(Arene)Ru(II) Complexes of P-N Ligands

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Ligands containing both phosphorus and nitrogen donors have shown excellent catalytic properties. We have set out to synthesize a series of P-N ligands known as “phosphino hydrazones”. Some of these ligands, for example, Z-PPh₂CH₂C(Buᵗ)=NNMe₂ I and Z-PPh₂CH₂C(Buᵗ)=NNH₂ II have shown interesting coordination chemistry with transition metals such as Cr, Mo, W, Rh, Ir, Pd and Pt. Here we report the synthesis of novel η⁶-arene complexes of I and II with ruthenium. Treatment of 0.5 equivalent of $[(\eta^6\text{-p-cymene})\text{RuCl}_2]_2$ with I in refluxing benzene gave the ruthenium (II) complex (1). The chelating complex $[(\eta^6\text{-p-cymene})\text{RuCl}\{Z\text{-PPh}_2\text{CH}_2\text{C(Bu}^t)\text{=}\text{NNMe}_2\}]\text{PF}_6$ (2) with a 6-membered ring was made by treating (1) with NH₄PF₆ in methanol. Treatment of II with 0.5 equiv. of $[(\eta^6\text{-p-cymene})\text{RuCl}_2]_2$ gave the chelating complex $[(\eta^6\text{-p-cymene})\text{RuCl}\{Z\text{-PPh}_2\text{CH}_2\text{C(Bu}^t)\text{=}\text{NNH}_2\}]\text{Cl}$ (3). We have found that the ligand I has the potential to act as either a modentate ligand or a bidentate ligand. The ligand II forms chelating complexes as the NH₂ group is sterically less demanding.

Introduction

Recently, there has been a considerable interest in the use of P-N ligands to generate new coordination and organometallic chemistry. P-N ligands contain at least one soft phosphorus donor and a hard nitrogen donor. Nitrogen donors are relatively good σ-donors but they do not act as π-acceptors. Thus, nitrogen donors do not prefer to coordinate to metal centres with low oxidation states. The coordination chemistry of phosphino hydrazones (e.g. Z-PPh₂CH₂C(Buᵗ)=NNR¹R²) with Group 6, 8, 9 and 10 metal centres have been reported (Hii et al, 1992, Hii et al, 1994, Ike et al, 1998, Perera & Shaw, 1995). This paper describes the syntheses of (p-cymene)Ru(II)- complexes of the phosphino dimethylhydrazone Z-PPh₂CH₂C(Buᵗ)=NNMe₂ I and the phosphino hydrazone Z-PPh₂CH₂C(Buᵗ)=NNH₂ II.

The noteworthy features of these two ligands are (i) the NMe₂ group is a better σ-donor than the NH₂ group, and (ii) the NMe₂ group is sterically more demanding than the NH₂ group. (Arene)ruthenium(II)-complexes of several bidentate ligands have been reported (Davenport et al, 2000,

$$\begin{align*}
\text{But} & \text{PPh}_2 \\
\text{N} & \text{NR}_2 \\
\text{I} & \text{Me} \\
\text{II} & \text{H} \\
\text{Ru} & \text{Cl} \\
\text{Cl} & \text{PPh}_2 \\
\text{NMe}_2 & \text{Ru} \\
\text{But} & \text{R} \\
\text{NH}_2 & \text{N} \\
\text{Ru} & \text{Cl} \\
\text{Ph}_2 \text{P} & \text{Cl} \\
\text{Me}_2 \text{N} & \text{N} \\
\text{Bu}^t & \text{N} \\
\text{Ru} & \text{Cl} \\
\text{PPh}_2 & \text{N} \\
\text{But} & \text{R} \\
\text{NH}_2 & \text{N} \\
\text{Ru} & \text{Cl} \\
\text{Ph}_2 \text{P} & \text{Cl} \\
\text{Me}_2 \text{N} & \text{N} \\
\text{Bu}^t & \text{N}
\end{align*}$$

**Experimental**

All the reactions were carried out in an inert atmosphere of dry nitrogen or dry argon. NMR spectra were recorded using a Bruker ARX-250 spectrometer (operating frequencies for $^1\text{H}$, $^{31}\text{P}$ and $^{13}\text{C}$ are 250.6, 101 and 62.9 MHz, respectively) or a Bruker AM-400 spectrometer (operating frequencies for $^1\text{H}$, $^{31}\text{P}$ and $^{13}\text{C}$ are 400.1, 161.9 and 100.6 MHz, respectively). $^1\text{H}$ and $^{13}\text{C}$ chemical shifts are relative to
tetramethylsilane and $^{31}$P shifts are relative to 85% phosphoric acid. Infrared spectra were recorded using a Perkin-Elmer model 257 grating spectrometer (4000-6000 cm$^{-1}$) or a Pye Unicam SP2000 (4000-2000 cm$^{-1}$). Mass spectra were recorded on a VG Autospec mass spectrometer using 8kV acceleration. For metal complexes, the $m/z$ values are quoted for $^{102}$Ru and $^{35}$Cl.

$$\left[\{\eta^6-p-\text{MeC}_6\text{H}_4\text{CH(Me)}_2\}\text{RuCl}_2\{\text{PPh}_2\text{CH}_2\text{C(Bu')}=\text{NNMe}_2\}\right]$$ (1).

A mixture of $\left[\{\eta^6-p\text{-cymene}\}\text{RuCl}_2\right]$ [5] (0.23 g, 0.38 mmol) and the phosphino dimethylhydrazone I (0.25 g, 0.76 mmol) in benzene (3 mL) was heated under reflux for 35 min. The complex (1) crystallized as red microcrystals, (0.43 g, 89%). (Found: C, 58.7; H, 6.45; Cl, 10.6; N, 4.0. $C_{30}H_{41}Cl_2N_p$Ru.0.5$C_6H_6$ requires C, 59.0; H, 6.6; Cl, 10.55; N, 4.15%). Mass (FAB): m/z 632 (M$^+$) and 597 (M-Cl). IR (Nujol): $\nu$(Ru-Cl) = 280 cm$^{-1}$. $^{31}$P-$^1$H NMR (101 MHz, CDCl$_3$), $\delta_P$ (ppm): 22.7 (s).

$$\left[\{\eta^6-\text{MeC}_6\text{H}_4\text{CH(Me)}_2\}\text{RuCl}\{\text{PPh}_2\text{CH}_2\text{C(Bu')}=\text{NNMe}_2\}\right]$$–P, N $\text{PF}_6$ (2).

A mixture of (1) (50 mg, 0.08 mmol) and of $\text{NH}_4\text{PF}_6$ (12 mg, 0.08 mmol) in methanol (3 mL) was heated at ca. 60 °C for 15 min. The required product (2) crystallized as orange microcrystals and was collected. Yield (34 mg, 58%). (Found: C, 49.0; H, 5.6; Cl, 4.9; N, 3.85. $C_{30}H_{41}Cl_6N_2P_2Ru$ requires C, 48.55; H, 5.55; Cl, 4.8; N, 3.8%). Mass (FAB): m/z 597 (M-$\text{PF}_6$). IR (Nujol): $\nu$(Ru-Cl) = 290 cm$^{-1}$. $^{31}$P-$^1$H NMR (101 MHz, CDCl$_3$), $\delta_P$ (ppm): 22.7 (s). $^1$H-NMR (250 MHz, CDCl$_3$), $\delta_H$ (ppm): 17.3(1C, s, $4\text{-MeC}_6\text{H}_4$), 22.2 (2C, s, $\text{CH}_2\text{Me}_2$), 24.6 [1C, d, $^3J(\text{PH})$ 19.6, $\text{CH}_2\text{P}$], 28.0 (3C, s, $\text{CMe}_3$), 30.1 (1C, s, CHMe$_2$), 39.3 [1C, d, $^3J(\text{PC})$ 1.6, $\text{CMe}_3$], 45.5 (2C, s, NMe$_2$) and 172.9 [1C, d, $^2J(\text{PH})$ 13.6, C=N].
\[ \{\eta^6-p-\text{CH}_3C_6\text{H}_4\text{CH(Me)}_2\}\text{RuCl}\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)\text{=NNH}_2\}-\text{P}, \text{N} \}\text{Cl} \quad (3). \]

A mixture of \([\eta^6-p\text{-cymene}]\text{RuCl}_2\] (50 mg, 0.08 mmol) and the phosphino hydrazone II (49 mg, 0.16 mmol) in benzene (1.5 mL) was heated at ca. 60 °C for 5 min. The complex (3) crystallized out immediately as yellow microcrystals. It was collected and washed with ether. Yield (67 mg, 69%). (Found: C, 55.1; H, 5.9; Cl, 11.5; N, 4.45. C\(_{28}\)H\(_{37}\)Cl\(_2\)N\(_2\)PRu requires C, 55.6; H, 6.1; Cl, 11.7; N, 4.6%). Mass (FAB): m/z 569 (M-Cl) and 533 (M-Cl-HCl). IR (Nujol): v(Ru-Cl) = 275 cm\(^{-1}\). \(^{31}\)P-\(^1\)H NMR (101 MHz, CDCl\(_3\)), \(\delta_p\) (ppm): 60.8 (s). \(^1\)H-NMR (250 MHz, CDCl\(_3\)), \(\delta_p\) (ppm): 0.80 (9H, s, Bu\(_t\)), 1.13 [3H, d, \(^3\)J (HH) 6.8, CHMe\(_2\)], 1.30 [3H, d, \(^3\)J (HH) 6.8, CHMe\(_2\)], 2.26 (3H, s, 4-\text{MeC}_6\text{H}_4), 2.85 (1H, m, d, \(^3\)J (PH) 14.0, CH\(_2\)P), 3.18 [1H, t, \(^2\)J (HH) = \(^2\)J (PH) 14.0, CH\(_2\)P], 10.10 (1H, t, \(^2\)J (HH) = \(^3\)J (PH) 9.9, NH\(_2\)). \(^{13}\)C-\(^1\)H NMR (62.9 MHz, CDCl\(_3\)), NMR (62.9 MHz, CDCl\(_3\)) \(\delta_p\) (ppm): 18.2 (1C, s, CH\(_3\)), 22.3 (1C, s, CH\(_3\)), 22.8 (1C, s, CH\(_3\)), 25.0 [1C, d, \(^1\)J (PC) 18.1, CH\(_2\)P], 27.4 (3C, s, CMe\(_3\)), 30.4 (1C, s, CHMe\(_2\)), 39.5 [1C, d, \(^3\)J (PC) 2.4, CMe\(_3\)], and 172.9 [1C, d, \(^2\)J (PC) 3.0, C=N].

**Results and Discussion**

Treatment of 0.5 equivalent of \([\eta^6-p\text{-cymene}]\text{RuCl}_2\] with the ligand I in refluxing benzene gave the ruthenium (II) complex (1) as red microcrystals in 89% yield. Micro-analytical data and mass spectral data suggest that the complex (1) is with the composition [RuCl\(_2\)(p-cymene){PPh\(_2\)CH\(_2\)C(Bu\(_t\))=NNMe\(_2\)}]. In the mass spectrum, the parent ion gave a profile at m/z 632 Dalton. The \(^{31}\)P-\(^1\)H NMR spectrum showed a singlet at 22.7 ppm. The low-field shift of 32.4 ppm (\(\delta_p\) of the free ligand I is -9.7 ppm) of the phosphorus chemical shift indicates the coordination of PPh\(_2\) group to Ru centre. In the proton NMR spectrum, the tert-butyl and NMe\(_2\) groups gave singlets at 0.56 and 1.84 ppm. The two protons of the CH\(_2\)P group were chemically equivalent and appeared as a doublet at 3.61 ppm, \(^2\)J (PH) = 13.0 Hz. The two-methyl groups of the isopropyl group of the p-cymene ligand gave a doublet at 1.11 ppm with a \(^3\)J (HH) value of 6.9 Hz. In this red complex (1), the ligand I is coordinated to the Ru(II) centre in a monodentate fashion through the P-donor as indicated by the characterizing data. This phosphino dimethylhydrazone ligand I formed chelating complexes readily with a number of metal centres (Hii et al, 1992, Hii et al, 1994, Ike et al, 1998, Perera & Shaw, 1995). We hoped that the ligand I in the complex (1) could form a six-membered chelate ring by removing.
one of the chloride ligands. The orange chelating complex \( [(\eta^6-p\text{-cymene}) \text{RuCl}\{Z\text{-PPh}_2\text{CH}_2\text{C(Bu}^\text{t})=\text{NNMe}_2\}]\text{PF}_6 \) (2) with a six-membered ring was prepared by treating the complex (1) with \( \text{NH}_4\text{PF}_6 \) in methanol. As expected, the phosphorus-31 resonance showed a large low field shift and appeared at 52.4 ppm. The two protons of the CH\(_2\)P group are now not chemically equivalent and in the \(^1\text{H}-^{31}\text{P} \) NMR spectrum they showed a AB pattern with \(^3\text{J(HH)} = 16.2\text{Hz} \). Treatment of the ligand II with 0.5 equivalent of \( [(\eta^6-p\text{-cymene}) \text{RuCl}_2]_2 \) gave the chelating complex \( [(\eta^6-p\text{-cymene}) \text{RuCl}\{Z\text{-PPh}_2\text{CH}_2\text{C(Bu}^\text{t})=\text{NNH}_2\}]\text{Cl} \) (3) as yellow microcrystals in 69\% yield. The spectral data are in good agreement with the proposed structure, where the sterically less demanding \( \text{NH}_2 \) group prefers to be coordinated to the ruthenium centre by displacing a chloride ligand.

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