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Synthesis and characterization of iron and ruthenium complexes bearing P–N ligands based on 8-hydroxyquinoline

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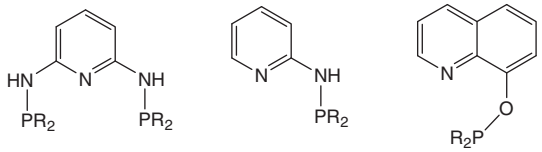
ABSTRACT

The synthesis of bidentate aminophosphine ligands (PN^{quin}) based on 8-hydroxyquinoline is described. These ligands react with *cis*-$Fe(CO)_4Br_2$ to give selectively octahedral complexes of the type *cis*,*cis*-$Fe(PN^{quin})(CO)_2Br_2$. There is only one isomer formed where the two CO and the two bromide ligands adopt a *cis* configuration. The reaction of $[RuCp(CH_3CN)_3]PF_6$ with PN^{quin} ligands affords the halfsandwich complexes $[RuCp(PN^{quin})(CH_3CN)]PF_6$ in high isolated yields. Likewise, treatment of $[Ru(\eta^6\text{-}p\text{-cymene})(\mu\text{-}Cl)Cl]_2$ with PN^{quin} in the presence of $AgCF_3SO_3$ affords halfsandwich complexes of the type $[Ru(\eta^6\text{-}p\text{-cymene})(PN^{quin})Cl]CF_3SO_3$. All ligands and complexes are characterized by NMR and IR spectroscopy. The X-ray structure of representative compounds is reported. In addition, the relative stability of isomeric structures and conformers of $Fe(PN^{quin}\text{-Ph})(CO)_2Br_2$ is studied by means of DFT calculations.

1. Introduction

The construction of phosphorus–nitrogen and phosphorous–oxygen bonds, in contrast to phosphorus–carbon bonds, is generally achieved by rather simple synthetic procedures, i.e., primary or secondary amines or primary alcohols are reacted with R_2PCl in the presence of base. R_2PCl may contain both bulky and/or electron-rich dialkyl phosphines as well as P–O and P–N bond containing achiral and chiral phosphite units derived from diols, aminoalcohols, and diamines [1]. It is thus not surprising that in recent years such compounds have attracted increasing attention as ligands because of their bonding versatility with metal centers allowing them to form a large number of complexes with interesting and unique properties [2].

In this context, we have recently focused on the synthesis of a series of tridentate (pincer) PNP ligands (**I**) [3] and bidentate PN^{py} ligands (**II**) [4,5] in which an amine acts as spacer between the aromatic pyridine ring and the phosphines. With PNP ligands we have thus far studied their reactivity towards different transition metal fragments which has resulted in the preparation of a range of new pincer complexes, including the first heptacoordinated molybdenum pincer complexes [3a], various iron complexes capable of acting as CO sensors [3d], and several pentacoordinated nickel complexes [6]. As PN^{py} ligands are concerned, the synthesis of a series of square planar Ni(II) and Pd(II) complexes [4] and octahedral molybdenum complexes of the type $Mo(PN^{py})(CO)_4$ [5] have been reported. Woollins and co-workers described the synthesis of several Pd, Pt, and Au complexes featring the PN^{py} ligand PPh_2NHpy [7].



I (PNP) **II** (PN^{py}) **III** (PN^{quin})

In the present work we extend our ongoing studies on PN complexes and describe the synthesis of several iron(II) and ruthenium(II) complexes of the types *cis*,*cis*-$Fe(PN^{quin})(CO)_2Br_2$, $[RuCp(PN^{quin})(CH_3CN)]PF_6$, and $[Ru(\eta^6\text{-}p\text{-cymene})(PN^{quin})Cl]CF_3SO_3$ featuring phosphinito quinoline ligands PN^{quin} (**III**). Some ligands of the type **III** and Ru(II), Ni(II), and Pd(II) complexes thereof have been already described in the recent literature [8–12].

2. Experimental

2.1. General procedure

All manipulations were performed under an inert atmosphere of argon by using Schlenk techniques. The solvents were purified

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according to standard procedures [13]. *cis*-$Fe(CO)_4Br_2$ [14] $[RuCp(CH_3CN)_3]PF_6$ [15], and $[Ru(\eta^6\text{-}p\text{-cymene})(\mu\text{-Cl})Cl]_2$ [16] were prepared according to the literature. The deuterated solvents were purchased from Aldrich and dried over 4 Å molecular sieves. ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker AVANCE-250 spectrometer and were referenced to $SiMe_4$ and H_3PO_4 (85%), respectively.

2.2. Syntheses

2.2.1. PN^{quin}-Ph (**1a**)

To a solution of 8-hydroxyquinoline (1.6 g, 11.1 mmol) and triethylamine (1.5 mL, 11.1 mmol) in toluene (50 mL) PPh_2Cl (2.0 mL, 11.1 mmol) was added dropwise at 0 °C and the mixture was then stirred for additional 3 h at 80 °C. After that the solution was filtered and the solvent was removed under vacuum to give **1a** as a pale yellow oil. Yield: 2.7 g (74%). *Anal.* Calc. for $C_{21}H_{16}NOP$: C, 76.59; H, 4.90; N, 4.25. Found: C, 76.70; H, 4.81; N, 4.29%. ^1H NMR (δ, $CDCl_3$, 20 °C): 8.96 (dd, J = 1.5 Hz, J = 4.3 Hz, 1H, quin), 8.13 (dd, J = 1.8 Hz, J = 8.2 Hz, 1H, quin), 7.87–7.81 (m, 4H, quin), 7.52–7.26 (m, 10H, Ph). ^{13}C NMR (δ, $CDCl_3$, 20 °C): 149.4 (quin), 147.9 (quin), 141.8 (d, J = 18.4 Hz, Ph), 135.8 (quin), 130.8 (d, J = 22.4 Hz, Ph), 129.6 (Ph), 128.4 (d, J = 6.9 Hz, Ph), 126.5 (quin), 122.1 (quin), 121.5 (quin), 117.9 (quin), 117.3 (d, J = 13.4 Hz, quin), 110.0 (quin). ^{31}P NMR (δ, $CDCl_3$, 20 °C): 118.4.

2.2.2. PN^{quin}-iPr (**1b**)

This ligand has been prepared analogously to **1a** with 8-hydroxyquinoline (1.1 g, 7.6 mmol), *i*Pr_2PCl (1.2 mL, 7.6 mmol) and triethylamine (1.1 mL, 7.6 mmol) as the starting materials. Yield: 1.4 g (69%). *Anal.* Calc. for $C_{15}H_{20}NOP$: C, 68.95; H, 7.71; N, 5.36. Found: C, 69.04; H, 7.80; N, 5.25%. ^1H NMR (δ, $CDCl_3$, 20 °C): 8.92 (dd, J = 1.5 Hz, J = 4.0 Hz, 1H, quin), 8.07 (dd, J = 1.5 Hz, J = 8.2 Hz, 1H, quin), 7.55–7.41 (m, 1H, quin), 7.39–7.32 (m, 3H, quin), 2.17 (m, J = 7.2 Hz, 2H, C*H*$(CH_3)_2$), 1.30 (dd, J = 7.0 Hz, J = 11.3 Hz, 6H, CH$(CH_3)_2$), 1.14 (dd, J = 7.0 Hz, J = 15.9 Hz, 6H, CH$(CH_3)_2$). ^{13}C NMR (δ, $CDCl_3$, 20 °C): 149.3 (quin), 147.8 (quin), 141.5 (quin), 135.7 (quin), 126.5 (quin), 121.3 (quin), 120.8 (quin), 116.3 (d, J = 18.8 Hz, quin), 109.9 (quin), 28.9 (*C*H$(CH_3)_2$), 28.6 (*C*H$(CH_3)_2$), 17.8 (d, J = 23.4 Hz, CH$(CH_3)_2$), 17.5 (d, J = 11.1 Hz, CH$(CH_3)_2$). ^{31}P NMR (δ, $CDCl_3$, 20 °C): 158.2.

2.2.3. PN^{quin}-BIPOL (**1c**)

This ligand has been prepared analogously to **1a** with 8-hydroxyquinoline (1.0 g, 6.9 mmol), 2-chlorodibenzo[d,f][1,3,2] dioxaphosphepine (1.7 g, 6.9 mmol) and triethylamine (1.0 mL, 6.9 mmol) as the starting materials. Yield: 2.0 g (82%). *Anal.* Calc. for $C_{21}H_{14}NO_3P$: C, 70.20; H, 3.92; N, 3.90. Found: C, 70.11; H, 3.80; N, 3.89%. ^1H NMR (δ, $CDCl_3$, 20 °C): 9.05 (dd, J = 1.2 Hz, J = 4.3 Hz, 1H, quin), 8.17 (dt, J = 1.2 Hz, J = 7.3 Hz, 1H, quin), 7.57–7.28 (m, 12H, quin and Ph). ^{13}C NMR (δ, $CDCl_3$, 20 °C): 149.6 (d, J = 4.6 Hz, quin), 149.3 (Ph), 149.1 (quin), 147.9 (quin), 135.9 (quin), 131.5 (d, J = 3.4 Hz, Ph), 129.9 (d, J = 1.2 Hz, Ph), 129.1 (Ph), 128.3 (quin), 126.8(quin), 125.2 (Ph), 122.5 (d, J = 1.2 Hz, Ph), 121.8 (quin), 118.7 (d, J = 4.0 Hz, quin), 110.0 (quin). ^{31}P NMR (δ, $CDCl_3$, 20 °C): 142.1.

2.2.4. cis,cis-Fe(PN^{quin}-Ph)$(CO)_2Br_2$ (**2a**)

To a solution of *cis*-$Fe(CO)_4Br_2$ (318 mg, 0.97 mmol) in toluene (15 mL) **1a** (318 mg, 0.97 mmol) was added whereupon an immediate evolution of CO was observed. Once the CO evolution subsided the reaction mixture was stirred at room temperature for 1 h and the solvent was decanted from the resulting brown solid, which was washed twice with Et_2O and dried under vacuum. Yield: 478 mg (82%). *Anal.* Calc. for $C_{23}H_{16}Br_2FeNO_3P$: C, 45.96; H, 2.68; N, 2.33. Found: C, 45.09; H, 2.70; N, 2.41%. ^1H NMR (δ, acetone-d_6, 20 °C): 10.57 (s, 1H, quin), 8.80 (s, 1H, quin), 7.88–7.73 (m, 10H, Ph), 7.35–7.18 (m, 4H, quin). ^{13}C NMR (δ, acetone-d_6, 20 °C): 212.0 (d, J = 24.2 Hz, *C*O), 211.2 (d, J = 25.0 Hz, *C*O). All other resonances are not informative and have not been assigned. ^{31}P NMR (δ, acetone-d_6, 20 °C): 172.3. IR (attenuated total reflection (ATR), cm^{-1}): 2003 (ν_{CO}), 2061 (ν_{CO}).

2.2.5. cis,cis-Fe(PN^{quin}-iPr)$(CO)_2Br_2$ (**2b**)

This complex was prepared analogously to **2a** with **1b** (225 mg, 0.86 mmol) and *cis*-$Fe(CO)_4Br_2$ (282 mg, 0.86 mmol) as the starting materials. Yield: 408 mg (89%). *Anal.* Calc. for $C_{17}H_{20}Br_2FeNO_3P$: C, 38.31; H, 3.78; N, 2.63. Found: C, 38.29; H, 3.70; N, 2.69%. ^1H NMR (δ, acetone-d_6, 20 °C): 10.51 (s, 1H, quin), 8.78 (d, J = 5.5 Hz, 1H, quin), 8.00 (s, 1H, quin), 7.83–7.79 (m, 3H, quin), 3.07 (s, 1H, C*H*$(CH_3)_2$), 2.86 (s, 1H, C*H*$(CH_3)_2$), 1.59 (dd, J = 3.1 Hz, J = 15.5 Hz, CH$(CH_3)_2$), 1.44 (dd, J = 4.1 Hz, J = 18.4 Hz, CH$(CH_3)_2$), 1.25 (dd, J = 5.0 Hz, J = 13.4 Hz, CH$(CH_3)_2$), 0.68 (dd, J = 5.9 Hz, J = 16.0 Hz, CH$(CH_3)_2$). ^{13}C NMR (δ, acetone-d_6, 20 °C): 213.8 (d, J = 21.8 Hz, *C*O), 211.6 (d, J = 23.5 Hz, *C*O), 164.1 (quin), 147.8 (d, J = 5.2 Hz, quin), 141.5 (quin), 138.6 (quin), 130.1 (quin), 128.9 (quin), 125.5 (quin), 122.8 (quin), 122.1 (quin), 34.0 (d, J = 16.1 Hz, *C*H$(CH_3)_2$), 31.8 (d, J = 29.9 Hz, *C*H$(CH_3)_2$), 17.5 (CH$(CH_3)_2$), 17.2 (CH$(CH_3)_2$), 16.9 (CH$(CH_3)_2$), 15.0(CH$(CH_3)_2$). ^{31}P NMR (δ, acetone-d_6, 20 °C): 214.9. IR (ATR, cm^{-1}): 1998 (ν_{CO}), 2050 (ν_{CO}).

2.2.6. cis,cis-Fe(PN^{quin}-BIPOL)$(CO)_2Br_2$ (**2c**)

This complex was prepared analogously to **2a** with **1c** (325 mg, 0.90 mmol) and *cis*-$Fe(CO)_4Br_2$ (296 mg, 0.90 mmol) as the starting materials. Yield: 431 mg (76%). *Anal.* Calc. for $C_{23}H_{14}Br_2FeNO_5P$: C, 43.78; H, 2.24; N, 2.22. Found: C, 43.89; H, 2.30; N, 2.18%. ^1H NMR (δ, acetone-d_6, 20 °C): 10.47 (s, 1H, quin), 8.80 (s, 1H, quin), 7.78–7.18 (m, 12H, quin and Ph). ^{13}C NMR (δ, acetone-d_6, 20 °C): 209.6 (d, J = 19.5 Hz, *C*O), 209.0 (d, J = 13.2 Hz, *C*O). All other resonances are not informative and have not been assigned. ^{31}P NMR (δ, acetone-d_6, 20 °C): 191.3. IR (ATR, cm^{-1}): 2018 (ν_{CO}), 2065 (ν_{CO}).

2.2.7. $[RuCp(PN^{quin}\text{-}Ph)(CH_3CN)]PF_6$ (**3a**)

A solution of $[RuCp(CH_3CN)_3]PF_6$ (0.382 g, 0.881 mmol) und **1a** (0.290 g, 0.881 mmol) in CH_2Cl_2 (5 mL) was stirred at room temperature for 2 h. After that time the solution was filtered and the solvent was removed under vacuum. After redissolving the residue in CH_2Cl_2, the yellow product was precipitated by addition of Et_2O, collected on a glass frit, washed twice with Et_2O and dried under vacuum. Yield: 0.482 g (80%). *Anal.* Calc. for $C_{28}H_{24}F_6N_2OP_2Ru$: C, 49.35; H, 3.55; N, 4.11. Found: C, 49.21; H, 3.61; N, 4.22%. ^1H NMR (δ, CD_2Cl_2, 20 °C): 9.67 (d, $^1J_{HH}$ = 4.34 Hz, 1H, quin), 8.39 (dd, $^1J_{HH}$ = 8.34 Hz, $^4J_{PH}$ = 1.26 Hz, 1H, quin), 7.80–7.40 (m, 14H, Ph, quin), 4.49 (s, 5H, Cp), 2.08 (s, 3C, CH_3CN). ^{13}C NMR (δ, CD_2Cl_2, 20 °C): 161.9 (s, quin), 148.7 (s, quin), 146.5 (s, Ph), 139.4 (s, quin), 134.4 (s, quin), 131.0–128.2 (m, Ph + quin), 124.7 (s, quin), 122.4 (s, quin), 121.1 (s, quin), 79.7 (d, J_{CP} = 2.87 Hz, Cp), 3.3 (s, *C*H_3CN). ^{31}P NMR (δ, CD_2Cl_2, 20 °C): 160.0, −142.8 (m, PF_6^-).

2.2.8. $[RuCp(PN^{quin}\text{-}iPr)(CH_3CN)]PF_6$ (**3b**)

This complex was prepared analogously to **3a** with $[RuCp(CH_3CN)_3]PF_6$ (0.245 g, 0.565 mmol) and **1b** (0.147 g, 0.565 mmol) as starting materials. Yield: 0.324 g (94%). *Anal.* Calc. for $C_{22}H_{28}F_6N_2OP_2Ru$: C, 43.78; H, 2.24; N, 2.22. Found: C, 43.67; H, 2.30; N, 2.16%. ^1H NMR (δ, CD_2Cl_2, 20 °C): 9.75 (d, $^1J_{HH}$ = 4.11 Hz, 1H, quin), 8.33 (d, $^1J_{HH}$ = 7.99 Hz, 1H, quin), 7.65–7.40 (m, 4H, quin), 4.69 (s, 5H, Cp), 2.72 (m, $^1J_{HH}$ = 7.42 Hz, 2H, *C*H$(CH_3)_2$), 2.31 (s, 3C, CH_3CN), 1.45–1.10 (m, 12H, *C*H_3). ^{13}C NMR (δ, CD_2Cl_2, 20 °C): 161.8 (d, J_{CP} = 1.15 Hz, quin), 149.9 (d, $^2J_{CP}$ = 4.02 Hz, quin), 139.1 (s, quin), 139.0 (d, $^3J_{CP}$ = 5.17 Hz, quin), 131.0 (s, quin), 128.6 (s, CH_3CN), 128.1 (s, quin), 123.7 (s, quin), 121.2 (d, J_{CP} = 4.60 Hz, quin), 120.9 (s, quin), 78.0 (d, J_{CP} = 2.30 Hz, Cp), 34.4 (d,

$^1J_{CP}$ = 25.86 Hz, $CH(CH_3)_2$), 32.2 (d, $^1J_{CP}$ = 23.56 Hz, $CH(CH_3)_2$), 17.5 (d, $^2J_{CP}$ = 3.45 Hz, CH_3), 17.0 (d, $^2J_{CP}$ = 8.62 Hz, CH_3), 16.2 (d, $^2J_{CP}$ = 4.60 Hz, CH_3), 3.9 (s, CH_3CN). ^{31}P NMR (δ, CD_2Cl_2, 20 °C): 194.3, −142.8 (m, PF_6^-).

2.2.9. [RuCp(PN^{quin}-BIPOL)(CH_3CN)]PF_6 (**3c**)

This complex was prepared analogously to **3a** with [RuCp(CH_3CN)$_3$]PF_6 (0.387 g, 0.891 mmol) and **1c** (0.320 g, 0.891 mmol) as starting materials. Yield: 0.590 g (93%). *Anal.* Calc. for $C_{28}H_{22}F_6N_2O_3P_2Ru$: C, 47.27; H, 3.12; N, 3.94. Found: C, 47.09; H, 3.08; N, 4.07%. ^{1}H NMR (δ, CD_2Cl_2, 20 °C): 9.79 (d, $^1J_{HH}$ = 4.80 Hz, 1H, Quin^1), 8.44 (dd, $^1J_{HH}$ = 8.22 Hz, $^4J_{PH}$ = 1.14 Hz, 1H, quin^3), 7.90–7.10 (m, 14H, Ph, quin), 4.74 (d, J_{PH} = 0.69 Hz, 5H, Cp), 2.53 (s, 3C, CH_3CN). ^{13}C NMR (δ, CD_2Cl_2, 20 °C): 162.7 (s, 1C, quin^1), 149.6 (d, $^2J_{CP}$ = 12.64 Hz, 1C, Ph^1), 147.6 (d, $^2J_{CP}$ = 6.90 Hz, 1C, Ph$^{1'}$), 146.2 (d, $^2J_{CP}$ = 1.72 Hz, 1C, quin^8), 139.7 (s, 1C, quin^3), 139.5 (s, 1C, quin^9), 131.0 (s, 1C, quin^4), 130.5–121.7 (m, 13C, Ph + quin), 121.5 (s, 1C, quin^7), 79.9 (d, J_{CP} = 3.45 Hz, 5C, Cp), 4.3 (s, 1C, CH_3CN). ^{31}P NMR (δ, CD_2Cl_2, 20 °C): 175.6, −142.8 (m, PF_6^-).

2.2.10. [Ru(η^6-p-cymene)(PN^{quin}-Ph)Cl]CF_3SO_3 (**4a**)

A solution of [Ru(η^6-*p*-cymene)(μ-Cl)Cl]$_2$ (0.237 g, 0.387 mmol) and **1a** (0.255 g, 0.775 mmol) in CH_2Cl_2 (2 mL) was treated with $AgCF_3SO_3$ (0.199 g, 0.775 mmol) and was stirred at room temperature for 2 h. After that time the solution was filtered and the solvent was removed under vacuum. After redissolving the residue in CH_2Cl_2, the yellow product was precipitated by addition of Et_2O, collected on a glass frit, washed twice with Et_2O and dried under vacuum. Yield: 0.500 g (0.667 mmol; 86%). *Anal.* Calc. for $C_{32}H_{30}ClF_3NO_4PRuS$: C, 51.31; H, 4.04; N, 1.87. Found: C, 50.89; H, 4.12; N, 1.81%. ^{1}H NMR (δ, CD_2Cl_2, 20 °C): 10.07 (d, $^1J_{HH}$ = 5.25 Hz, 1H, quin), 8.57(d, $^1J_{HH}$ = 7.54 Hz, 1H, quin), 8.14 (m, 2H, Ph), 7.90–7.90 (m, 8H, Ph), 7.30–7.10 (m, 4H, quin), 5.90 (d, $^1J_{HH}$ = 6.62 Hz, 1H, cym), 5.55 (d, $^1J_{HH}$ = 6.17 Hz, 1H, cym), 5.47 (d, $^1J_{HH}$ = 6.40 Hz, 1H, cym), 5.13 (d, $^1J_{HH}$ = 6.17 Hz, 1H, cym), 2.39 (m, $^1J_{HH}$ = 6.80 Hz, 1H, $CH(CH_3)_2$), 1.53 (s, 3H, CH_3), 1.12 (d, $^1J_{HH}$ = 7.08 Hz, 3H, $CH(CH_3)_2$), 0.96 (d, $^1J_{HH}$ = 6.85 Hz, 3H, $CH(CH_3)_2$). ^{13}C NMR (δ, CD_2Cl_2, 20 °C): 162.8 (s, quin), 145.1 (s, quin), 141.3 (s, quin), 137.1–128.0 (m, Ph + quin), 126.0 (s, quin), 123.2 (d, J_{CP} = 6.32 Hz, quin), 122.8 (s, quin), 114.1 (s, Cym), 101.6 (s, cym), 96.8 (d, $^2J_{CP}$ = 5.17 Hz, cym), 96.5 (d, $^2J_{CP}$ = 6.90 Hz, cym), 92.8 (d, $^2J_{CP}$ = 3.45 Hz, cym), 89.2 (d, $^2J_{CP}$ = 2.30 Hz, cym), 30.7 (s, $CH(CH_3)_2$), 22.3 (s, $CH(CH_3)_2$), 20.7 (s, $CH(CH_3)_2$), 17.7 (s, CH_3). ^{31}P NMR (δ, CD_2Cl_2, 20 °C): 126.2.

2.2.11. [Ru(η^6-p-cymene)(PN^{quin}-iPr)Cl]CF_3SO_3 (**4b**)

This complex was prepared analogously to **4a** with [$RuCl_2$(η^6-*p*-cymene)]$_2$ (0.251 g, 0.409 mmol), **1b** (0.213 g, 0.818 mmol) and $AgCF_3SO_3$ (0.210 g, 0.818 mmol) as starting materials. Yield: 0.494 g (89%). *Anal.* Calc. for $C_{26}H_{34}ClF_3NO_4PRuS$: C, 45.85; H, 5.03; N, 2.06. Found: C, 45.74; H, 5.11; N, 2.09%. ^{1}H NMR (δ, CD_2Cl_2, 20 °C): 9.97 (d, $^1J_{HH}$ = 4.80 Hz, 1H, quin), 8.55 (d, $^1J_{HH}$ = 8.22 Hz, 1H, quin), 7.90–7.60 (m, 4H, quin), 3.45 (m, $^1J_{HH}$ = 7.22 Hz, 1H, $CH(CH_3)_2$), 2.28 (m, $^1J_{HH}$ = 7.42 Hz, 1H, $CH(CH_3)_2$), 2.16 (m, $^1J_{HH}$ = 6.91 Hz, 1H, $CH(CH_3)_2$), 1.85–1.60 (m, 6H, CH_3), 1.62 (s, 3H, CH_3), 1.20–1.00 (m, 6H, CH_3), 0.92 (d, $^1J_{HH}$ = 7.08 Hz, 1H, CH_3), 0.80–0.65 (m, 3H, CH_3).^{13}C NMR (δ, CD_2Cl_2, 20 °C): 162.2 (s, quin), 146.8 (d, $^2J_{CP}$ = 5.17 Hz, quin), 140.9 (s, quin), 137.2 (d, $^3J_{CP}$ = 6.32 Hz, quin), 131.1 (s, quin), 129.0 (s, quin), 124.9 (s, quin), 122.2 (s, quin), 122.1 (d, J_{CP} = 5.17 Hz, quin), 113.5 (s, cym), 99.1 (s, cym), 94.8 (d, $^2J_{CP}$ = 4.02 Hz, cym), 93.6 (d, $^2J_{CP}$ = 3.45 Hz, cym), 92.1 (d, $^2J_{CP}$ = 6.32 Hz, cym), 87.5 (d, $^2J_{CP}$ = 2.87 Hz, cym), 34.5 (d, $^1J_{CP}$ = 28.74 Hz, $CH(CH_3)_2$), 32.6 (d, $^1J_{CP}$ = 16.67 Hz, $CH(CH_3)_2$), 30.8 (s, $CH(CH_3)_2$), 21.7 (s, $CH(CH_3)_2$), 21.2 (s, $CH(CH_3)_2$), 17.8 (s, CH_3), 17.8–17.1 (m, CH_3). ^{31}P NMR (δ, CD_2Cl_2, 20 °C): 160.2.

2.2.12. [Ru(η^6-p-cymene)(PN^{quin}-BIPOL)Cl]CF_3SO_3 (**4c**)

This complex was prepared analogously to **4a** with [$RuCl_2$(η^6-*p*-cymene)]$_2$ (0.152 g, 0.248 mmol), **1c** (0.178 g, 0.495 mmol), and $AgCF_3SO_3$ (0.127 g, 0.495 mmol) as starting materials. Yield: 0.328 g (0.421 mmol; 85%). *Anal.* Calc. for $C_{32}H_{28}ClF_3NO_6PRuS$: C, 49.33; H, 3.62; N, 1.80. Found: C, 49.21; H, 3.72; N, 1.91%. ^{1}H NMR (δ, CD_2Cl_2, 20 °C): 9.90 (d, $^1J_{HH}$ = 5.03 Hz, 1H, quin), 8.57 (d, $^1J_{HH}$ = 7.99 Hz, 1H, quin), 7.92–7.48 (m, 12H, Ph, quin), 6.40 (d, $^1J_{HH}$ = 6.17 Hz, 1H, cym), 6.18 (d, $^1J_{HH}$ = 6.40 Hz, 1H, cym), 5.94 (d, $^1J_{HH}$ = 6.40 Hz, 1H, cym), 5.37 (d, $^1J_{HH}$ = 6.17 Hz, 1H, cym), 1.93 (m, $^1J_{HH}$ = 6.85 Hz, 1H, $CH(CH_3)_2$), 1.79 (s, 3H, CH_3), 0.78 (d, $^1J_{HH}$ = 6.94 Hz, 3H, $CH(CH_3)_2$), 0.76 (d, $^1J_{HH}$ = 6.17 Hz, 3H, $CH(CH_3)_2$). ^{13}C NMR (δ, CD_2Cl_2, 20 °C): 163.9 (s, quin), 149.3 (s, Ph), 146.7 (s, Ph), 144.3 (s, quin), 141.1 (s, quin), 137.8 (s, quin), 131.1 (s, quin), 130.9 (d, $^4J_{CP}$ = 1.72 Hz, Ph), 130.4 (d, $^4J_{CP}$ = 1.72 Hz, Ph), 130.1 (s, Ph), 129.5 (s, Ph), 129.1 (s, Ph), 128.6 (s, quin), 126.5 (s, quin), 127.4 (s, Ph), 123.7 (d, $^4J_{CP}$ = 4.60 Hz, Ph), 123.1 (s, quin), 122.5 (d, $^4J_{CP}$ = 5.75 Hz, Ph), 121.5 (s, quin), 111.3 (s, cym), 108.4 (s, cym), 99.4 (d, $^2J_{CP}$ = 9.20 Hz, cym), 98.3 (d, $^2J_{CP}$ = 5.75 Hz, cym), 94.4 (d, $^2J_{CP}$ = 4.60 Hz, cym), 90.0 (d, $^2J_{CP}$ = 4.60 Hz, cym), 30.5 (s, $CH(CH_3)_2$), 21.7 (s, $CH(CH_3)_2$), 20.7 (s, $CH(CH_3)_2$), 18.3 (s, H_3). ^{31}P NMR (δ, CD_2Cl_2, 20 °C): 153.8.

2.3. X-ray structure determination for **2a** and **3c**·½(C_2H_5)$_2$O

X-ray data were collected on a Bruker Smart APEX CCD area detector diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) and 0.3° ω-scan frames. Corrections for absorption, $\lambda/2$ effects, and crystal decay were applied [17]. After structure solution with program SHELXLS97 refinement on F^2 was carried out with the program SHELXL97 [18]. Non-hydrogen atoms were refined anisotropically. All H atoms were placed in calculated positions and thereafter treated as riding.

Important crystallographic data are: **2a**: $C_{23}H_{16}Br_2FeNO_3P$, M_r = 601.01, orange prism, 0.36 × 0.23 × 0.20 mm, monoclinic, space group $P2_1/c$ (No. 14), a = 10.2554(5) Å, b = 10.9390(5) Å, c = 19.7572(10) Å, β = 93.306(1)°, V = 2212.8(2) Å^3, Z = 4, μ = 4.391 mm^{-1}, d_x = 1.804 g cm^{-3}, T = 173(2) K. Of 28777 reflections were collected up to θ_{max} = 30.0° and, after applying absorption corrections, merged to 6221 independent data (R_{int} = 0.028); final R indices: R_1 = 0.0422 (5595 reflections with $I > 2\sigma(I)$), wR_2 = 0.0803 (all data), 296 parameters. One bromide (Br2) and one carbonyl group (C23–O3) in *trans*-disposition to each other and cis to P and N were partly disordered with a 73/27% complementary occupation by CO and Br, respectively. Distance restraints were used to stabilize the refinement of these two CO groups. **3c**·½(C_2H_5)$_2$O: $C_{30}H_{27}F_6N_2O_{3.5}P_2Ru$, M_r = 784.55, orange plates, 0.42 × 0.30 × 0.20 mm, monoclinic, space group $P2_1/c$ (No. 14), a = 7.4420(6) Å, b = 13.5287(11) Å, c = 29.226(2) Å, β = 95.399(1)°, V = 2929.5(4) Å^3, Z = 4, μ = 0.721 mm^{-1}, d_x = 1.697 g cm^{-3}, T = 100(2) K. Of 31247 reflections were collected up to θ_{max} = 30.0° and, after applying absorption corrections, merged to 8496 independent data (R_{int} = 0.020); final R indices: R_1 = 0.0297 (7997 reflections with $I > 2\sigma(I)$), wR_2 = 0.0770 (all data), 416 parameters.

2.4. Computational details

Calculations were performed using the GAUSSIAN 03 software package on the Phoenix Linux Cluster of the Vienna University of Technology [19]. The geometries and relative energies of **2a–c**, and isomers thereof were optimized at the B3LYP level [20] with the Stuttgart/Dresden ECP (SDD) basis set [21] to describe the electrons of the iron atom. For all other atoms the 6-31g** basis set was employed [22]. Frequency calculations were performed to confirm the nature of the stationary points yielding no imaginary frequency for the minima. A scaling factor of 0.9614 was applied for the CO

frequencies [23]. Solvent effects (toluene) were considered through single point energy calculations with the optimized geometries using the Polarizable Continuum Model (PCM) initially devised by Tomasi and co-workers [24] as implemented in GAUSSIAN 03 [25] and, thus, the energy values can be taken as free energy [26]. The molecular cavity was based on the united atom topological model applied on UAHF radii, optimized for the HF/6-31G(d) level.

3. Results and discussion

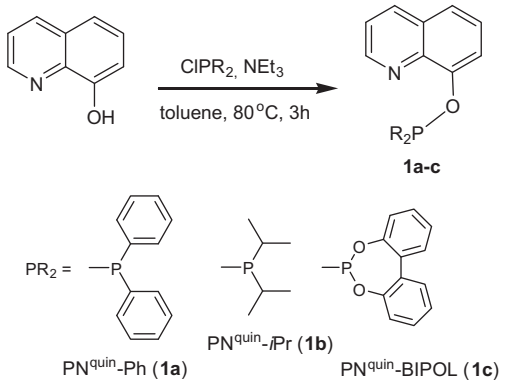
3.1. Ligands

The PN^{quin} ligands **1a–c** were prepared in 69–82% yield by reacting 8-hydroxyquinoline with 1 equiv. of the respective chlorophosphine or chlorophosphite in the presence of the base NEt_3 (Scheme 1). The reactions were carried out in toluene at 80 °C for 3 h. It has to be noted that the synthesis of PN^{quin}-Ph (**1a**) and PN^{quin}-*i*Pr (**1b**) has been reported elsewhere by a slightly different methodology [8]. The ligands **1a–c** were isolated as moderately air stable solids or oils and were characterized by ^1H, ^{13}C and ^{31}P NMR spectroscopy. Most diagnostic is the ^{31}P NMR spectrum, which exhibits a single resonance at 118.4 (**1a**), 158.2 (**1b**), and 142.1 ppm (**1c**), respectively (*cf.* 120.7 and 160.5 ppm for **1a** and **1b** in Ref. [8]). All other resonances are unremarkable and are not discussed here.

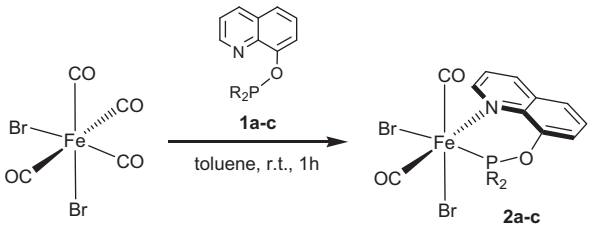
3.2. Iron complexes

Treatment of *cis*-$Fe(CO)_4Br_2$ with 1 equiv of the respective PN^{quin} ligands in toluene at room temperature for 1 h afforded the dicarbonyl dibromo complexes *cis,cis*-$Fe(PN^{quin})(CO)_2Br_2$ (**2a–c**) in good isolated yields (76–82%) (Scheme 2). All complexes are dark brown solids that are air stable in the solid state for several days but decompose in solution within a few hours to intractable materials. Their identity was unequivocally established by ^1H, ^{13}C and ^{31}P NMR, IR spectroscopy, and elemental analysis.

In the ^{31}P NMR spectra, **2a–c** exhibit singlets which show the expected low-field shifts relative to the free uncoordinated ligands [**2a**: 172.3 ppm ($\Delta\delta$ = 53.9 ppm), **2b**: 214.9 ppm ($\Delta\delta$ = 56.7 ppm), **2c**: 191.3 ppm ($\Delta\delta$ = 49.2 ppm)]. In the ^{13}C NMR spectra of **2a–c** the carbon atoms of the two CO ligands give rise to two characteristic low-field doublets. For instance, **2a** exhibits signals at 213.8 (J_{PC} = 21.8 Hz) and 211.6 (J_{PC} = 23.5 Hz) ppm. The small coupling constants are diagnostic for the phosphorus atom being in *cis* position with respect to the two CO ligands. The IR spectrum of **2a–c** displays the two expected peaks for a *cis* dicarbonyl structure. The scaled calculated frequencies ν_{CO} together with the experimentally observed values are given in Table 1 and show a reasonably good agreement.



Scheme 1.



Scheme 2.

The molecular structure of **2a** as determined by X-ray crystallography confirms that the two CO and the two bromide ligands are *cis* to one another with one CO ligand *trans* to the quinoline nitrogen atom and one *trans* to a bromide ligand. A structural view is shown in Fig. 1 with selected bond lengths and angles given in the caption This Figure and the subsequent discussion concern the predominant conformer of the solid state structure; by disorder, a second conformer with Br2 and C23–O3 in interchanged positions is present in the solid for about quarter of all complexes. The coordination geometry around the iron center corresponds to a slightly distorted octahedron. All *cis*-bond angles about Fe are close to 90° varying between 84° and 95°. The bite angle N–Fe–P is 85.8°. The Fe–P, Fe–N1, Fe–C22, Fe–C23, Fe–Br1, and Fe–Br2 bond distances are 2.167(1), 2.076(2), 1.786(3), 1.786(4), 2.510(1), 2.446(1) Å, respectively. The complex exhibits significant strain with the result that the quinoline moiety is notably twisted (r.m.s. non-planarity 0.05 Å; interplanar angle between its two 6-membered rings is 5.2(1)°) and that the iron and the phosphorus deviate much from the mean plane of the quinoline, namely by +0.37 Å for Fe and −0.73 Å for P. The angle between the mean

Table 1
Comparison of the calculated and experimental ν_{CO} absorptions.

Complex	calcd. ν_{sym}	calcd. ν_{asym}	exptl. ν_{sym}	exptl. ν_{asym}
2a	2068	2023	2061	2003
2b	2051	2014	2050	1998
2c	2072	2048	2065	2018

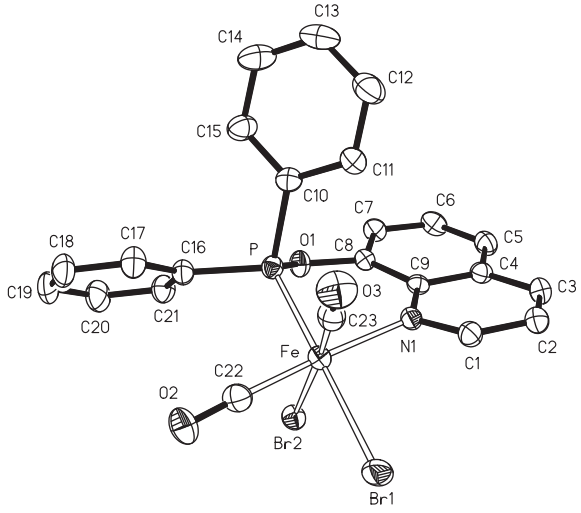
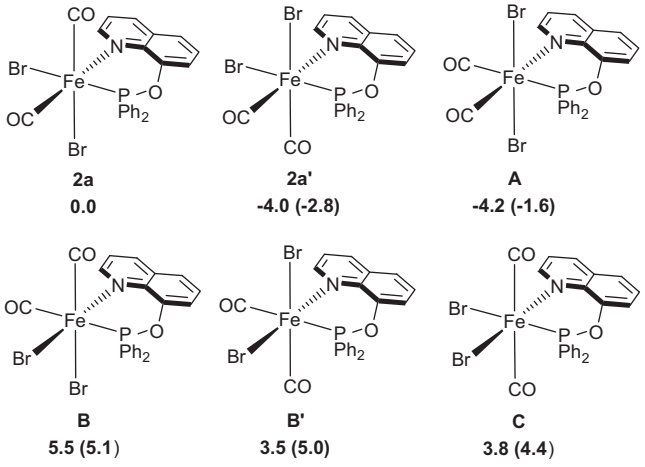


Fig. 1. Molecular structure of Fe(PN^{quin}-Ph)$(CO)_2Br_2$ (**2a**) showing 40% displacement ellipsoids. Selected distances and angles (Å, deg): Fe–P 2.167(1), Fe–N1 2.076(2), Fe–C22 1.786(3), Fe–C23 1.786(4), Fe–Br1 2.510(1), Fe–Br2 2.446(1), N1–Fe–P 85.83(7), N1–Fe–C22 176.1(1), Br1–Fe–P 178.09(3), Br2–Fe–C23 172.5(2).

planes of the quinoline and O1–P–Fe–Br1 is 50.8(1)°. In the six-membered chelate ring N1–C9–C8–O1–P–Fe the angles C8–C9–O1 = 124.0(2)° and C9–N1–Fe = 128.3(2)° are notably bigger than the corresponding *exo*-angles, C7–C8–O1 = 114.3(2)° and C1–N1–Fe = 114.3(2)°.

Both NMR and IR spectroscopy and X-ray crystallography clearly reveal that the reaction of *cis*-$Fe(CO)_4Br_2$ with PN^{quin} ligands **1a–c** resulted in all cases in the selective formation of *cis*,-*cis*-$Fe(PN^{quin})(CO)_2Br_2$. In principle, however, several isomers are conceivable. We therefore determined the geometries and relative free energies (in kcal/mol) of **2a** and possible isomers and conformers thereof by means of DFT/B3LYP calculations. These results are shown in Scheme 3. The reliability of the computational method (details in Section 2) can be checked by comparing the X-ray structure of **2a** (Fig. 1) with its calculated geometry (Fig. 2). In addition, the geometries of *cis*,*cis*-$Fe(PN^{quin}$-*i*Pr$)(CO)_2Br_2$ (**2b**) and *cis*,*cis*-$Fe(PN^{quin}$-BIPOL$)(CO)_2Br_2$ (**2c**) have also been determined (Fig. 2).

Relevant data are given in the caption. According to our calculations, **2a**′ (a conformer of **2a**) and **A** are thermodynamically more stable than **2a** by 4.0 and 4.2 kcal/mol, respectively (numbers in parenthesis refer to toluene as solvent), while **B**, **B**′ (a conformer of **B**), and **C** are less stable by 5.5, 3.5, and 3.8 kcal/mol, respectively. However, since in the starting material *cis*-$Fe(CO)_4Br_2$ as well as in **2a** and **2a**′, respectively, the two bromide ligands adopt a *cis* geometry, isomerization processes apparently do not take place in the course of the substitution reactions. Thus, the formation of **A** – having a *trans*-bromide arrangement – is presumably kinetically disfavored, while the formation of **B**, **B**′, and **C** is thermodynamically unfavorable.

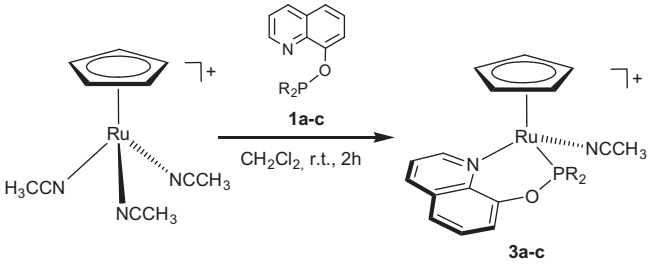


Scheme 3.

3.3. Ruthenium complexes

The reaction of $[RuCp(CH_3CN)_3]PF_6$ with 1 equiv. of PN^{quin} ligands in CH_2Cl_2 at room temperature for 2 h yields, on workup, the halfsandwich complexes $[RuCp(PN)(CH_3CN)]PF_6$ (**3a–c**) in 80–94% isolated yields (Scheme 4). Complexes **3** are orange solids which are air-stable both in the solid state and in solution for several days. They have been characterized by ^1H, ^{13}C and ^{31}P NMR spectroscopy, and elemental analysis. The ^1H NMR spectra of **3a–c** bear no unusual features.

Thus, the Cp ligand exhibits a singlet at about 4.6 ppm and the proton resonance of the CH_3CN ligand gives a doublet in the range of 2.1–2.5 ppm. In the ^{31}P NMR spectra of **3a–c** the PN^{quin} ligand exhibits, respectively, a singlet at 160.0, 194.3, and 175.6 ppm.



Scheme 4.

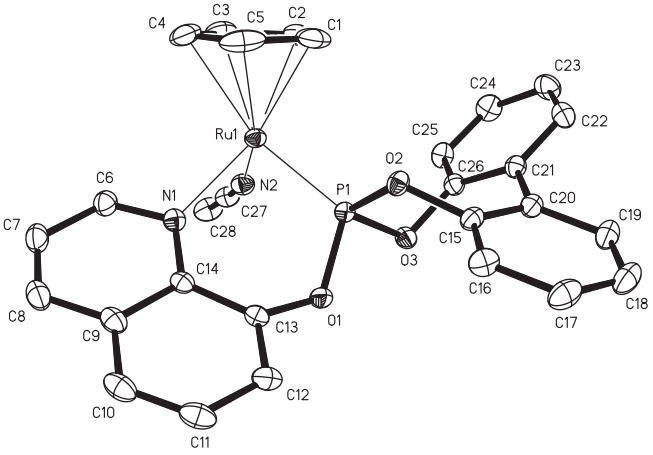


Fig. 3. Molecular structure of $[RuCp(PN^{quin}$-BIPOL$)(CH_3CN)]PF_6 \cdot ½(C_2H_5)_2O$ (**3c**$\cdot ½(C_2H_5)_2O$) showing 50% displacement ellipsoids (PF_6^- and solvent omitted for clarity). Selected distances and angles (Å, deg): Ru–C(1–5)$_{av}$ 2.206(2), Ru–N1 2.149(2), Ru–N2 2.059(1), Ru–P1 2.1681(4), P1–Ru–N1 89.02(4), P1–Ru–N2 95.63(4), N1–Ru–N2 84.34(6).

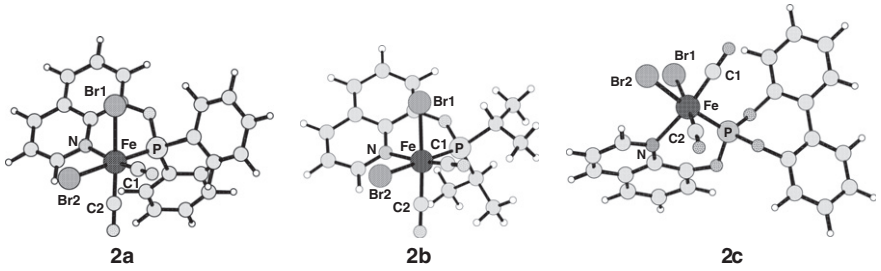
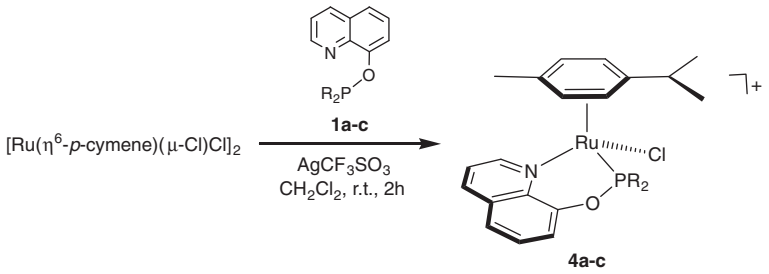


Fig. 2. Optimized geometries of **2a–c** calculated at the B3LYP level of theory (Fe sdd; C, N, P, O, Br, H 6-31g**). Selected distances and angles (Å, deg): **2a**: Fe–P 2.223, Fe–N 2.142, Fe–C1 1.816, Fe–C2 1.801, Fe–Br1 2.491, Fe–Br2 2.532, N–Fe–P 86.7, N–Fe–C1 170.3, Br2–Fe–P 178.2, Br1–Fe–C2 173.6. **2b**: Fe–P 2.248, Fe–N 2.146, Fe–C1 1.812, Fe–C2 1.796, Fe–Br1 2.492, Fe–Br2 2.537, N–Fe–P 88.8, N–Fe–C1 170.0, Br2–Fe–P 177.5, Br1–Fe–C2 175.4. **2c**: Fe–P 2.175, Fe–N 2.188, Fe–C1 1.816, Fe–C2 1.815, Fe–Br1 2.475, Fe–Br2 2.546, N–Fe–P 90.3, N–Fe–C1 171.1, Br2–Fe–P 172.5, Br1–Fe–C2 176.1.



Scheme 5.

The solid state structure of **3c**·½$(C_2H_5)_2O$ was determined by single-crystal X-ray diffraction. An ORTEP diagram is depicted in Fig. 3 with selected bond distances and angles reported in the caption.

Complex **3c**·½$(C_2H_5)_2O$ adopts a typical three legged piano stool conformation with CH_3CN and the N and P atoms of the PN^{quin} ligand as the legs. The Ru–N(1), Ru–N(2), and Ru–P(1) distances are 2.149(2), 2.059(2), and 2.1681(4) Å, respectively, with P(1)–Ru–N(1), P(1)–Ru–N(2), and N(1)–Ru–N(2) angles of 89.02(4)°, 95.63(4)°, and 84.34(6)°. The Ru–C distances range from 2.163(2) to 2.257(2) Å (mean 2.206 Å). Similar like in 2**a**, the chelate ring Ru1–P1–O1–C13–C14–N1 is notably non-planar and the quinoline moiety remarkably twisted (r.m.s. non-planarity 0.065 Å, interplanar angle between its two 6-membered rings 7.0(1)°). Ru1, P1, and O1 deviate by 0.77, 0.37, and −0.42 Å from the mean plane through quinoline.

Treatment of [Ru(η^6-*p*-cymene)(μ-Cl)Cl]$_2$ with 2 equiv. of PN^{quin} ligands in the presence of 2 equiv. of $AgCF_3SO_3$ in CH_2Cl_2 at room temperature for 2 h affords the halfsandwich complexes [Ru(η^6-*p*-cymene)(PN^{quin})Cl]CF_3SO_3 (**4a–c**) in 85–86% isolated yields as orange air-stable complexes (Scheme 5). Complexes **4** have been characterized by ^1H, ^{13}C and ^{31}P NMR spectroscopy, and elemental analysis. In the ^1H NMR spectrum **4a–c**, the *p*-cymene ligand typically gives rise to four multiplets. The methyl groups of the *i*Pr moiety are diastereotopic exhibiting two distinct doublets centered at about 0.90 and 1.20 ppm. The ^{13}C NMR spectrum does not bear any unusual features and is not discussed here. In the ^{31}P NMR spectrum, **4a–c** exhibit singlets at 126.2, 160.2, and 153.8 ppm, respectively.

In summary, we have shown that the reaction of *cis*-Fe$(CO)_4Br_2$ with PN^{quin} ligands resulted in the selective formation of *cis*,*cis*-Fe(PN^{quin})$(CO)_2Br_2$ complexes which have been characterized by NMR and IR spectroscopy. The X-ray structure of *cis*,*cis*-Fe(PN^{quin}-Ph)$(CO)_2Br_2$ is reported. Based on DFT calculations, the relative stability of four isomers of Fe(PN^{quin}-Ph)$(CO)_2Br_2$ has been established suggesting that the formation of these complexes is kinetic rather than thermodynamic in origin. In addition, we have shown that PN^{quin} ligands are able to react with [RuCp$(CH_3CN)_3$]PF_6 to afford the halfsandwich complexes [RuCp(PN^{quin})(CH_3CN)]PF_6 in high isolated yields. In similar fashion, halfsandwich complexes of the type [Ru(η^6-*p*-cymene)(PN^{quin})Cl]CF_3SO_3 are obtained upon treatment of PN^{quin} ligands with [Ru(η^6-*p*-cymene)(μ-Cl)Cl]$_2$ in the presence of $AgCF_3SO_3$.

Acknowledgements

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Appendix A. Supplementary material

CCDC 735393 and 753281contain the supplementary crystallographic data for the crystal structure of **2a** and **3c**·½$(C_2H_5)_2O$. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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