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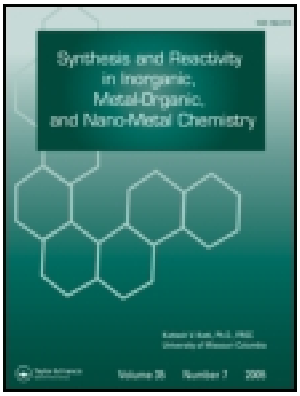

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SYNTHESIS AND CHARACTERIZATION OF RUTHENIUM(II) PYRAZOLE TERTIARY PHOSPHINE COMPLEXES

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SYNTHESIS AND CHARACTERIZATION OF RUTHENIUM(II) PYRAZOLE TERTIARY PHOSPHINE COMPLEXES

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ABSTRACT

The product of the reaction of $[RuCl_2(PPh_3)_3]$ with two equivalents of pyrazole (Hpz) in toluene, when precipitated from a toluene/hexane mixture was characterised as $[RuCl_2(Hpz)_2(PPh_3)_2] \cdot \frac{1}{2}C_6H_{14}$ (**1**); the same reaction, effected in acetone, produced the acetone coordinated species $[RuCl_2(Hpz)(Me_2CO)(PPh_3)_2]$ (**2**). When the reaction was carried out using 3,5-dimethylpyrazole (HDMpz), in either acetone or toluene as solvent, the yellow five-coordinate complex $[RuCl_2(HDMpz)(PPh_3)_2]$ (**3**) was produced. The bromo compounds $[RuBr_2(Hpz)_2(PPh_3)_2] \cdot \frac{1}{2}C_6H_{14}$ (**4**) and $[RuBr_2(HDMpz)(PPh_3)_2]$ (**5**) have also been prepared using

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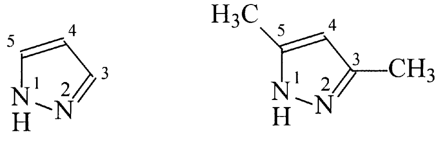
$[RuBr_2(PPh_3)_3]$ as precursor. Attempts to make the iodo analogues from $[RuI_2(PPh_3)_2]_n$, resulted in a species identified as $[RuI_2(HDMpz)(PPh_3)_2]$ on the basis of NMR and infrared measurements. The novel derivatives (**1**)–(**5**) have been characterised using microanalyses and infrared, ^1H and ^{31}P NMR spectroscopy.

Reaction of (**1**) with CO resulted in displacement of Hpz to eventually produce *cis*-$[RuCl_2(CO)_2(PPh_3)_2]$. The reaction appeared to proceed through the a monosubstituted product $[RuCl_2(CO)(Hpz)(PPh_3)_2]$, distinguished from spectroscopic measurements. The reaction of (**1**) with oxygen is discussed.

INTRODUCTION

Ruthenium complexes containing tertiary phosphines have long been found to have applications in the field of homogeneous catalysis whilst neutral pyrazoles have been widely used as monodentate ligands in coordination chemistry[1], coordinating through the azomethine nitrogen atom, N2 (Fig. 1). Moreover, 1-unsubstituted pyrazoles are weak acids; deprotonation produces the pyrazolate anion which may be used as a bridging ligand between metal centres over a wide range of intermetallic separations[2]. In addition, ruthenium(II) complexes containing $(\eta^5$-pyrazole ligands recently have been reported[3]. For these reasons, therefore, the preparation and characterisation of ruthenium/phosphine/pyrazole species and their interactions with small molecules, such as CO, are of interest[4]. Here we report results of the reactions of $[RuCl_2(PPh_3)_3]$ with pyrazole (Hpz) and 3,5-dimethylpyrazole (HDMpz), in acetone and toluene, together with investigations of the geometry of the products. Two bromo and one iodo analogues have also been synthesised from the



Pyrazole (Hpz) 3,5-Dimethylpyrazole (HDMpz)

Figure 1. Pyrazoles.

reactions of $[RuBr_2(PPh_3)_3]$ and $[RuI_2(PPh_3)_2]_n$ with Hpz and HDMpz, respectively. The reactions of $[RuCl_2(Hpz)_2(PPh_3)_2] \cdot \frac{1}{2}C_6H_{14}$ (**1**), with O_2 and CO are also discussed.

RESULTS AND DISCUSSION

Structure of Pyrazole Complexes

The reaction of two equivalents of a nitrogen-donating ligand, such as pyridine, with $[RuCl_2(PPh_3)_3]$ in acetone has been reported to result in six-coordinate species with *cis* coordination of the nitrogen ligands; the same reaction in toluene has resulted in the formation of the *trans* isomers[5]. In this study, in an attempt to prepare the two isomers containing *cis* and *trans* pyrazole groups, the same ruthenium compound was reacted with pyrazole in both solvents. In toluene the diamagnetic, six-coordinate *trans*-species $[RuCl_2(Hpz)_2(PPh_3)_2] \cdot \frac{1}{2}C_6H_{14}$ (**1**) was formed after addition of hexane, whilst reaction of Hpz with $[RuCl_2(PPh_3)_3]$ in acetone gave the acetone-coordinated species $[RuCl_2(Hpz)(Me_2CO)(PPh_3)_2]$ (**2**). Reaction of $[RuCl_2(PPh_3)_3]$ with HDMpz instead of Hpz, in either solvent, produced the five-coordinate species $[RuCl_2(HDMpz)(PPh_3)_2]$ (**3**); presumably the steric bulk of HDMpz, as compared with Hpz, prevents six-coordination. Both of the bromo compounds $[RuBr_2(Hpz)_2(PPh_3)_2] \cdot \frac{1}{2}C_6H_{14}$ (**4**) and $[RuBr_2(HDMpz)(PPh_3)_2]$ (**5**) have been prepared by reaction of the appropriate pyrazoles with $[RuBr_2(PPh_3)_3]$. Difficulty was encountered in preparing the iodo analogues in a high degree of purity by the reaction of the appropriate pyrazoles with $[RuI_2(PPh_3)_2]_n$. Reaction of Hpz with $[RuI_2(PPh_3)_2]_n$ gave an impure product with a ^{31}P NMR resonance at 54 δ, suggesting a completely different structure as compared with the other pyrazole complexes under consideration. Possibilities include five-coordinate and cationic species of Ru(II) which tend to have similar ^{31}P chemical shifts[6,7]; such species might form because of the overcrowding resulting from the increased size of the halogen. In contrast, ^1H NMR of the product of the reaction of HDMpz with $[RuI_2(PPh_3)_2]_n$ indicated that an iodo analogue of (**3**) and (**5**), probably $[RuI_2(HDMpz)(PPh_3)_2]$, had been formed.

Spectral information for the pyrazole products is shown in Table I. The presence of a medium-intense band for ν(N-H) at around 3200 cm^{-1} in the infrared spectrum of each one of the complexes is taken as evidence of η^1-coordination of the pyrazoles[7]. Evidence for the *trans* configuration (D_{2h} symmetry, assuming the pyrazoles behave as point masses) of the complexes (**1**) and (**4**) comes from ^{31}P NMR and far-infrared (600–250 cm^{-1}) measurements: a single resonance, at an appropriate chemical shift value for

Table I. Spectroscopic Data Describing the Ruthenium(II) Phosphine/Pyrazole Complexes

Compound	^{1}H NMR (δ)^a	^{31}P NMR (δ)^b	Infrared Data (cm^{-1})
(**1**)	11.7 (br, 2H, NH) 8.1 (d, 2H, C3{Hpz}) 7.3 (m, 32H, [2H, C5{Hpz}; 30H,{PPh_3}]) 5.9(t, 2H,C4{Hpz})	28.4^c	ν(N-H) 3270 m ν(Ru-Cl) 326^d w
(**2**)	11.7 (br, 1H, NH) 8.1 (d, 1H, C3{Hpz}) 7.1 (m, 31H, [1H, C5{Hpz}; 30H,{PPh_3}]) 5.9 (s, 1H, C4{Hpz}) 1.5 (s, 6H, {Me_2CO)^f	29.1^c	ν(N-H) 3260 m ν(C = O) 1710^e s ν(Ru-Cl) 330 w
(**3**)	10.8 (br, 1H, NH) 7.1 (m, 30H, {PPh_3}) 5.3 (s, 1H, C4{HDMpz}) 1.8 (s, 6H, -CH3{HDMpz})	26.1	ν(N-H) 3250 m ν(Ru-Cl) 300 w, 312^d w
(**4**)	11.7 (br, 2H, NH) 8.1 (d, 2H, C3{Hpz}) 7.3 (m, 32H, [2H, C5{Hpz}; 30H, {PPh_3}]) 5.9 (t, 2H, C4{Hpz})	28.4^c	ν(N-H) 3260 m
(**5**)	10.9 (br, 1H, NH) 7.2 (m, 30H, {PPh_3}) 5.4 (s, 1H, C4{HDMpz}) 1.8 (s, 6H, -CH3{HDMpz})	26.0	ν(N-H) 3255 m

^{a}In $CDCl_3$, ^{b}in $CDCl_3$ relative to 85% H_3PO_4, ^{c}appropriate to *trans*-phosphines[8], ^{d}*trans* to another chlorine atom[5], ^{e}acetone in CCl_4 exhibited ν(C=O) at 1720 cm^{-1}, ^{f}free acetone occurs at 2.1δ.

equivalent *trans*-phosphine groups[8], is found in the ^{31}P NMR spectra of each species; for the chloro complex (**1**), one appropriate value for ν(Ru-Cl) *trans* to another Cl atom[5] is shown in the far-infrared spectrum. The structures of (**1**) and (**3**) are shown in Fig. 2.

In transition metal pyrazole complexes, often the hydrogen atom on the pyrrole-type nitrogen forms hydrogen bonds with anionic ligands. Also apparent in the infrared spectrum of (**1**) is a medium-intensity broad band at 2850 cm^{-1}, possibly indicating N-H···Cl association[9–11]. Similar bands are not observed in the infrared spectra of any of the other pyrazole species reported.

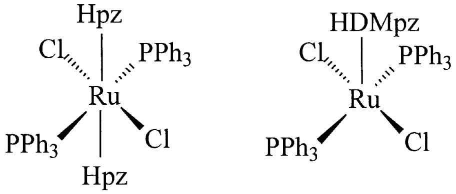


Figure 2. Suggested structures of (**1**) and (**3**).

Reactivity of Pyrazole Complexes with Air

The species (**1**)-(**5**) proved stable to air in the solid state, but in solution turned green. The coordinatively unsaturated HDMpz species (**3**) and (**5**) proved particularly unstable; their solutions rapidly changed colour in the presence of air. Investigation of the oxidation of (**1**) and (**3**) in $CDCl_3$ solution was carried out using ^{31}P NMR. When exposed to air, a solution of (**1**) turned from yellow to dark green over a period of 1–2 h. The green solution showed resonances at δ 29 and δ -6, assigned to free $O{=}PPh_3$ and free PPh_3[12], respectively. The same spectrum showed a signal at δ 42 which could not be identified; this may be due to a [Ru-$OPPh_3$] species, which resonates in this area–such complexes have been identified as products of the oxidation[13] of $[RuCl_2PPh_3)_3]$. Coordinatively unsaturated (**3**) proved even more sensitive to oxidation than (**1**), solutions turned green very rapidly when exposed to air and an unidentified resonance at δ 36 together with signals indicative of free phosphine and phosphine oxide were observed in the ^{31}P NMR spectrum.

Reaction of CO with $[RuCl_2(Hpz)_2(PPh_3)_2] \cdot {}^1\!/_2C_6H_{14}$ (1)

The reaction of CO with (**1**) in toluene solution at ambient temperature leads to the replacement of Hpz by CO (a stronger-field ligand and softer base) and spectroscopic measurements indicate that initially monosubstituted $[RuCl_2(CO)(Hpz)(PPh_3)_2]$ is formed. Under more forcing conditions further substitution occurs and pale green *cis*-$[RuCl_2(CO)_2(PPh_3)_2]$ is the product[13]; the infrared of which shows no ν(N-H) band and ν(C≡O) absorptions at 2000 and 2064 cm^{-1}; also ν(Ru-Cl) is evident in the far-infrared at 300 and 280 cm^{-1}.

EXPERIMENTAL

Reactions and manipulations were carried out in a dry nitrogen atmosphere, using standard Schlenk-type apparatus. Solvents were distilled, dried and degassed, prior to use. ^{1}H and ^{31}P NMR spectra were obtained in $CDCl_3$ at 298 K using a JEOL EX 270 MHz Fourier transform spectrophotometer. Infrared spectra (4000-250 cm^{-1}) were recorded on Perkin Elmer 881 and 457 instruments using KBr and CsI discs, respectively. All products were dried *in vacuo*. Analyses were carried out by Butterworth Laboratories Ltd., Middlesex and MEDAC Ltd., Brunel University, Middlesex. The complexes $[RuCl_2(PPh_3)_3]$ and $[RuBr_2(PPh_3)_3]$ were prepared as described in the literature[14] from commercial $RuCl_3 \cdot xH_2O$, obtained from Aldrich. Magnetic susceptibilities were measured using a Johnson Matthey magnetic susceptibility balance.

Preparation[15] of $[RuI_2(PPh_3)_2]_n$

Ruthenium trichloride hydrate (0.20 g) was stirred with $AgClO_4$ (0.48 g, 2.30 mmol) in methanol (30 mL) for 24 h. The resulting white precipitate was removed by centrifugation and filtration and potassium iodide (0.38 g, 6.00 mmol) added to the filtrate. This mixture was refluxed under nitrogen for 15 min and triphenylphosphine added (1.20 g, 4.57 mmol). The mixture was then refluxed for 4 h and the dark brown precipitate obtained washed with methanol (20 mL) and diethyl ether, then dried under suction. Yield, 0.65 g (96%).

Preparation of Ruthenium Chloro and Bromo Pyrazole Compounds

Two methods could be employed for the preparation of the pyrazole derivatives:

(a) $[RuX_2(PPh_3)_3]$ (0.20 mmol) was added to two equivalents of the pyrazole dissolved in degassed acetone (30 mL) and the mixture refluxed for 2 h. The yellow/orange/brown precipitate obtained was filtered, washed with acetone and dried *in vacuo* at 353 K.

(b) The pyrazole (0.40 mmol) was reacted with $[RuX_2(PPh_3)_3]$ (0.20 mmol) in degassed toluene (25 mL) as solvent. The mixture was stirred for 30 min at room temperature. Concentration of the solution to *ca.* 5 mL and addition of degassed hexane gave yellow

Table II. Physical and Analytical Data Relating to Ru(II) Pyrazole Derivatives

Compound	Empirical Formula Formula Weight Decomp. Temp.	Magnetic Moment	Colour/Yield%	Found (Calcd.)%		
				C	H	N
$[RuCl_2(Hpz)_2(PPh_3)_2] \cdot {}^1/_2C_6H_{14}$ (**1**)	$C_{45}H_{45}Cl_2N_4P_2Ru$ 876 dec. > 140°C	diamagnetic	yellow/60	61.7 (61.7)	5.1 (5.1)	6.3 (6.4)
$[RuCl_2\ (Hpz)(Me_2CO)(PPh_3)_2]$ (**2**)	$C_{42}H_{40}Cl_2N_2OP_2Ru$ 822 dec. > 125°C	diamagnetic	yellow/65	61.3 (61.3)	5.1 (4.9)	3.5 (3.4)
$[RuCl_2(HDMpz)(PPh_3)_2]$ (**3**)	$C_{41}H_{38}Cl_2N_2P_2Ru$ 792 dec. > 195°C	diamagnetic	yellow/64	62.1 (62.1)	5.1 (4.8)	3.8 (3.5)
$[RuBr_2(Hpz)_2(PPh_3)_2] \cdot {}^1/_2C_6H_{14}$ (**4**)	$C_{45}H_{45}Br_2N_4P_2Ru$ 965 dec. > 120°C	diamagnetic	light brown/65	56.5 (56.0)	4.6 (4.7)	6.3 (5.8)
$[RuBr_2(HDMpz)(PPh_3)_2]$ (**5**)	$C_{41}H_{38}Br_2N_2P_2Ru$ 881 dec. > 175°C	diamagnetic	orange/65	56.4 (55.9)	4.3 (4.3)	3.7 (3.2)

microcrystals. The product was filtered, washed with a small amount of hexane (5 mL) and dried *in vacuo* at 353 K.

Method (a) proved the most convenient for the isolation of most of the pyrazole complexes and reported yields are based on this method. However method (b) had to be employed for the preparation of $[RuCl_2(Hpz)_2(PPh_3)_2] \cdot \frac{1}{2}C_6H_{14}$ (**1**); the reaction of $[RuCl_2(PPh_3)_3]$ with Hpz in acetone gave the acetone coordinated species $[RuCl_2(Hpz)(Me_2CO)(PPh_3)_2]$ (**2**). For analytical data relating to (**1**)–(**5**), see Table II.

Reaction of $[RuI_2(PPh_3)_2]_n$ with HDMpz

This was effected by refluxing 3,5-dimethylpyrazole (0.08 g, 0.83 mmol) with $[RuI_2(PPh_3)_2]_n$ (0.52 g) in acetone (25 mL), under nitrogen, for 6 h. The resulting light brown precipitate was obtained by filtration and washed with acetone (5 mL). Identified as $[RuI_2(HDMpz)(PPh_3)_2]$ from: IR (cm^{-1}): 3245 m, ν(N-H). ^{1}H NMR (δ ppm):10.9, br, 1H, (NH{HDMpz}); 7.3, m, 30H, (PPh_3); 5.4, s, 1H, C4(HDMpz);1.8, s, 6H, -CH_3(HDMpz). ^{31}P NMR (δ ppm): 25.0. Yield, 0.38 g (65%).

Reaction of $[RuCl_2(Hpz)_2(PPh_3)_2] \cdot \frac{1}{2}C_6H_{14}$, (1) with CO

(i) Carbon monoxide was bubbled through a solution of (**1**) (0.18 g, 0.20 mmol) in degassed toluene (20 mL) for 2 h at ambient temperature and pressure. A pale yellow product was obtained by concentration of the toluene solution to about 2 mL and addition of a few drops of hexane. This product was thought to contain $[RuCl_2(CO)(Hpz)(PPh_3)_2]$ as identified from the following spectroscopic measurements: IR (cm^{-1}): 3270 w, ν(N-H); 1940 s, ν(C≡O); 1430 s, (P-aryl); 327 w, ν(Ru-Cl). ^{1}H NMR (δ ppm): 11.3, br, 1H, (NH, {Hpz}); 7.3, m, 31H, (C3{Hpz} and 30H, {PPh_3}); 6.8, s, 1H, C5 (Hpz); 5.8, br, 1H, C4(Hpz). ^{31}P NMR (δ ppm): 31.0, appropriate for *trans*-phosphines[8].

(ii) A mixture prepared as in (i), was refluxed for three hours. A pale green product was obtained by concentration of the solution and precipitation with hexane. The product was subsequently characterised as cis-$[RuCl_2(CO)_2(PPh_3)_2]$, by comparison with published spectroscopic data[13].

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