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(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, $Z\text{-}PPh_2CH_2C(Bu^t){=}NNMe_2$ ***I*** *and* $Z\text{-}PPh_2CH_2C(Bu^t){=}NNH_2$ ***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* η^6*-arene complexes of* ***I*** *and* ***II*** *with ruthenium. Treatment of 0.5 equivalent of* $[(\eta^6\text{-}p\text{-cymene})RuCl_2]_2$ *with* ***I*** *in refluxing benzene gave the ruthenium (II) complex* ***(1)****. The chelating complex* $[(\eta^6\text{-}p\text{-cymene})RuCl\{Z\text{-}PPh_2CH_2C(Bu^t){=}NNMe_2\}]PF_6$ ***(2)*** *with a 6-membered ring was made by treating* ***(1)*** *with* NH_4PF_6 *in methanol. Treatment of* ***II*** *with 0.5 equiv. of* $[(\eta^6\text{-}p\text{-cymene})RuCl_2]_2$ *gave the chelating complex* $[(\eta^6\text{-}p\text{-cymene})RuCl\{Z\text{-}PPh_2CH_2C(Bu^t){=}NNH_2\}]Cl$ ***(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* NH_2 *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.* $Z\text{-}PPh_2CH_2C(Bu^t){=}NNR^1R^2$) 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 $Z\text{-}PPh_2CH_2C(Bu^t){=}NNMe_2$ **I** and the phosphino hydrazone $Z\text{-}PPh_2CH_2C(Bu^t){=}NNH_2$ **II**.

The noteworthy features of these two ligands are (i) the NMe_2 group is a better σ-donor than the NH_2 group, and (ii) the NMe_2 group is sterically more demanding than the NH_2 group. (Arene)ruthenium(II)-complexes of several bidentate ligands have been reported (Davenport et al, 2000,

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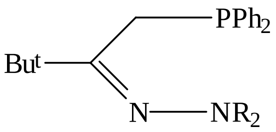
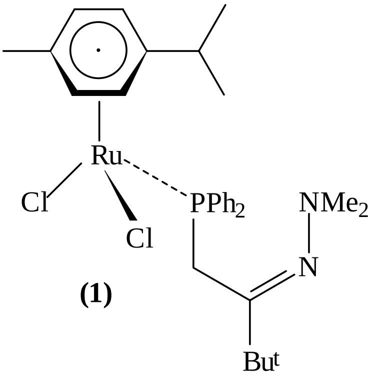
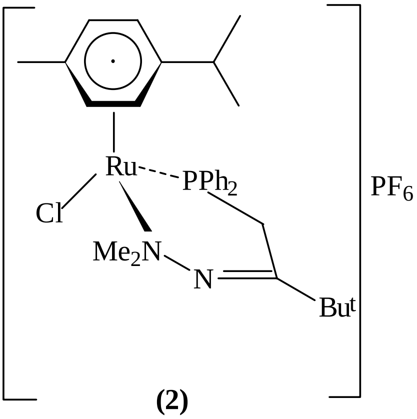
Davies et al, 2001). Some examples include (i) asymmetric transfer hydrogenation of ketones, with enantiomeric excesses (ee) of > 99%, using chiral diamine ligands (Noyori & Hashiguchi, 1997); (ii) asymmetric hydrogenation with $[RuCl(binap)(arene)]^+$ (Mashima, et al, 1989)]; (iii) enantioselective Diels-Alder reactions catalysed by $[RuCl(pyridyloxazoline)(arene)][SbF_6]$(Davenport, et al, 2000).



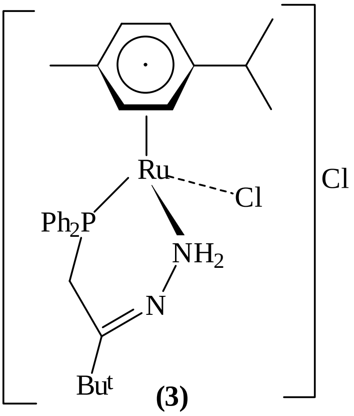
	R
I	Me
II	H



(1)



(2)



(3)

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 ^1H, ^{31}P and ^{13}C are 250.6, 101 and 62.9 MHz, respectively) or a Bruker AM-400 spectrometer (operating frequencies for ^1H, ^{31}P and ^{13}C are 400.1, 161.9 and 100.6 MHz, respectively). ^1H and ^{13}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 (4000-600 cm^{-1}) or a Pye Unicam SP2000 (4000-200 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.

$[\{\eta^6\text{-}p\text{-}MeC_6H_4CH(Me)_2\}RuCl_2\{\underline{P}Ph_2CH_2C(Bu^t)=NNMe_2\}]$ (1).

A mixture of $[(\eta^6\text{-p-cymene})RuCl_2]_2$ [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. $C_{30}H_{41}Cl_2N_2PRu.0.5C_6H_6$ 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): v(Ru-Cl) = 280 cm^{-1}. $^{31}P\text{-}\{^1H\}$ NMR (101 MHz, $CDCl_3$), δ_P (ppm): 22.7 (s). ^1H-NMR (250 MHz, $CDCl_3$), δ_H (ppm): 0.56 (9H, s, Bu^t), 1.11 [6H, d, ^3J (HH) 6.9, $CH\mathit{Me}_2$], 1.67 (3H, s, 4-$\mathit{Me}C_6H_4$), 1.84 (6H, s, $N\mathit{Me}_2$), 2.44 (1H, m, $CH\mathit{Me}_2$) and 3.61 [2H, d, ^2J(PH) 13.0, CH_2P]. $^{13}C\text{-}\{^1H\}$ NMR (62.9 MHz, $CDCl_3$) δ_C (ppm): 17.3(1C, s, 4-$\mathit{Me}C_6H_4$), 22.2 (2C, s, $CH\mathit{Me}_2$), 24.6 [1C, d, ^1J(PC) 19.6, CH_2P], 28.0 (3C, s, $C\mathit{Me}_3$), 30.1 (1C, s, $\mathit{C}HMe_2$), 39.3 [1C, d, ^3J(PC) 1.6, $\mathit{C}Me_3$], 45.5 (2C, s, $N\mathit{Me}_2$) and 172.9 [1C, d, ^2J(PC) 13.6, C=N].

$[\{\eta^6\text{-}MeC_6H_4CH(Me)_2\}RuCl\{\underline{P}Ph_2CH_2C(Bu^t)=N\underline{N}Me_2\}\text{–}P, N]\ PF_6$ (2).

A mixture of **(1)** (50 mg, 0.08 mmol) and of NH_4PF_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. $C_{30}H_{41}ClF_6N_2P_2Ru$ requires C, 48.55; H, 5.55; Cl, 4.8; N, 3.8%). Mass (FAB): m/z 597 ($M\text{-}PF_6$). IR (Nujol): v(Ru-Cl) = 290 cm^{-1}. $^{31}P\text{-}\{^1H\}$ NMR (101 MHz, $CDCl_3$), δ_P (ppm): 52.4 (s). ^1H-NMR (250 MHz, $CDCl_3$), δ_H (ppm): 0.82 (9H, s, $C\mathit{Me}_3$), 1.16 [6H, d, ^3J (HH) 7.0, $CH\mathit{Me}_2$], 1.19 (3H, s, 4-$\mathit{Me}C_6H_4$), 1.21 (3H, s, $N\mathit{Me}_2$), 1.22 (3H, s, $N\mathit{Me}_2$), 2.53 (1H, m, $CH\mathit{Me}_2$) 2.59 [1H, dd, ^2J(PH) 10.6, ^2J(HH) 16.2, CH_2P] and 3.47 [1H, t, ^2J(PH) = ^2J(HH) 16.2, CH_2P]. $^{13}C\text{-}\{^1H\}$ NMR (62.9 MHz, $CDCl_3$) δ_C (ppm): 18.2(1C, s, CH_3), 19.9 [1C, d, ^1J(PC) 21.2, CH_2P], 22.8 (2C, s, $CH\mathit{Me}_2$), 27.4 (3C, s, $C\mathit{Me}_3$), 30.4 (1C, s, $\mathit{C}HMe_2$), 39.5 [1C, d, ^3J(PC) 2.4, $\mathit{C}Me_3$], 45.5 (2C, s, $N\mathit{Me}_2$) and 170.8 (1C, s, C=N).

$[\{\eta^6\text{-}p\text{-}CH_3C_6H_4CH(Me)_2\}RuCl\{\underline{P}Ph_2CH_2C(Bu^t)=N\underline{N}H_2\}\text{–}P, N]\ Cl$ (3).

A mixture of $[(\eta^6\text{-}p\text{-cymene})RuCl_2]_2$ (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, 11.55; N, 4.45. $C_{28}H_{37}Cl_2N_2PRu$ requires C, 55.6; H, 6.15; Cl, 11.7; N, 4.65%). Mass (FAB): m/z 569 (M-Cl) and 533 (M-Cl-HCl). IR (Nujol): v(Ru-Cl) = 275 $cm^{-1.}$ $^{31}P\text{-}\{^1H\}$ NMR (101 MHz, $CDCl_3$), δ_P (ppm): 60.8 (s). ^1H-NMR (250 MHz, $CDCl_3$), δ_H (ppm): 0.80 (9H, s, Bu^t), 1.13 [3H, d, ^3J (HH) 6.8, $CH\mathit{Me}_2$], 1.30 [3H, d, ^3J (HH) 6.8, $CH\mathit{Me}_2$], 2.26 (3H, s, 4-$\mathit{Me}C_6H_4$), 2.85 (1H, m, d, ^3J (HH) 6.8, $C\mathit{H}Me_2$), 3.36 [1H, t, $^2J(HH) = {}^2J(PH)$ 14.0, CH^2P], 3.81 [1H, t, $^2J(HH) = {}^2J(PH)$ 14.0, CH_2P], 10.10 (1H, t, $^2J(HH) = {}^3J(PH)$ 9.9, NH_2). $^{13}C\text{-}\{^1H\}$ (101 MHz, $CDCl_3$), NMR (62.9 MHz, $CDCl_3$) δ_C (ppm): 18.2 (1C, s, CH_3), 22.3 (1C, s, CH_3), 22.8 (1C, s, CH_3), 25.0 [1C, d, $^1J(PC)$ 18.1, CH_2P], 27.4 (3C, s, $C\mathit{Me}_3$), 30.4 (1C, s, $\mathit{C}HMe_2$), 39.5 [1C, d, $^3J(PC)$ 2.4, $\mathit{C}Me_3$], and 172.9 [1C, d, $^2J(PC)$ 3.0, $\mathit{C}{=}N$].

Results and Discussion

Treatment of 0.5 equivalent of $[(\eta^6\text{-}p\text{-cymene})RuCl_2]_2$ 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 $[RuCl_2(p\text{-cymene})\{PPh_2CH_2C(Bu^t)=NNMe_2\}]$. In the mass spectrum, the parent ion gave a profile at m/z 632 Dalton. The $^{31}P\text{-}\{^1H\}$ NMR spectrum showed a singlet at 22.7 ppm. The low-field shift of 32.4 ppm (δ_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_2P group were chemically equivalent and appeared as a doublet at 3.61 ppm, $^2J(PH) = 13.0$ Hz. The two-methyl groups of the isopropyl group of the *p*-cymene ligand gave a doublet at 1.11 ppm with a $^3J(HH)$ 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 [(η^6-*p*-cymene)RuCl{Z-$PPh_2CH_2C(Bu^t)$= $NNMe_2$}]PF_6 **(2)** with a six-membered ring was prepared by treating the complex **(1)** with NH_4PF_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_2P group are now not chemically equivalent and in the ^1H-{^{31}P} NMR spectrum they showed a AB pattern with $^3J(HH)$ = 16.2Hz. Treatment of the ligand **II** with 0.5 equivalent of [(η^6-*p*-cymene)$RuCl_2$]$_2$ gave the chelating complex [(η^6-*p*-cymene)RuCl{Z-$PPh_2CH_2C(Bu^t)$= NNH_2}]Cl **(3)** as yellow microcrystals in 69% yield. The spectral data are in good agreement with the proposed structure, where the sterically less demanding NH_2 group prefers to be coordinated to the ruthenium centre by displacing a chloride ligand.

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