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# Coordination study of ruthenium(II) complexes containing a mixed donor (**P–N**) ligand

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ABSTRACT

A series of ruthenium(II) complexes containing an *o*-(diphenylphosphino)aniline (**P–N**) ligand have been prepared to elucidate the geometric coordination isomers and substitution reactions. Thus, [(**P–N**)$RuCl_2(CO)_2$] (**1**), [(**P–N**)$RuCl_2(dmso)_2$] (**2**) and [(**P–N**)$RuCl_2(PPh_3)$] (**3**) were synthesized by the reactions of various Ru(II) precursors with **P–N**. Treatment of **2** with $CH_3CN$ yielded the substitution product [(**P–N**)$RuCl_2(dmso)(CH_3CN)$] (**4**). The rate of the dmso ligand self-exchange of **2** was investigated, and $\Delta G^{\neq}$ was estimated to be 23.7 kcal/mol, whereas $\Delta G^{\neq}$ for the $CH_3CN$ ligand self-exchange of **4** was 25 kcal/mol. Replacement of CO in **1** with dmso directly yielded [(**P–N**)$RuCl_2(dmso)(CO)$] (**8**). Of course, complex **8** could also be prepared by substitutions of **2** and **4** with CO, but through various intermediates. Furthermore, the substitution reaction of **3** with CO and dmso led to the formation of **8**, and complexes **2** and **3** were inter-convertible. The stereochemistry of all the Ru(II) complexes has been established by elemental, spectroscopic and X-ray crystal structural analyses.

## 1. Introduction

The development of phosphorus-containing ligands has played an important role in homogeneous catalysis. Although phosphines still dominate the field of late transition metal-based catalysis, there is growing interest in the search for new catalysts with unsymmetrical bidentate ligands, particularly with phosphorus–nitrogen (**P–N**) donors [1–12]. Unlike the symmetrical counterparts, the *trans*-effect natures of phosphorus and nitrogen are expected to influence the binding properties of the substrates around the metal center, which might manipulate the activity of the catalysts [1–12]. Ruthenium complexes containing **P–N** ligands have been established on complexation [13–24], but few investigations involve the coordination study of related ruthenium(II) species with **P–N** ligands.

We have found that palladium complexes containing **P–N** ligands (Chart 1) showed unusual properties in controlling the insertions of alkene, alkyne and/or CO, providing an understanding of ligand effects [25–29]. Compared to the four-coordinated palladium species, the coordination variety of ruthenium ions is rather complicated. Continuing the study of ligand effects, we explore the coordination chemistry of **P–N** toward Ru(II).

## 2. Experimental

### 2.1. Methods and materials

All reactions, manipulations and purifications steps were performed under a dry nitrogen atmosphere. Tetrahydrofuran was distilled under nitrogen from sodium benzophenone ketyl. Dichloromethane and acetonitrile were dried over $CaH_2$ and distilled under nitrogen. Other chemicals and solvents were of analytical grade and were used after the degassing process. The ligand **P–N** [30], [$RuCl_2(dmso)_4$] [31], [$RuCl_2(CO)_3(THF)$] [32] and [$RuCl_2(PPh_3)_3$] [33] were prepared accordingly to the method reported previously.

Nuclear magnetic resonance spectra were recorded in $CDCl_3$ or acetone-$d_6$ on a Bruker AVANCE 400 spectrometer. Chemical shifts are given in parts per million relative to $Me_4Si$ for $^1H$ and $^{13}C$ NMR, and relative 85% $H_3PO_4$ for $^{31}P$ NMR. Infrared spectra were measured on a Nicolet Magna-IR 550 spectrometer (Series-II) as KBr pellets, unless otherwise noted.

### 2.2. Synthesis and characterization

#### 2.2.1. Complex *1*

A mixture of **P–N** (100 mg, 0.36 mmol) and $RuCl_2(CO)_3(THF)$ (118 mg, 0.36 mmol) in anhydrous THF (3 mL) was heated to reflux for 6 h. During the reaction, white solids precipitated, which were collected by filtration and washed with ether (1 mL × 3). The desired complex was obtained as yellow solids (k158 mg, 87%): IR (KBr, $cm^{-1}$): 2058, 1996 ($\nu_{CO}$). $^1H$ NMR (400 MHz, $d_6$-dmso) $\delta$:

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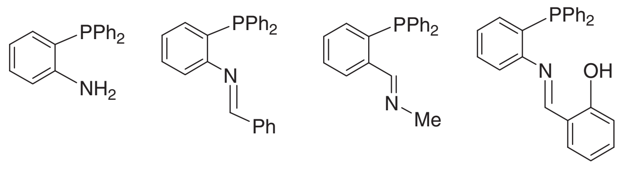

**P–N** **P–N=CPh** **P–N=CMe** **P–N–O**

**Chart 1.** Some **P–N** type ligands.

8.11 (d, 1H, $J_{H-H}$ = 12 Hz, N*H*–), 7.88 (dd, 2H, *J* = 8.0 Hz, *J* = 12.0 Hz, Ar *H*), 7.76 (m, 1H, Ar *H*), 7.69–7.47 (m, 9H, Ar *H*), 7.30 (m, 2H, Ar *H*), 6.70 (d, 1H, $J_{H-P}$ = 12 Hz, N*H*–); $^{31}$P NMR (161 MHz, $d_6$-dmso) $\delta$: 53.9; $^{13}$C NMR (100 MHz, $d_6$-dmso) $\delta$: 195.8 (d, $J_{C-P}$ = 12.0 Hz, *C*O), 191.4 (d, $J_{C-P}$ = 11.0 Hz, *C*O), 150.6 (d, $J_{C-P}$ = 18.0 Hz, *C*–NH$_2$), 134.9 (d, $J_{C-P}$ = 57.0 Hz), 134.7 (d, $J_{C-P}$ = 10.0 Hz), 133.3, 133.2, 132.3, 131.7, 131.6 (d, $J_{C-P}$ = 10.0 Hz), 129.8 (d, $J_{C-P}$ = 11.0 Hz), 129.0 (d, $J_{C-P}$ = 11.0 Hz), 128.8 (d, $J_{C-P}$ = 3.0 Hz), 128.7 (d, $J_{C-P}$ = 10.0 Hz), 128.3 (d, $J_{C-P}$ = 6.0 Hz), 127.8 (d, $J_{C-P}$ = 7.0 Hz). *Anal.* Calc. for $C_{20}H_{16}Cl_2NO_2PRu$: C, 47.54; H, 3.19; N, 2.77; Found: C, 47.23; H, 2.99; N, 2.47.

### 2.2.2. Complex **2**

A mixture of **P–N** (100 mg, 0.36 mmol) and RuCl$_2$(dmso)$_4$ (174 mg, 0.36 mmol) in anhydrous THF (3 mL) was heated to reflux for 6 h. During the reaction, yellow solids precipitated, which were collected by filtration and washed with acetone. The desired complex was obtained as yellow solids (181 mg, 83%): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.89 (dd, 2H, $J_{H-H}$ = 8.0 Hz, $J_{H-H}$ = 12.0 Hz, Ar–*H*), 7.76 (dd, 2H, $J_{H-H}$ = 8.0 Hz, $J_{H-H}$ = 12.0 Hz, Ar *H*), 7.66 (dd, 1H, $J_{H-H}$ = 4.0 Hz, $J_{H-H}$ = 8.0 Hz, Ar–*H*), 7.57–7.27 (m, 9H, Ar *H*), 6.35 (d, 1H, $J_{H-H}$ = 12 Hz, N*H*–), 5.64 (d, 1H, $J_{H-H}$ = 12 Hz, N*H*–), 3.47 (s, 3H, dmso), 3.39 (s, 3H, dmso), 3.01 (s, 3H, dmso), 2.11 (s, 3H, dmso). $^{31}$P NMR (161 MHz, CDCl$_3$) $\delta$: 54.3. $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 149.0 (d, $J_{C-P}$ = 16.0 Hz, *C*–NH$_2$), 135.1 (d, $J_{C-P}$ = 9.0 Hz), 134.4, 133.9 (d, $J_{C-P}$ = 9.0 Hz), 133.0 (d, $J_{C-P}$ = 45.0 Hz), 132.3, 132.0 (d, $J_{C-P}$ = 48.0 Hz), 131.0, 130.2, 128.9 (d, $J_{C-P}$ = 10.0 Hz), 127.6 (d, $J_{C-P}$ = 10.0 Hz), 127.4 (d, $J_{C-P}$ = 6.0 Hz), 127.3 (d, $J_{C-P}$ = 14.0 Hz), 48.5 (dmso), 47.7 (dmso), 47.3 (dmso), 45.6 (dmso). HR-ESI-MS *m/z*: 611.0292 ([M−Cl+CH$_3$CN]$^+$, calc. for $C_{24}H_{31}ClN_2O_2PRuS_2$: 611.0297). *Anal.* Calc. for $C_{22}H_{28}Cl_2NO_2PRuS_2$: C, 43.64; H, 4.66; N, 2.31. Found: C, 43.40; H, 4.77; N, 1.91.

### 2.2.3. Complex **3**

A mixture of **P–N** (100 mg, 0.36 mmol) and RuCl$_2$(PPh$_3$)$_3$ (345 mg, 0.36 mmol) in THF (3 mL) was heated to reflux for 6 h. After completion of the reaction, the solvent was removed and the residue was washed with ether several times to remove triphenylphosphine. The desired complex was precipitated by the addition of acetone to an ether solution as dark-green solids (133 mg, 52%). Due to the fluxional nature of the complex, the NMR data was too complicated to be analyzed. HR-ESI-MS *m/z*: 717.0921 ([M−Cl+MeCN]$^+$, calc. for $C_{38}H_{34}ClN_2P_2Ru$: 717.0929), *Anal.* Calc. for $C_{36}H_{31}Cl_2NP_2Ru$: C, 60.77; H, 4.39; N, 1.97. Found: C, 60.60; H, 4.36; N, 1.68.

### 2.2.4. Complex **4**

Complex **2** (100 mg, 0.2 mmol) was placed in a 50 mL flask and degassed. A mixed solution of THF and acetonitrile (*V*:*V* = 1:1) was then syringed into the above vessel. The resulting solution was heated to reflux for 6 h. Upon concentration, yellow precipitates were formed and collected (77 mg, 72%): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.89 (m, 2H Ar–*H*), 7.77 (m, 1H Ar–*H*), 7.61 (m, 2H), 7.26–7.47 (m, 9H, Ar–*H*), 5.93 (d, 1H, $J_{H-H}$ = 14 Hz, –N*H*), 4.71 (d, 1H, $J_{H-H}$ = 14 Hz, –N*H*), 3.35 (s, 3H, dmso), 2.99 (s, 3H, dmso), 1.67 (s, 3H, C*H*$_3$CN). $^{31}$P NMR (161 MHz, CDCl$_3$) $\delta$: 63.0. $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 148.4 (d, $J_{C-P}$ = 17.0 Hz, *C*–NH$_2$), 134.6 (d, $J_{C-P}$ = 9.0 Hz), 134.1 (d, $J_{C-P}$ = 46.0 Hz), 133.2, 132.8 (d, $J_{C-P}$ = 10.0 Hz), 132.4 (d, $J_{C-P}$ = 48.0 Hz), 131.6, 130.4, 129.5, 128.2 (d, $J_{C-P}$ = 10.0 Hz), 127.9 (d, $J_{C-P}$ = 10.0 Hz), 127.9 (d, $J_{C-P}$ = 6.0 Hz), 127.1 (d, $J_{C-P}$ = 6.0 Hz), 123.0 (CH$_3$*C*N), 46.5 (dmso), 46.3 (dmso), 4.6 (*C*H$_3$CN). HR-ESI-MS *m/z*: 574.0422 ([M−Cl]$^+$, calc. for $C_{24}H_{28}ClN_3OPRuS$: 574.0423). *Anal.* Calc. for $C_{22}H_{25}Cl_2N_2OPRuS$: C, 46.48; H, 4.43; N, 4.93. Found: C, 46.06; H, 4.46; N, 4.62.

### 2.2.5. Complex **5**

Complex **3** (50 mg, 0.07 mmol) in CH$_2$Cl$_2$ (3 mL) was treated with an atmospheric pressure of carbon monoxide with stirring at room temperature for 3 days. Addition of ether to the above solution readily provided dark-green solids as the desired product (41 mg, 78%): IR (KBr, cm$^{-1}$): 1959 ($\nu_{CO}$). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 8.11 (m, 6H, Ar *H*), 7.99 (m, 2H, Ar *H*), 7.89 (m, 1H, Ar *H*), 7.64 (m, 4H, Ar *H*), 7.48–7.30 (m, 15H, Ar *H*), 6.56 (m, 1H, Ar *H*), 4.40 (d, 1H, $J_{H-H}$ = 12 Hz, N*H*–), 2.78 (d, 1H, $J_{H-H}$ = 12 Hz, N*H*–). $^{31}$P NMR (161 MHz, CDCl$_3$) $\delta$: 34.9 (d, $J_{P-P}$ = 355 Hz), 21.9 (d, $J_{P-P}$ = 355 Hz). $^{13}$C NMR (100 MHz, CDCl$_3$/CD$_2$Cl$_2$ = 1:1) $\delta$: 199.8 (t, $J_{C-P}$ = 13.5 Hz, *C*O), 148.9 (d, $J_{C-P}$ = 16.0 Hz, *C*–NH$_2$), 134.9, 134.8 (d, $J_{C-P}$ = 9.9 Hz), 134.2 (d, $J_{C-P}$ = 9.8 Hz), 133.3 (d, $J_{C-P}$ = 40.6 Hz), 132.9 (d, $J_{C-P}$ = 9.8 Hz), 132.2, 131.5 (d, $J_{C-P}$ = 41.0 Hz), 130.8, 130.6, 130.4, 129.5 (d, $J_{C-P}$ = 4.5 Hz),128.9 (d, $J_{C-P}$ = 9.1 Hz), 128.7 (d, $J_{C-P}$ = 9.8 Hz), 128.2 (d, $J_{C-P}$ = 9.9 Hz), 128.2 (d, $J_{C-P}$ = 4.5 Hz), 125.5 (d, $J_{C-P}$ = 9.9 Hz), 47.4 (dmso). *Anal.* Calc. for $C_{37}H_{31}Cl_2NOP_2Ru$: C, 60.09; H, 4.22; N, 1.89. Found: C, 59.70; H, 4.37; N, 1.73.

### 2.2.6. Complex **6**

Complex **4** (50 mg, 0.09 mmol) in CDCl$_3$ (1 mL) was placed in a 100 mL bomb and then pressurized with CO (150 psi). The mixture was stirred at an ambient temperature for 3 days. Addition of ether caused the precipitation of light yellow solids (37 mg, 73%): Conductivity: 86.1 ohm$^{-1}$ cm$^2$ mol$^{-1}$ ($3.6 \times 10^{-4}$ M in CH$_3$OH, 27 °C). IR (KBr, cm$^{-1}$): 2045 ($\nu_{CO}$). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 9.68 (d, 1H, $J_{H-H}$ = 12 Hz, N*H*–), 7.83–7.19 (m, 14H, Ar *H*), 5.51 (d, 1H, $J_{H-H}$ = 12 Hz, N*H*–), 3.33 (s, 3H, dmso), 2.91 (s, 3H, dmso), 1.83 (s, 3H, C*H*$_3$CN). $^{31}$P NMR (161 MHz, CDCl$_3$) $\delta$: 36.5. $^{13}$C NMR (100 MHz) $\delta$: 191.4 (d, $J_{C-P}$ = 111.0 Hz, *C*O), 149.6 (d, $J_{C-P}$ = 20.8 Hz), 134.2 (d, $J_{C-P}$ = 9.5 Hz), 133.7 (d, $J_{C-P}$ = 10.2 Hz), 133.2, 131.4 (d, $J_{C-P}$ = 2.9 Hz), 130.8 (d, $J_{C-P}$ = 2.5 Hz), 128.9 (d, $J_{C-P}$ = 9.7 Hz), 128.9, 128.6 (d, $J_{C-P}$ = 10.4 Hz), 128.4 (d, $J_{C-P}$ = 5.3 Hz), 128.1 (d, $J_{C-P}$ = 31.9 Hz), 127.7 (d, $J_{C-P}$ = 6.1 Hz), 127.36 (d, $J_{C-P}$ = 32.8 Hz), 126.9 (d, $J_{C-P}$ = 46.5 Hz), 51.2 (dmso), 46.6 (dmso), 5.0 (*C*H$_3$CN). *Anal.* Calc. for $C_{23}H_{25}Cl_2N_2O_2PRuS$ + (CH$_3$SOCH$_3$): C, 44.51; H, 4.63; N, 4.15. Found: C, 44.85; H, 4.48; N, 4.33.

### 2.2.7. Complexes **7** and **8**

Complex **2** (50 mg, 0.08 mmol) in CH$_2$Cl$_2$ (3 mL) was placed in a 100 mL bomb and then pressurized with CO (150 psi). The mixture was stirred at an ambient temperature for 5 days. After releasing the CO, the reaction mixture was centrifuged and decanted to yield white solids as complex **8** (21 mg, 47%). Addition of ether to the solution portion gave light yellow solids as complex **7** (22 mg, 48%). Complex **7**: IR (KBr, cm$^{-1}$): 1996 ($\nu_{CO}$). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.61 (t, 2H, $J_{H-H}$ = 10 Hz, Ar–*H*), 7.44 (m, 1H, Ar *H*), 7.35–7.18 (m, 11H, Ar *H*), 6.15 (s, 2H, N*H*–), 3.07 (s, 6H, dmso). $^{31}$P NMR (161 MHz, CDCl$_3$) $\delta$: 32.5. $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 194.8 (d, $J_{C-P}$ = 118.0 Hz, *C*O), 149.2 (d, $J_{C-P}$ = 22.0 Hz, *C*–NH$_2$), 134.4, 134.0 (d, $J_{C-P}$ = 10.0 Hz), 131.4, 129.7 (d, $J_{C-P}$ = 1.0 Hz), 129.0 (d, $J_{C-P}$ = 44.0 Hz), 128.8 (d, $J_{C-P}$ = 40.0 Hz), 127.4 (d, $J_{C-P}$ = 10.0 Hz), 126.8 (d, $J_{C-P}$ = 6.0 Hz), 126.6 (d, $J_{C-P}$ = 9.0 Hz), 47.4 (dmso). *Anal.* Calc. for $C_{21}H_{22}Cl_2NO_2PRuS$: C, 45.41; H, 3.99; N, 2.52. Found: C, 45.68; H, 4.03; N, 2.34. Complex **8**: IR (KBr, cm$^{-1}$): 1994 ($\nu_{CO}$). $^1$H NMR (400 MHz, dmso-$d_6$) $\delta$: 7.80 (m, 2H,