Synthesis and structure of a ruthenium(II) complex incorporating κ*N* bound 2-pyridonato ligands; a new catalytic system for transfer hydrogenation of ketones

Eric P. Kelson * and Proma P. Phengsy

Department of Chemistry, California State University Northridge, Northridge,
18111 Nordhoff Street, California 91330-8262, USA. E-mail: eric.kelson@csun.edu

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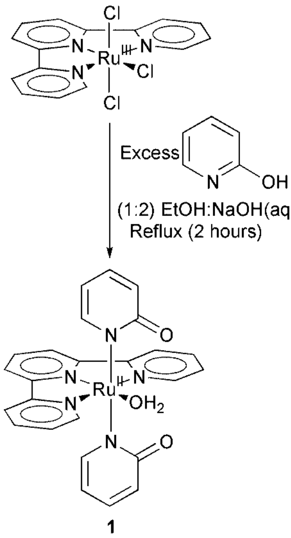
The preparation of *trans*-[(terpy)Ru(NC_5H_4O-κ*N*)$_2$(OH_2)] 1 provides the first structurally characterized example of monodentate κ*N* bound 2-pyridonato ligands on ruthenium(II) and a new catalyst for the transfer hydrogenation of ketones featuring a saturated hard donor ligand set.

The anion of 2-pyridone exhibits a range of coordination modes and is especially prone to bridging between metal centers.[1] The monodentate κ*N* bound ligand, however, is rare with only a few structural examples reported in platinum, osmium, and cobalt complexes.[2] Aside from simple transformations of the complexes themselves, the chemistry of κ*N* bound pyridonato complexes is largely unexplored. As part of our effort to investigate the influence of hydroxylated pyridine ligands on neighboring groups, we report here the synthesis and crystallographic characterization of a ruthenium complex incorporating two monodentate κ*N* bound 2-pyridonato ligands.[3] We also present this complex as the first catalyst for transfer hydrogenation of ketones by 2-propanol with a saturated coordination environment exclusively comprised of hard donor ligands.

The κ*N* bound pyridonato complex **1** is prepared in high yield by treatment of (terpy)$RuCl_3$ with excess 2-hydroxypyridine and sodium hydroxide in a refluxing 2:1 mixture of ethanol and water [eqn. (1)]. Removal of the ethanol under vacuum affords the product as a dark purple microcrystalline hemihydrate.†



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(1)

Vapor diffusion of toluene into a saturated solution of **1**·0.5H_2O in acetone afforded crystals of **1**·$(CH_3)_2CO$·H_2O suitable for single crystal X-ray determination.‡ Complex **1**·$(CH_3)_2CO$·H_2O crystallizes in the triclinic $P\bar{1}$ space group with the asymmetric unit containing two nearly identical ruthenium complexes. Each complex (one is shown in Fig. 1) is approximately octahedral with the ruthenium bound by a meridonal terpy ligand, two κ*N* coordinated 2-pyridonato ligands and one aquo ligand. The terpy ligand is coordinated in the usual planar, tridentate fashion with the central nitrogen closest to ruthenium. The pyridonato ligands are arranged *trans* to each other with a N–Ru–N angle of 176.6° and *cis* to the aquo ligand with N–Ru–O angles of 89.4 and 87.9°. The pyridonato rings are planar (with maximum out-of-plane deviations of only 0.041 and 0.026 Å) and exhibit the alternating long [1.434(6) to 1.392(6) Å] and short [1.376(5) to 1.347(7) Å] C–C bond distances and short C–O bond lengths [1.259(5) and 1.280(4) Å] expected for the κ*N* tautomers. These ligand bond lengths are comparable to those reported for *mer*-[Pt(NH_3)$_2$(NC_5H_4O-κ*N*)Cl_3].[2b] The long Ru–O distance [2.160(2) Å] is typical for aquo ligands in polypyridyl ruthenium complexes, and structure refinement from the low temperature (200 K) data located hydrogens on the aquo

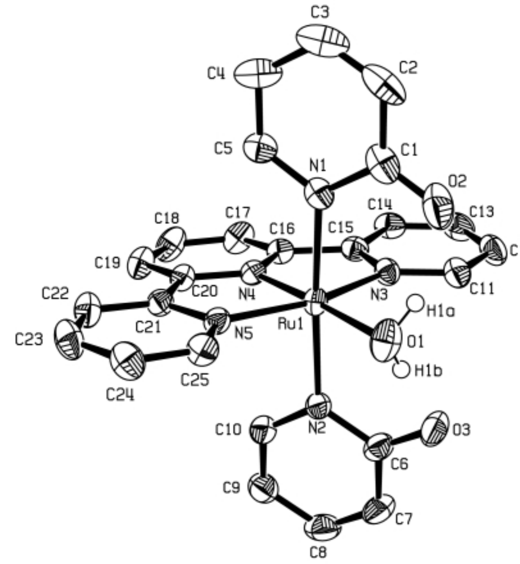

Fig. 1 The molecular structure of **1**. Selected bond lengths (Å) and angles (°) are: Ru(1)–O(1) 2.160(2), Ru(1)–N(1) 2.125(3), Ru(1)–N(2) 2.126(3), Ru(1)–N(3) 2.089(2), Ru(1)–N(4) 1.917(2), Ru(1)–N(5) 2.043(2), O(1)–H(1a) 0.85(6), O(1)–H(1b) 0.74(6), O(2)–C(1) 1.259(5), O(3)–C(6) 1.280(4), N(1)–C(1) 1.381(4), N(1)–C(5) 1.367(4), N(2)–C(6) 1.380(4), N(2)–C(10) 1.362(4), C(1)–C(2) 1.434(6), C(2)–C(3) 1.347(7), C(3)–C(4) 1.392(6), C(4)–C(5) 1.376(5), C(6)–C(7) 1.433(5), C(7)–C(8) 1.350(6), C(8)–C(9) 1.396(5), C(9)–C(10) 1.356(5); O(1)–Ru(1)–N(1) 89.4(1), O(1)–Ru(1)–N(2) 87.9(1), O(1)–Ru(1)–N(3) 103.2(1), O(1)–Ru(1)–N(4) 176.6(1), O(1)–Ru(1)–N(5) 96.0(1), N(1)–Ru(1)–N(2) 176.6(1), N(1)–Ru(1)–N(3) 89.7(1), N(1)–Ru(1)–N(4) 91.7(1), N(1)–Ru(1)–N(5) 90.6(1), N(2)–Ru(1)–N(3) 88.9(1), N(2)–Ru(1)–N(4) 91.0(1), N(2)–Ru(1)–N(5) 91.8(1), N(3)–Ru(1)–N(4) 80.0(1), N(3)–Ru(1)–N(5) 160.7(1), N(4)–Ru(1)–N(5) 80.8(1).

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Table 1 Results of transfer hydrogenation of selected ketones by 2-propanol catalyzed by **1**[a]

Substrate	Product	t/min	Yield (%)[b]	Turnovers/TO	Av. rate/TO h^{-1}
Acetophenone	1-Phenylethanol	5	31	65	780
		29	94	197	408
Cyclohexanone	Cyclohexanol	10	24	50	300
		60	99	209	209
2-Adamantanone	2-Adamantanol	10	7	15	90
		180	99	209	70
Benzophenone	Diphenylmethanol	11	59	124	676
		60	96	202	202
2-Decanone	2-Decanol	12	42	88	440
		71	94	202	171

[a] General conditions: 10.0 µmol **1** in 2.0 mL of 2-propanol refluxed for 30 min under argon, 2.1 mmol substrate and 200 µmol NaOH in 3 mL 2-propanol added anaerobically, and reaction refluxed. [b] Yields were measured by GC-FID with a HP-5 column of 30 m length, 0.32 mm diameter, and 0.25 µm film thickness except for those from 2-adamantanone that were measured with a HP-Wax column of 30 m length, 0.32 mm diameter, and 0.25 µm film thickness.

oxygen oriented toward the pyridonato oxygens.[4] The short O–O distances between the aquo ligand and the pyridonato oxygens [2.558(5) and 2.543(4) Å] and the large O–H–O angles [154(5) and 173(6)°] suggest hydrogen bonding between these ligands. As a result of being constrained by these interactions, the pyridonato rings appear eclipsed with a dihedral angle of only 1° between their least square planes.§ Overall, complex **1** represents the first example of monodentate κ*N* bound pyridonato ligands on ruthenium and provides a verification of the ligand ring structure in such complexes.¶ The structure reported here also presents an interesting mode of intramolecular hydrogen bonding that appears to have an important influence on the structure and stability of this complex. In the few reported κ*N* pyridonato platinum and cobalt complexes these ligands are also *cis* to hydrogen bond donors and exhibit intermolecular hydrogen bonds.[2a,c,d] This structural motif may be applicable as a design strategy to stabilize κ*N* binding of pyridonato ligands in other systems.

In addition to its structural novelty, complex **1** was found to catalyze the reduction of ketones by 2-propanol (Table 1). In the reduction of acetophenone, total turnover numbers have been observed to exceed 1000 with little to no indication of catalyst degradation. Surprisingly, this system also reduces ketones with significant steric bulk (such as 2-adamantanone). Cyclohexene and styrene, however, are not reduced by this system, and excess cyclohexene does not impede the reduction of acetophenone. This reactivity suggests **1** could be used for selective reductions. Though several catalytic systems have been reported to support transfer hydrogenation of ketones, complex **1** is novel for its saturated hard donor coordination environment.[5] This is in contrast to more familiar catalytic systems that incorporate soft ligands and often require *in situ* preparation. Complex **1** could represent a new family of transfer hydrogenation catalysts supported by hard donor ligand sets and/or κ*N* bound pyridonates. The scope and mechanism of the catalytic activity of **1** are currently under investigation.

Acknowledgements

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Notes and references

† Synthesis of **1**·$0.5H_2O$: Solid (terpy)$RuCl_3$ (0.79 g, 1.79 mmol) was added to a solution of 2-hydroxypyridine (28 mM, 300 cm^3, 8.3 mmol) in absolute ethanol, and the suspension was stirred at reflux for 1 hour. A solution of NaOH (300 mM, 150 cm^3, 45 mmol) in water was added, and the suspension was stirred at reflux for another 2 hours. The solution was filtered while hot, and the filtrate was reduced to 50 cm^3 volume by rotoevaporation to afford purple crystals of **1**·0.5 H_2O (0.71 g, 73%), (Found: C, 55.03; H, 4.26; N, 12.44%. $C_{25}H_{22}N_5O_{3.5}Ru$ requires C, 54.64; H, 4.04; N, 12.74%); λ_{max}/nm (acetone) 365 (ε/dm^3 mol^{-1} cm^{-1}, 16 900), 526 (6940); $\tilde{\nu}_{max}$/cm^{-1} (in KBr) 3423m, 3067w, 1606s, 1537m, 1479s, 1446s, 1377w, 1360w, 1278s, 1148w, 1114w, 1037w, 1009m, 972w, 846m, 765s, 741m, 646w, 579w, 528m; δ_H(200 MHz; solvent acetone-d_6) 9.24 (2 H, d, *J* 5.0 Hz), 8.48 (4 H, m), 7.92 (2 H, td, *J* 7.8 and 1.6 Hz), 7.75 (1 H, t, *J* 8.0 Hz), 7.59 (2 H, m), 6.75 (2 H, m), 5.97 (2 H, br s), 5.74 (2 H, m), 5.43 (2 H, td, *J* 6.1 and 0.8 Hz).

‡ Crystal data for **1**·$(CH_3)_2CO\cdot H_2O$: $C_{28}H_{29}N_5O_5Ru$, dark purple prism, 0.2 × 0.2 × 0.09 mm, $M = 616.64$, triclinic, $a = 9.6425(2)$, $b = 16.5602(5)$, $c = 18.7869(6)$ Å, $\alpha = 65.1871(12)$, $\beta = 89.7847(18)$, $\gamma = 89.3632(18)°$, $U = 2722.81(13)$ Å^3, $T = 200$ K, space group $P\bar{1}$ (no. 2), $Z = 4$, μ(Mo-Kα) = 0.623 cm^{-1}, 19324 reflections measured, 16393 unique ($R_{int} = 0.032$), final $R_1 = 0.0518$ for 11652 [$I > 2.0\sigma(I)$] observed reflections, $wR_2 = 0.1081$ (based on F^2) for all unique reflections using the SHELXL-97 program package.[6] Axial photographs along the *a*-axis did not show a mirror image. The angles β and γ are close to 90° an indication of a pseudo monoclinic structure, but systematic absences were consistent with the compound having crystallized in the triclinic space group $P\bar{1}$. The placement of ruthenium atoms suggests a higher space group with pseudo-*a* centering and an apparent glide plane, but the ligands do not conform to this symmetry. Intensity data were collected on a Nonius KappaCCD diffractometer equipped with Mo-Kα radiation ($\lambda = 0.71073$ Å). Ten frames of data were collected with an oscillation range of 1 deg/frame and an exposure time of 20 sec/frame.[7] CCDC reference number 186/2197. See http://www.rsc.org/suppdata/dt/b0/b007041f/ for crystallographic files in .cif format.

§ Each molecule of **1** appears paired with a counterpart in an adjacent asymmetric unit *via* hydrogen bonds to bridging waters of solvation. The acetone of solvation has no apparent role in hydrogen bonding.

¶ Among the few reported κ*N* pyridonato complexes, the ligand bond distances were crystallographically determined only for *mer*-[Pt-$(NH_3)_2(NC_5H_4O$-κ*N*)Cl_3].[2d] In the case of *trans*-[$(CH_3NH_2)_2Pt(C_5H_4$-NO-κ*N*)(C_5H_5NO-κ*N*)](NO_3) ambiguity in the proton placement resulted in the ring geometries being between those of a 2-pyridonato and a neutral 2-hydroxypyridine.[2a] Crystallographic difficulties with *cis*-$(PMe_3)_4Os(H)(NC_5H_4O$-κ*N*) required that the ring C–C distances be fixed to a constant value, and the nature of the coordinated 2-pyridonato in [$(NH_3)_5Co(NC_5H_4O$-κ*N*)]$(ClO_4)_2\cdot H_2O$ was deduced spectroscopically.[2b,c]

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