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Synthesis and characterization of Ru(arene) complexes of bispyrazolylazines: Catalytic hydrogen transfer of ketones ☆

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Dedicated to Prof. Jerry Trofimenko

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ABSTRACT

The bis(pyrazol-1-yl)azine ligands 2,3-bis(pyrazol-1-yl)quinoxaline (bpzqnx), 2,3-bis(pyrazol-1-yl)pyrazine (bpzprz) and 3,6-bis(3,5-dimethylpyrazol-1-yl)pyridazine (bpz*pdz) were prepared by the reaction of pyrazolate salts and the corresponding azine dichloride derivatives. The reaction of these ligands with Ru(arene) precursors led to the mononuclear complexes [RuCl(arene)(L)]BPh_4 (arene = *p*-cymene, L = bpzqnx, **1**, bpzprz, **5**, bpz*pdz, **7**; arene = C_6H_6, L = bpzqnx, **2**, bpzprz, **6**, bpz*pdz, **8**) with the N-donor ligand coordinated in a bidentate chelate way. In general, the ligands coordinate through one pyrazole ring and the azine, except in the cases of **1** and **2** where the two pyrazolyl rings are coordinated to the metal in a symmetrical way. When the reactions between the ruthenium precursors and bpzqnx are carried out in MeOH, the complexes [RuCl(arene)(OMepzqnx)]BPh_4 with partially methanolyzed ligands are isolated (arene = *p*-cymene, **3**; C_6H_6, **4**). In this process a methoxy group has replaced one of the pyrazole groups in the ligand. The X-ray structures of **6** and **7** have been determined. These compounds have a three-legged piano-stool structure with cations and anions packed through weak interactions. Complexes **1**–**8** are active in ketone hydrogenation transfer processes even in the absence of base.

1. Introduction

Ru(arene) derivatives constitute a family of interesting precursors in a variety of catalytic processes [1]. Noyori and other authors have designed very active systems with basic centres (N-donor mainly) in the asymmetric catalytic reduction of ketones using alcohols as the hydrogen source [2]. This situation has raised interest in the preparation of systems bearing N-donor centres that could participate in one or more steps of these hydrogenation processes [3]. However, the use of arene ruthenium derivatives with heterocyclic auxiliary ligands as polypyridines in catalytic hydrogenation processes has not been explored very much [4]. Our experience in the preparation of Ru(arene) complexes with N-donor ligands and their use in hydrogen transfer reactions [5] inspired the work described here, which focuses on the study of the effect that uncoordinated basic centres could have in hydrogen transfer catalytic processes. With this aim in mind, a family of bis(pyrazol-1-yl)azines, which are easily prepared, have been chosen. The preparation of mononuclear [RuCl(arene)(L)]BPh_4 derivatives was carried out and these compounds were used as precursors in hydrogen transfer reaction processes with and without a base as co-catalyst.

2. Experimental

2.1. General procedures

All manipulations were carried out under an atmosphere of dry oxygen-free nitrogen using standard Schlenk techniques. Elemental analyses were performed with a Carlo Erba Instruments EA 1108 CHNS/O microanalyzer. IR spectra were recorded on a Shimadzu IRPRESTIGE-21 spectrophotometer deposing a pure solid sample over an ATR device (4000–700 cm^{-1} range). FAB+ mass spectra (position of the peaks in Da) were recorded with a VG Biotech Quattro Spectrometer. NMR spectra were recorded at room temperature (25 °C) on Varian Unity Inova-400 (400 MHz for ^1H; 100.6 MHz for ^{13}C) and Varian Inova FT-500 (500 MHz for ^1H; 125 MHz for ^{13}C) spectrometers. ^1H shifts (ppm) were recorded using the residual proton signal of the solvent as an internal standard (see numbering of protons and carbons in Scheme 1). For the acquisition of the COSY, *g*-HMBC and *g*-HMQC spectra the standard VARIAN pulse sequences were used (VNMR 6.1 C software). The following parameters were used for COSY: acquisition time 0.214 s, pulse width 10 μs, relaxation delay 1 s, 16 scans, 512 increments. For the *g*-HMBC and *g*-HMQC the spectra were acquired using 7996-Hz (^1H) and 25133.5-Hz (^{13}C) widths; 16 transients of 2048 data points were collected for each of the 128 increments. The nOe difference spectra were recorded with 5000 Hz, acquisition time 3.27 s, pulse width 90°, relaxation delay 4 s, and irradiation power 5–10 dB. All the $^{13}C\{^1H\}$ NMR resonances are singlets.

☆ In memoriam of our friend and master Jerry Trofimenko.

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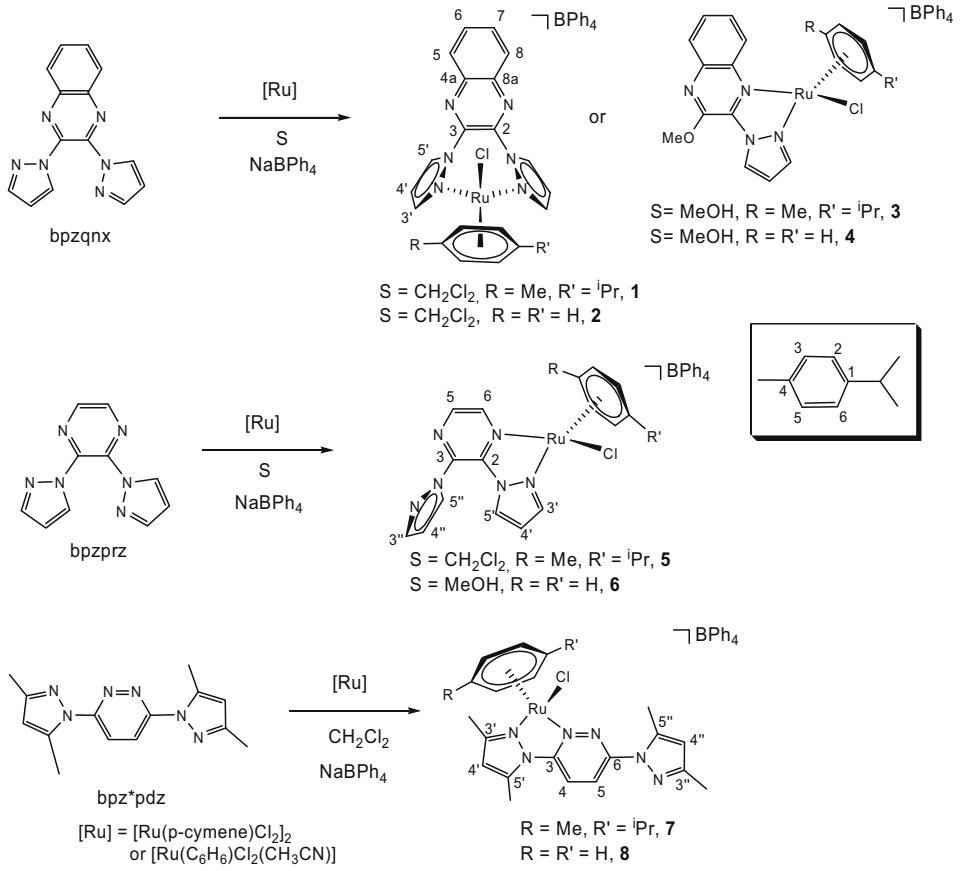

Scheme 1.

2.2. Solvents and reagents

Solvents were supplied by SDS (reagent grade) and distilled from the appropriate drying agents and degassed before use. Starting materials $[RuCl_2(p\text{-cymene})]_2$ [6] and $[RuCl_2(C_6H_6)]_2$ [7] were prepared according to literature procedures. $NaBPh_4$, acetophenone and benzophenone were purchased from Aldrich.

2.3. Structure solution and refinement

Suitable single crystals of the title compounds for X-ray study were grown from the vapour transfer of pentane over a methanol solution of **6** or the slow evaporation of a methanol solution of **7**. Crystal data and refinement are summarized in Table S1 for compound **6** and in Table S2 for compound **7**. A yellow prism ($0.33 \times 0.29 \times 0.08$ mm) of compound **6** and a yellow irregular block ($0.33 \times 0.23 \times 0.20$ mm) of compound **7** were selected and mounted on a Bruker SMART-CCD area diffractometer. Unit cell parameters were determined from 1271 frames of intensity data covering 0.3° in ω over a hemisphere of the reciprocal space by combination of three exposure sets, and refined by the least-squares method. Intensities were collected with graphite monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å) using the $\omega/2\theta$ scan-technique. A total of 40 592 reflections for **6** were measured in the range $1.21 \leqslant \theta \leqslant 26.37$ and 26 018 reflections for **7** were measured in the range $1.68 \leqslant \theta \leqslant 26.37$. Lorentz-polarization and absorption corrections were made.

The structures were solved by direct methods using the SHELXS computer program [8] and refined by the full-matrix least-squares method with the SHELX97 computer program [8], using 6786 reflections for **6** and 8471 reflections for **7**. The function minimized was $\sum w||Fo|^2 - |Fc|^2|^2$, where $w = [\sigma^2(I) + (0.0355P)^2 + 9.1687P]^{-1}$ for **6** and $w = [\sigma^2(I) + (0.0327P)^2 + 5.8723P]^{-1}$ for **7**, and $P = (|Fo|^2 + 2|Fc|^2)/3$. The values of f, f' and f'' were taken from International Tables of X-ray Crystallography [9]. All hydrogen atoms were computed and refined using a riding model. For compound **6**, the final R (on F) factor was 0.0354, wR (on $|F|^2$) = 0.0969 and goodness of fit = 1.243 for all observed reflections. The number of refined parameters was 442. Max. shift/esd = 0.002, Mean shift/esd = 0.00. Max. and Min. peaks in final difference synthesis were 0.871 and -0.592 eÅ^{-3}, respectively. For compound **7**, the final R (on F) factor was 0.0343, wR (on $|F|^2$) = 0.079 and goodness of fit = 1.021 for all observed reflections. The number of refined parameters was 514. Max. shift/esd = 0.001, Mean shift/esd = 0.00. Max. and Min. peaks in final difference synthesis were 1.517 and -1.092 eÅ^{-3}, respectively.

2.4. Preparation of ligands and complexes

2.4.1. Synthesis of 2,3-bis(pyrazol-1-yl)quinoxaline (bpzqnx)

A solution of pyrazole (729.1 mg, 10.71 mmol) in 10 ml of THF was added dropwise to a suspension of NaH (257.2 mg, 10.71 mmol) in 10 ml of THF. After 2 h of reaction at room temperature the solution was filtered and 2,3-dichloroquinoxaline (0.710 g, 3.57 mmol) was added to the solution. The mixture was refluxed during 4 h and then the solvent was removed under vacuum. The product was extracted with CH_2Cl_2 (3×10 ml), then the solvent was evaporated and finally the solid was washed with 2 ml of ethylacetate to remove the excess of pyrazole. Yield: 0.655 g (70%). *Anal.* Calc. for $C_{14}H_{10}N_6$: C, 64.10; H, 3.84; N, 32.04. Found: C, 63.94; H, 3.83; N, 31.92%. IR (Nujol, cm^{-1}): 1554 (m), 1526 (m). ^{1}H NMR ($CDCl_3$) δ (ppm): 8.08 (m, 2H, $H^{5,8}$), 7.77 (m, 2H,