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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-PPh$_2$CH$_2$C(Bu$^t$)=NNMe$_2$* ***1*** *and Z-PPh$_2$CH$_2$C(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 rf-arene complexes of* ***I*** *and* ***II*** *with ruthenium. Treatment of 0.5 equivalent of [(n$^6$-p-cymene)RuCl$_2$]$_2$ with* ***I*** *in refluxing benzene gave the ruthenium (II) complex* ***(1).*** *The chelating complex [(n$^6$-p-cymene)RuCl {Z-PPh$_2$CH$_2$C(Bu$^t$)=NNMe$_2$}]PF6* ***(2)*** *with a 6-membered ring was made by treating* ***(1)*** *with NH4PF6 in methanol. Treatment of* ***II*** *with 0.5 equiv. of [(n$^6$-p-cymene)RuCl$_2$]$_2$ gave the chelating complex [(n$^6$-p-cymene)RuCl {Z-PPh3CH2C(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 o-donors but they do not act as n-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-PPh$_2$CH$_2$C(Bu$^t$)=NNR$^1$R$^2$) 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-PPh$_2$CH$_2$C(Bu$^t$)=NNMe$_2$ **I** and the phosphino hydrazone Z-PPh$_2$CH$_2$C(Bu$^t$)=NNH$_2$ **II.**

The noteworthy features of these two ligands are (i) the NMe$_2$ group is a better o-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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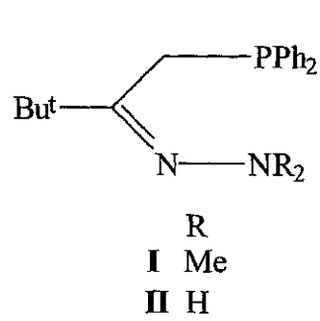
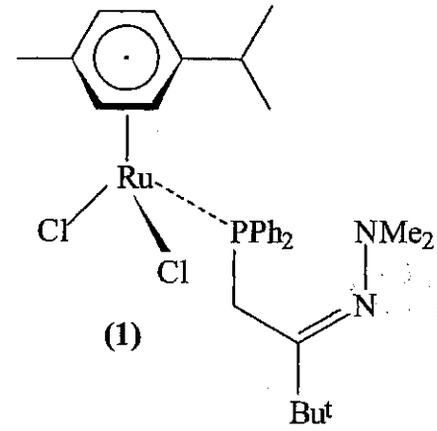
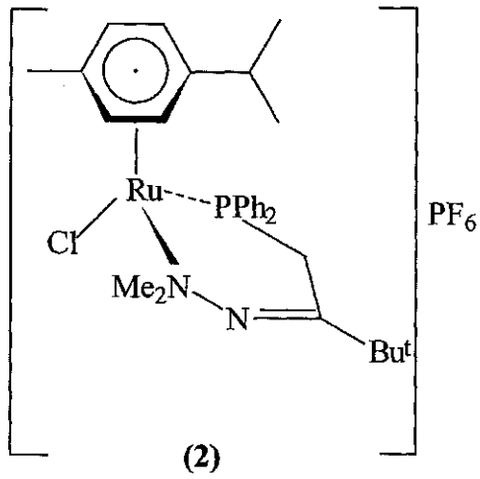
Davies et al, 2001). Some examples include (i) asymmetric transfer hydrogenation of ketones, with enantiomeric excesses (ee) of > 99%, using chiral diamine ligands (Noyori & Hashiguchi, 1997); (ii) asymmetric hydrogenation with $[RuCl(binap)(arene)]^+$ (Mashima, et al, 1989)]; (iii) enantioselective Diels-Alder reactions catalysed by $[RuCl(pyridyloxazoline)(arene)][SbF_6]$(Davenport, et al, 2000).




(1)

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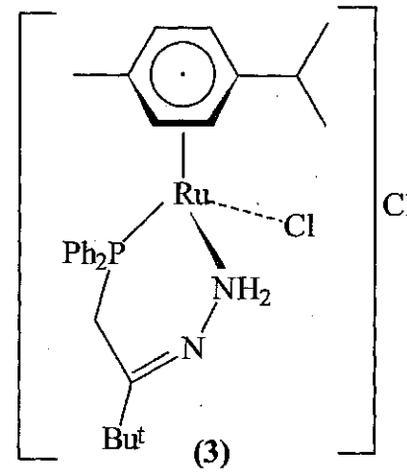


(3)

## 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 $^{1}H$, $^{31}P$ and $^{13}C$ are 250.6, 101 and 62.9 MHz, respectively) or a Bruker AM-400 spectrometer (operating frequencies for $^{1}H$, $^{31}P$ and $^{13}C$ are 400.1, 161.9 and 100.6 MHz, respectively). *H and $^{13}C$ chemical shifts are relative to

tetramethylsilane and 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 crnf 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 $^{35}$C1.

**[{$^{6}$-*p*-MeC$_6$H$_4$CH(Me)$_2$}RuCl$_2$-{PPh$_2$CH$_2$C(Bu$^t$) = NNMe$_2$}] (I).**

A mixture of [(n$^6$-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; CI, 10.6; N, 4.0. C$_3$oH4iCl$_2$N$_2$PRu.0.5C$_6$H$_6$ requires C, 59.0; H, 6.6; CI, 10.55; N, 4.15%). Mass (FAB): m/z 632 (M$^+$) and 597 (M-Cl). IR (Nujol): v(Ru-Cl) = 280 cmV'P-fH} NMR (101 MHz, CDC1$_3$), 6$_P$(ppm): 22.7 (s). $^J$H-NMR (250 MHz, CDC1$_3$), 6$_H$ (ppm): 0.56 (9H, s, *Bu),* 1.11 [6H, d, $^3$J (HH) 6.9, CHMe$_2$], 1.67 (3H, s, 4-MeC$_6$H$_4$), 1.84 (6H, s, NMe$_2$), 2.44 (1H, m, CHMe$_2$) and 3.61 [2H, d, $^2$J(PH) 13.0, CH$_2$P]. i3C-{iH} NMR (62.9 MHz, CDCI3) 8c (ppm): 17.3(1C, s, 4-MeC$_6$H$_4$), 22.2 (2C, s, CHMe$_2$), 24.6 [1C, d, U(PC) 19.6, CH$_2$P], 28.0 (3C, s, CMe$_3$), 30.1 (1C, s, CHMe$_2$), 39.3 [1C, d, 3J(PC) 1.6, CMe$_3$], 45.5 (2C, s, NMe$_2$) and 172.9 [1C, d, 2J(PQ 13.6, ON].

**[{n$^6$-MeC$_6$H$_4$CH(Me)$_2$}RuCl{PPh$_2$CH$_2$C(Bu$^t$)=NNMe$_2$}-P,N]PF$_6$ PF$_6$ (2).**

A mixture of **(1)** (50 mg, 0.08 mmol) and of NH$_4$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; CI, 4.9; N, 3.85. C$_3$oH4iClF$_6$N$_2$P$_2$Ru requires C, 48.55; H, 5.55; CI, 4.8; N, 3.8%). Mass (FAB): m/z 597 (M-PF$_6$). IR (Nujol): v(Ru-Cl) = 290 cm-$^1$. 3iP-{*H} NMR (101 MHz, CDCI3), 8$_P$ (ppm): 52.4 (s). $^X$H-NMR (250 MHz, CDC1$_3$), 8$_H$ (ppm): 0.82 (9H, s, CMe$_3$), 1.16 [6H, d, 3J (HH) 7.0, CHMe$_2$], 1.19 (3H, s, 4-MeC$_6$H$_4$), 1.21 (3H, s, NMe$_2$), 1.22 (3H, s, NMe$_2$), 2.53 (1H, m, CHMe$_2$) 2.59 [1H, dd, 2J(PH) 10.6, 2J(HH) 16.2, CH$_2$P] and 3.47 [1H, t, 2J(PH) = 2J(HH) 16.2, CH$_2$P]. $^{13}$C-{!H} NMR (62.9 MHz, CDC1$_3$) 8$_c$(ppm): 18.2(1C, s, CH$_3$), 19.9 [1C, d, U(PC) 21.2, CH$_2$P], 22.8 (2C, s, CHMe$_2$), 27.4 (3C, s, CMe$_3$), 30.4 (1C, s, CHMe$_2$), 39.5 [1C, d, 3J(PC) 2.4, CMe$_3$], 45.5 (2C, s, NMe$_2$) and 170.8 (1C, s, ON).

**[{$\eta^6$-P-$CH_3C_6H_4CH(Me)_2$}RuCl{$PPh_2CH_2C(Bu^t)$=NN<u>N</u>$H_2$}-P,*N*]Cl (3)-**

A mixture of [($\eta^6$-p-cymene)RuCl2]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; CI, 11.55; N, 4.45. C28H37CI2N2PRU requires C, 55.6; H, 6.15; CI, 11.7; N, 4.65%). Mass (FAB): m/z 569 (M-Cl) and 533 (M-C1-HC1). IR (Nujol): v(Ru-Cl) = 275 cm-$^1$- 3ip-{iH} NMR (101 MHz, CDC1$_3$), $6_P$ (ppm): 60.8 (s). iJH-NMR (250 MHz, CDCI3), $8_H$(ppm): 0.80 (9H, s, But), 1.13 [3H, d, 3J (HH) 6.8, $CHMe_2$], 1.30 [3H, d, $^3$J (HH) 6.8, $CHMe_2$], 2.26 (3H, s, 4-$MeC_6H_4$), 2.85 (1H, m, d, 3J (HH) 6.8, *$CHMe_2$),* 3.36 [1H, t, 2J(HH) = $^2$J(PH) 14.0, $CH^2$P], 3.81 [1H, t, 2J(HH) = 2J(PH) 14.0, $CH_2$P], 10.10 (1H, t, 2J(HH) = 3J(PH) 9.9, $NH_2$). $^{13}$C-{!H} (101 MHz, CDCI3), NMR (62.9 MHz, CDC1$_3$) $5_C$ (ppm): 18.2 (1C, s, $CH_3$), 22.3 (1C, s, $CH_3$), 22.8 (1C, s, $CM_3$), 25.0 [1C, d, iJ(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, 2J(PQ 3.0, ON].

## Results and Discussion

Treatment of 0.5 equivalent of [($\eta^6$-p-cymene)RuCl2]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 [RuCbtp-cymene){$PPh_2$CH2C($Bu^t$)=NNMe2}]. In the mass spectrum, the parent ion gave a profile at m/z 632 Dalton. The $^{31}$P-{$^X$H} NMR spectrum showed a singlet at 22.7 ppm. The low-field shift of 32.4 ppm ($5_P$ 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 CH2P 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 [($n^6$-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 NH4PF6 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 ^-{^P} NMR spectrum they showed a AB pattern with $^3J(HH)$ = 16.2Hz. Treatment of the ligand **II** with 0.5 equivalent of [($n^6$-p-cymene)$RuCl_2$]$_2$ gave the chelating complex [($n^6$-p-cymene)RuCl{Z-$PPh_2CH_2C(Bu^t)$= $NNH_2$}]C1 **(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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