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Mono and dinuclear half-sandwich platinum group metal complexes bearing pyrazolyl-pyrimidine ligands: Syntheses and structural studies

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ABSTRACT

Reactions of 0.5 eq. of the dinuclear complexes $[(\eta^6\text{-arene})\text{Ru}(\mu\text{-Cl})\text{Cl}]_2$ (arene = $\eta^6\text{-C}_6\text{H}_6$, $\eta^6\text{-}p\text{-}^i\text{PrC}_6\text{H}_4\text{Me}$) and $[(\text{Cp}^*)\text{M}(\mu\text{-Cl})\text{Cl}]_2$ (M = Rh, Ir; Cp* = $\eta^5\text{-C}_5\text{Me}_5$) with 4,6-disubstituted pyrazolyl-pyrimidine ligands (L) *viz.* 4,6-bis(pyrazolyl)pyrimidine (L1), 4,6-bis(3-methyl-pyrazolyl)pyrimidine (L2), 4,6-bis(3,5-dimethyl-pyrazolyl)pyrimidine (L3) lead to the formation of the cationic mononuclear complexes $[(\eta^6\text{-C}_6\text{H}_6)\text{Ru(L)Cl}]^+$ (L = L1, **1**; L2, **2**; L3, **3**), $[(\eta^6\text{-}p\text{-}^i\text{PrC}_6\text{H}_4\text{Me})\text{Ru(L)Cl}]^+$ (L = L1, **4**; L2, **5**; L3, **6**), $[(\text{Cp}^*)\text{Rh(L)Cl}]^+$ (L = L1, **7**; L2, **8**; L3, **9**) and $[(\text{Cp}^*)\text{Ir(L)Cl}]^+$ (L = L1, **10**; L2, **11**; L3, **12**), while reactions with 1.0 eq. of the dinuclear complexes $[(\eta^6\text{-arene})\text{Ru}(\mu\text{-Cl})\text{Cl}]_2$ and $[(\text{Cp}^*)\text{M}(\mu\text{-Cl})\text{Cl}]_2$ give rise to the dicationic dinuclear complexes $[\{(\eta^6\text{-C}_6\text{H}_6)\text{RuCl}\}_2(\text{L})]^{2+}$ (L = L1, **13**; L2, **14**; L3, **15**), $[\{(\eta^6\text{-}p\text{-}^i\text{PrC}_6\text{H}_4\text{Me})\text{RuCl}\}_2(\text{L})]^{2+}$ (L = L1, **16**; L2, **17**; L3, **18**), $[\{(\text{Cp}^*)\text{RhCl}\}_2(\text{L})]^{2+}$ (L = L1, **19**; L2, **20**; L3, **21**) and $[\{(\text{Cp}^*)\text{IrCl}\}_2(\text{L})]^{2+}$ (L = L1 **22**; L2, **23**; L3 **24**). The molecular structures of [**3**]PF_6, [**6**]PF_6, [**7**]PF_6 and [**18**]$(\text{PF}_6)_2$ have been established by single crystal X-ray structure analysis.

1. Introduction

During the last few decades there has been great interest in the chemistry of transition metals associated with polydentate ligands with sp^2-hybridized nitrogen atoms, for instance, polypyrazolylborates [1,2] and polypyridines [2–10]. In many cases the charge transfer properties of these compounds justify this interest. Especially with these nitrogen donor ligands have been shown to be effective catalysts for oxidation reactions [11–19] and for ring-opening metathesis polymerization [20] and recent studies of arene ruthenium complexes have shown that they are found to inhibit cancer cell growth [21–26], as non-linear optical (NLO) materials [27,28]. For a majority of the complexes studied, the metal centers are linked by a bridging ligand and the nature of the bridge has a fundamental influence on the electronic interaction between the metals and therefore on the characteristics of the material.

The ligand 4,6-bis(pyrazolyl)pyrimidine (L1) and its analogues, 4,6-bis(3-methyl-pyrazolyl)pyrimidine (L2) and 4,6-bis(3,5-dimethyl-pyrazolyl)pyrimidine (L3), are the subject of this investigation. They have a structural similarity to 3,6-bis(pyrazolyl)pyridazine (**A**) and 4,5-bis(pyrazolyl)quinoxaline (**B**) both of which have been previously studied [29,30]. In our previous work, we demonstrated that the ligand **A** does not yield dinuclear compounds with two half-sandwich platinum group metal atoms, since the steric nature of the ligand, resulted only in the formation of mononuclear complexes [29]. However it is true in the case of more sterically free ligand **B** also, because it also yielded mononuclear complexes, since the pyrazole rings of the ligand tilted with respect to the central quinoxaline ring because of the steric collide between the R' groups of the pyrazole rings. In the case of ligand **A** the pyrazolyl rings are bonded *para* to each other, where as in the case of ligand **B**, they are bonded *ortho* to each other on central six membered rings. But sterically less demanding ligand L (L1–L3) can coordinate to two half-sandwich platinum group metal centers, since the pyrazolyl rings of the ligand are bonded *meta* to each other, leading to reduced steric interaction, which enhances the stability of the dinuclear complexes.

In recent years, we have been carrying out arene ruthenium complexation reactions with a variety of nitrogen-based ligands [31–36] including pyridyl-pyridazine and pyrazolyl-pyridazine ligands. Ruthenium complexes of these types of nitrogen-based ligands have a capacity to function as catalysts for the oxidation of water to oxygen [37–39]. Although extensive studies have been made on ruthenium complexes containing polypyridyl ligands, complexes containing pyrazolyl-pyrimidine ligands have not yet been investigated.

In the present paper, we focus on the synthetic methodology applied for the development of homogeneous and immobilized half-sandwich ruthenium, rhodium and iridium complexes bearing bis(pyrazolyl)pyrimidine, as a specific *N,N*-bidentate bridging ligands (L) (Scheme 1).

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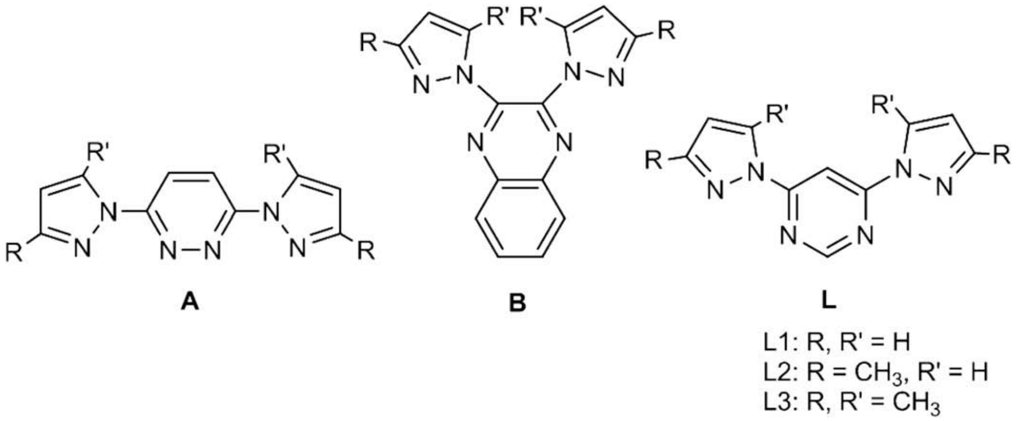

Scheme 1.

2. Experimental

2.1. General remarks

All solvents were dried and distilled prior to use. 3-methylpyrazole, 3,5-dimethylpyrazole and 4,6-dichloropyrimidine (Aldrich) were purchased and used as received. $[(\eta^6\text{-}C_6H_6)Ru(\mu\text{-}Cl)Cl]_2$, $[(\eta^6\text{-}p\text{-}^iPrC_6H_4Me)Ru(\mu\text{-}Cl)Cl]_2$ [40–42], and $[(Cp^*)M(\mu\text{-}Cl)Cl]_2$ (M = Rh, Ir) [43–45] were prepared according to literature methods. The preparation of ligand 4,6-bis(pyrazolyl)pyrimidine (L1) has been previously described [46] and ligand 4,6-bis(3,5-dimethyl-pyrazolyl)pyrimidine (L3) was prepared by the modified procedure of Oro et al. [47]. ^1H NMR spectra were recorded on Bruker AMX-400 MHz spectrometer. Infrared spectra were recorded as KBr pellets on a Perkin–Elmer 983 spectrophotometer; elemental analyses of the complexes were performed on a Perkin–Elmer-2400 CHN/S analyzer. Mass spectra were obtained from Waters ZQ 4000 mass spectrometer by ESI method. Absorption spectra were obtained at room temperature using a Perkin–Elmer Lambda 25 UV–Vis spectrophotometer.

2.2. Single crystal X-ray structure analyses

Crystals suitable for X-ray diffraction study for compounds [**3**]PF_6, [**6**]PF_6, [**7**]PF_6 and [**18**]$(PF_6)_2$ were grown by slow diffusion of diethylether/hexane into dichloromethane/acetone solution of complexes [**3**]$PF_6\cdot H_2O$, [**6**]PF_6, [**7**]PF_6 and [**18**]$(PF_6)_2\cdot H_2O$, respectively. The crystals were mounted on a Stoe Image Plate Diffraction system equipped with a ϕ circle goniometer, using Mo Kα graphite monochromated radiation (λ = 0.71073 Å) with ϕ range 0–200°. The structures were solved by direct methods using the program SHELXS–97 [48]. Refinement and all further calculations were carried out using SHELXL–97 [49]. The H-atoms were included in calculated positions and treated as riding atoms using the SHELXL default parameters. The non-H atoms were refined anisotropically, using weighted full-matrix least-square on F^2. Crystallographic details are summarized in Table 1 and selected bond lengths and angles are presented in Table 2. Figs. 1–4 were drawn with ORTEP [50] and Fig. 5 with the software MERCURY [51,52].

2.3. Preparation of ligands (L2 and L3)

2.3.1. 4,6-Bis(3-methyl-pyrazolyl)pyrimidine (L2)

To a solution of 3-methylpyrazole (1.20 g, 14.7 mmol) in 50 ml of THF was added fine pieces of potassium (0.600 g, 15.3 mmol), the mixture was refluxed at 50 °C until the potassium was completely dissolved. Then 4,6-dichloropyrimidine (1.094 g, 7.35 mmol) was added to the reaction mixture(pale-brown solution), which was refluxed for 5 h. Then 80 ml of water was added and the solution refrigerated overnight. The colorless solid was filtered and washed with water (2 × 10 ml) and dried under P_2O_5. The pure compound was obtained after recrystallization from chloroform/hexane.

Yield: 0.72 g, 57.8%.

Elemental Anal. Calc. for $C_{12}H_{12}N_6$: C, 59.99; H, 5.03; N, 34.98. Found: C, 59.63; H, 5.18; N, 34.72%. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.71 (s, 1H), 8.45 (d, 2H, ^3J = 2.4 Hz), 8.29 (s, 1H), 6.29 (d, 2H, ^3J = 2.4 Hz), 2.39 (s, 6H, CH_3); ESI-MS (*m*/*z*): 241.11 $[M+H]^+$; IR (KBr, cm^{-1}): 2924m, 1597s, 1464m, 1382m, 1211m, 1044s, 777s.

2.3.2. 4,6-Bis(3,5-dimethyl-pyrazolyl)pyrimidine (L3)

The L3 ligand was synthesized in a similar manner using 3,5-dimethylpyrazole (1.50 g, 15.6 mmol), potassium (0.60 g, 15.0 mmol) and 4,6-dichloropyrimidine (1.10 g, 7.35 mmol). However, after refluxing the THF solution for 5 h, the mixture was evaporated to dryness. The product was extracted three times with 30 ml of toluene. The solvent was removed, and the white solid obtained was dissolved in dichloromethane layering the resulting solution with hexane led to the precipitation of traces of pyrazole. L3 was obtained after filtration and evaporation to dryness of the resulting solution. The solid was recrystallized from chloroform/hexane.

Yield: 1.5 g, 55%.

Elemental Anal. Calc. for $C_{14}H_{16}N_6$: C, 62.67; H, 6.01; N, 31.32. Found: C, 62.68; H, 6.05; N, 31.28%. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.74 (s, 1H), 8.37 (s, 1H), 6.01 (s, 2H,), 2.67 (s, 6H, CH_3), 2.29 (s, 6H, CH_3); ESI-MS (*m*/*z*): 269.14 $[M+H]^+$); IR (KBr, cm^{-1}): 3446w, 2925m, 1593s, 1484s, 1385m, 1266m, 1019s, 771m.

2.4. General procedure for the preparation of the mononuclear complexes *1–6*

A mixture of $[(\eta^6\text{-}C_6H_6)Ru(\mu\text{-}Cl)Cl]_2$ (arene = C_6H_6 and $p\text{-}^iPrC_6H_4Me$) (0.07 mmol), ligand L (L1, L2 or L3) (0.15 mmol) and 2.5 equivalents of NH_4PF_6 in dry methanol (15 ml) was stirred at room temperature for 8 h resulting in the precipitation of a dark yellow solid. The precipitate was separated by filtration, washed with cold methanol, diethyl ether and dried *in vacuo*.

2.4.1. $[(\eta^6\text{-}C_6H_6)Ru(L1)Cl]PF_6$ ([**1**]PF_6)

Yield: 66 mg, 82.5%.

Elemental Anal. Calc. for $C_{16}H_{14}N_6RuClPF_6$ (571.97): C, 33.61; H, 2.47; N, 14.70. Found: C, 33.73; H, 2.65; N, 13.98%. ^1H NMR (400 MHz, $CDCl_3$): δ = 9.56 (d, 1H, ^3J = 2.4 Hz), 8.75 (d, 1H,