$); 1.35 (15H, $C_5Me_5$). $^{13}C\{^1H\}$-NMR ($C_6D_6$): 156.87 (s, $C^{6'}$); 148.29 (s, $C^{6'}$); 133.97 (s, $C^{4'}$); 133.48 (d, $^2J_{CP} = 9.5$ Hz, $C_{ortho\text{-}Ph}$); 126.5 (m, $C_{para\text{-}Ph}$ or $C_{meta\text{-}Ph}$, the other signal must be overlapped with that of the solvent);131.74 (s, $C^{4'}$); 126.42 (s, 2C, $C^{5'}$); 120.56 (2C, d, $^2J_{CP} = 3.0$ Hz, $C^{3'}$); 112.53 (d, $^3J_{CP} = 15$ Hz, –C$H$=CH–$_{cyclooct}$) 104.34 (–CH=CH–$_{cyclooct}$); 91.49 (s, $C_5Me_5$); 48.87 (d, $^2J_{CP} = 15.1$ Hz, Ru–C$H$–CH=$_{cyclooct}$); 30.5–23.4 ($CH_{2,phosphole} + CH_{2,cyclooct}$); 8.40 ($C_5Me_5$).

#### 4.2.7. *$RuCl_2$(NPN)$_2$ (**7**)*

Phosphole NPN (0.161 g, 0.44 mmol) was added to a suspension of $RuCl_2(PPh_3)_3$ (0.210 g, 0.22 mmol) in dichloromethane (20 ml). The mixture was stirred at 40 °C for 3 h. After evaporation to dryness and washing with diethylether (2 × 10 ml), **7** was obtained as a brown solid. Yield, 179.9 mg (90%). Anal. Calc. for $C_{48}H_{42}Cl_2N_4P_2Ru$ (908.45): C, 63.46; H, 4.62; N, 6.16 Found: C, 63.51; H, 4.94; N, 5.89%. IR ($cm^{-1}$): 1595, 1583 ($\nu CN_{phosphole}$). $^{31}P\{^1H\}$-NMR ($CDCl_3$): $\delta$ 79.8 (d, $^2J_{PP} = 33.6$ Hz), 75.6 (d). $^1H$-NMR ($CDCl_3$): 10.26 (d, $H^{6'}$), 9.92 (d, $H^{6'}$) and 8.57 (d, 2H, $H^{6'}$); 8.20–7.52 (m, Ph and pyridine); 3.44–1.24 (m, 16H, C–C$H_2$–C$H_2$).

#### 4.2.8. *RuClH(cod)(NPN) (**8**)*

Phosphole NPN (0.116 g, 0.31 mmol) was added to a solution of RuClH(cod)(bpzm) (0.124 g, 0.31 mmol) in thf (25 ml). The mixture was stirred at r.t. for 5 h. After evaporation to dryness and washing with hexane (2 × 10 ml), **8** was obtained as a red solid. Yield, 142.7 (75%). Anal. Calc. for $C_{32}H_{34}ClN_2PRu$ (613.84): C, 62.61; H, 5.54; N, 4.56 Found: C, 62.47; H, 6.01; N, 4.66%. IR ($cm^{-1}$): 1595, 1578 ($\nu CN_{phosphole}$); 2006 ($\nu$RuH). $^{31}P\{^1H\}$-NMR ($(CD_3)_2CO$): $\delta$ **8a**: 52.14 (s); **8b**: 44.2 (s); **8c**: 38.9 (s). $^1H$-NMR ($(CD_3)_2CO$): 9.32 (d, 1H, $^3J_{HH} = 5.1$ Hz, $H^{6'}$, **8b**); 8.61 (d, 1H, $^3J_{HH} = 3.9$ Hz, $H^{6'}$, **8a** or **8c**); 8.58 (d, 1H, $^3J_{HH} = 5.1$ Hz, $H^{6'}$, **8a** or **8c**); 8.37 (d, $^3J_{HH} = 4.7$ Hz, 1H, $H^{6'}$, **8b**); 8.35 (d, $^3J_{HH} = 5.7$ Hz, 1H, $H^{6'}$, **8a** or **8c**); 8.09 (d, 1H, $^3J_{HH} = 5.9$ Hz, $H^{6'}$, **8a** or **8c**); 8.06–7.0 (m, Ph and pyridine, **8a**, **8b** and **8c**); 4.67 (m, –C$H$=$_{cod}$, **8a**); 4.45 (m, –C$H$=$_{cod}$, **8b**); 4.37 (m, –C$H$=$_{cod}$, **8b**); 4.05 (–C$H$=$_{cod}$, **8a** or **8c**); 3.73 (–C$H$=$_{cod}$, **8c**); 3.33 (–C$H$=$_{cod}$, **8c**); 2.80 ($CH_{2,cod}$, **8a**); 3.41–3.0 (m, 4H, =C–C$H_{2,phosphole}$); 2.95–1.57 (C$H_{2,cod}$); 1.64–2.1 (m, 4H, =C–$CH_2$–C$H_{2,phosphole}$), −6.94 (**8a**, Ru$H$); −7.04 (**8b**, Ru$H$); −8.16 (**8c**, Ru$H$). $^{13}C\{^1H\}$-NMR ($(CD_3)_2CO$): **8b**: 154.98 (s, $C^{6'}$); 154.51 (s, $C^{6'}$); 145.36 (s, $C^{4'}$); 141.80 (s, $C^{4'}$); 138.04 (d, $^2J_{CP} = 11.5$ Hz, $C_{ortho\text{-}Ph}$); 135.16 (d, $^4J_{CP} = 3.0$ Hz, $C_{para\text{-}Ph}$); 133.40 (d, $^3J_{CP} = 9.4$ Hz, $C_{meta\text{-}Ph}$); 129.93 (d, $^3J_{CP} = 7.5$ Hz, $C^{3'}$); 127.15 (d, $^3J_{CP} = 6.0$ Hz, $C^{3'}$); 126.47 (s, $C^{5'}$); 126.53 (s, $C^{5'}$); 88.69 (d, $^2J_{CP} = 17.2$ Hz, =C$H_{cod}$); 84.49 (d, $^2J_{CP} = 9.0$ Hz, =C$H_{cod}$); 73.56 (s, =C$H_{cod}$); 72.11 (s, =C$H_{cod}$); 43.13 (d, $^3J_{CP} = 3.5$, –C$H_{2,cod}$); 38.33 (s, –C$H_{2,cod}$); 37.68 (s, –C$H_{2,cod}$); 35.15 (s, –C$H_{2,cod}$); 32.50 (d, $^3J_{CP} = 5.5$ Hz, =C–C$H_{2,phosphole}$); 28.36 (s, =C–$CH_2$–C$H_{2,phosphole}$); 27.69 (s, =C–$CH_2$–C$H_{2,phosphole}$). **8a** and **8c** (only resonances assigned): 159.46 (s, $C^{6'}$); 158.00 (s, $C^{6'}$); 154.77 (s, $C^{6'}$); 154.67 (s, $C^{6'}$); 147.76 (s, $C^{4'}$); 142.71 (s, $C^{4'}$); 142.11 (s, $C^{4'}$); 138.87 (d, $^2J_{CP} = 9.5$ Hz, $C_{ortho\text{-}Ph}$); 138.78 (d, $^2J_{CP} = 10.5$ Hz, $C_{ortho\text{-}Ph}$); 134.41 (d, $^4J_{CP} = 2.0$ Hz, $C_{para\text{-}Ph}$); 132.83 (d, $^3J_{CP} = 9.7$ Hz, $C_{meta\text{-}Ph}$); 132.27 (d, $^3J_{CP} = 9.7$ Hz, $C_{meta\text{-}Ph}$); 128.80 (d, $^3J_{CP} = 8.3$ Hz, $C^{3'}$); 128.48 (s, $C^{5'}$); 127.92 (s, $C^{5'}$); 127.84 (s, $C^{5'}$); 127.65 (d, $^3J_{CP} = 8.0$ Hz, $C^{3'}$); 90.34 (d, $^2J_{CP} = 16.5$ Hz, =C$H_{cod}$); 94.24–93.35 (3C, =C$H_{cod}$); 75.77 (s, =C$H_{cod}$); 74.44 (s, =C$H_{cod}$); 40.62 (d, $^3J_{CP} = 3.2$ Hz, –C$H_{2,cod}$); 41.11–27.45 (–C$H_{2,cod}$ + =C–C$H_{2,phosphole}$ + =C–$CH_2$=C$H_{2,phosphole}$).

#### 4.2.9. *Protonation of **8a–c***

To a solution of **8a–c** (0.015 g, 0.025 mmol) in $(CD_3)_2CO$ at −80 °C prepared in a NMR tube, 1.9 μl (0.025 mmol) of $CF_3COOH$ were added. The tube was introduced in the NMR probe previously cooled at −80 °C. The $^1H$-NMR spectra were registered at different temperatures.

## 5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic

Data Centre, CCDC no. 185566. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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