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2,6-Dipyrazinylpyridines and Their Ruthenium(II) Complexes: A New Polynucleating Ligand Family

Rocco Liegghio, Pierre G. Potvin,* and A. B. P. Lever*

Department of Chemistry, York University, 4700 Keele Street, Toronto, ON, Canada M3J 1P3

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Ruthenium complexes have been explored as photosensitizers and photocatalysts[1] and, more recently, as electrocatalysts.[2] The ligands used include polypyridines,[3,4] polypyrimidines,[5,6] polypyrazines,[6] dipyridinylpyrimidine,[7] dipyridinylpyrazine,[4,6,8,9] dipyrimidinylpyridine,[10] and tetrapyridinylpyrazine.[3] Some of these are polynucleating and have served in supramolecular constructs,[11] but most reports concern monometallic species with a limited number of electrons that can be mobilized.[8] Multiple-electron reductions are desirable, for instance in CO_2 reduction, to avoid the significant overpotentials associated with single-electron reductions.[12] 2,6-Dipyrazinylpyridines (Figure 1), curiously missing from the literature, are attractive in that they can potentially link three metals, allowing reactivity at the central core to be tuned and also providing an additional source or sink of electrons for multielectron catalysis. They also represent an important new gateway into supramolecular chemistry via linkage of additional metal−ligand units to the peripheral pyrazine nitrogen atoms. This pathway can also clearly lead to dendrimer formation. We report a one-step synthesis of such a ligand and the assembly of mono- and polymetallic complexes therefrom.

All attempts to make a ligand of this type using conventional routes to terpyridines failed, yielding instead only higher condensation products.[13] However, modified Chichibabin conditions (Scheme 1) provided, in one step, 4-*p*-tolyl-2,6-di(2-pyrazinyl)pyridine (L) in 84% isolated yield. We have successfully applied this process to the syntheses of the 4-(4-*tert*-butylphenyl) and 4-(4-hydroxyphenyl) analogues.[14] NMR, EI-MS, elemental analysis, and X-ray crystallographic analysis[15] (Figure 2) confirmed the structure of the L ligand.

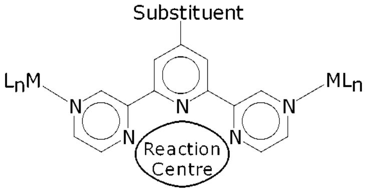
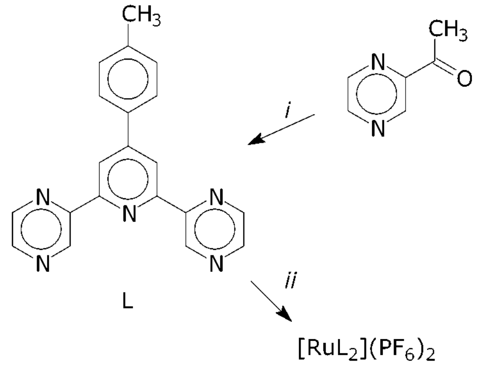


Figure 1. Tuning a reaction center with a dipyrazinylpyridine ligand.

Scheme 1 [a]



[a] Conditions: (i) 0.5 equiv of *p*-tolualdehyde, excess NH_4OH, 1:1 CH_3OH−5% KOH/room temperature/9 h, (ii) 0.5 equiv of $Ru(DMSO)_4Cl_2$, 1,2-ethanediol/reflux/16 h, then excess aqueous NH_4PF_6.

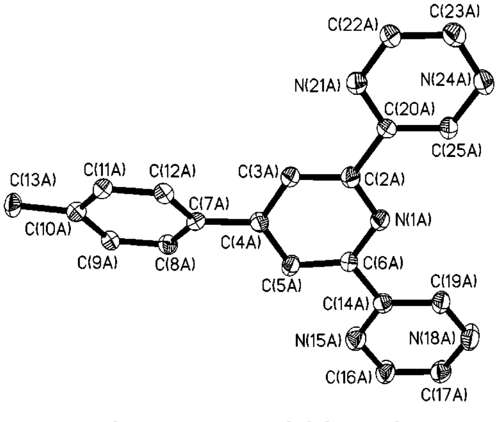


Figure 2. ORTEP drawing at 30% probability, with H atoms omitted, of one of two crystallographically distinct molecules in the crystal structure of L.

$[RuL_2](PF_6)_2$ was prepared by reaction of L with $Ru(DMSO)_4Cl_2$[16] (Scheme 1) in quantitative yield after recrystallization (hot CH_3CN/Et_2O). NMR, MALDI-MS, and X-ray crys-

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(15) $C_{20}H_{15}N_5$: *M* 325.37, triclinic, $a = 9.2990(4)$ Å, $b = 10.7650(4)$ Å, $c = 17.6110(9)$ Å, $\alpha = 102.400(3)°$, $\beta = 95.362(2)°$, $\gamma = 111.857(3)°$, $V = 1568.52(12)$ Å^3, $T = 150(2)$ K, space group $P\bar{1}$ (No. 2), $Z = 4$, μ(Mo K_α) $= 0.086$ mm^{-1}; 7009 unique reflections [$R_{int} = 0.032$]; $R_w(F^2) = 0.1443$ (all data), $R = 0.0997$ (all data), 0.0553 ($I > 2\sigma(I)$).

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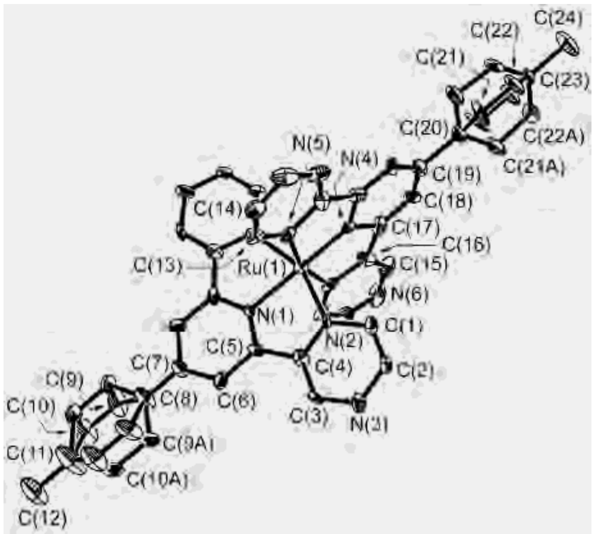

Figure 3. ORTEP drawing at 50% probability of the cation in the crystal structure of $[RuL_2](PF_6)_2{\cdot}2CH_3CN$, with H atoms omitted for clarity. Unlabeled atoms are symmetry related to labeled ones, and both phenyl rings are disordered. Selected bond lengths (and esd's): Ru(1)−N(1) 2.065(9) Å, Ru(1)−N(2) 2.066(7) Å, Ru(1)−N(4) 1.891(10) Å, Ru(1)−N(5) 2.074(7) Å.

tallography[17] (Figure 3) confirmed its structure. The Ru−N bond lengths averaged 1.98 Å to the pyridine nitrogen atoms and 2.07 Å to the pyrazine nitrogen atoms, i.e., entirely within the ranges found in terpyridine complexes.[18] The MLCT band of $[RuL_2](PF_6)_2$ at 498 nm (ϵ 1.66 × 10^5 M^{-1} cm^{-1}) was typical of species of this class. In the solid state, it emitted weakly at room temperature near 667 nm ($\tau = 18$ ns), albeit more strongly than did the terpyridine analogue $[Ru(ttpy)_2]^{2+}$ ($\tau = 0.95$ ns at 640 nm,[19] ttpy is 4′-*p*-tolyl-2,2′:6′,2″-terpyridine), intensifying to a strong structured emission at 77 K with a peak at 685 nm and a shoulder at 654 nm ($\tau = 697$ ns). This is evidently phosphorescence from the lowest lying MLCT state. The cyclic voltammogram consisted of a reversible $Ru^{III/II}$ couple (1.62 V vs SCE), and three reduction steps (−0.83, −1.04, and ca. −1.3 V vs SCE), all at more positive potentials than with $[Ru(ttpy)_2](PF_6)_2$,[20] owing to the electron-withdrawing effect of the pyrazine rings. We have also prepared[14] $RuL(CO)Cl_2$, its 4-octyloxyphenyl analogue, and $[RuL(CO)_2Cl]Cl$ as 2,6-dipyrazinylpyridine analogues of the known terpyridine complexes.[21]

An important feature of this new ligand family is the ability to bind other Lewis acids at the peripheral nitrogen atoms.[22] $[RuL_2](PF_6)_2$ was titrated with aqueous $Na_3[Fe(CN)_5NH_3]$, whose NH_3 ligand is labile under these conditions (Figure 4). UV−visible spectroscopy showed a new Fe-to-pyrazine charge-transfer band[22] near 720 nm. In the ^1H NMR spectrum, 1 equiv of $Na_3[Fe(CN)_5NH_3]$ caused a split of the aromatic signals into 1:2:1 (or, by fortuitous overlap, 1:3) clusters, as the unsymmetrical $[RuL(LFe(CN)_5)]^-$ formed exclusively and quantitatively. Further addition of $[Fe(CN)_5(NH_3)]^{3-}$ led to mixtures of pentacyanoferrated adducts, which are currrently being examined. $RuL(CO)Cl_2$ could likewise be titrated. The electrocatalytic and supramolecular properties of this new versatile ligand are being explored.

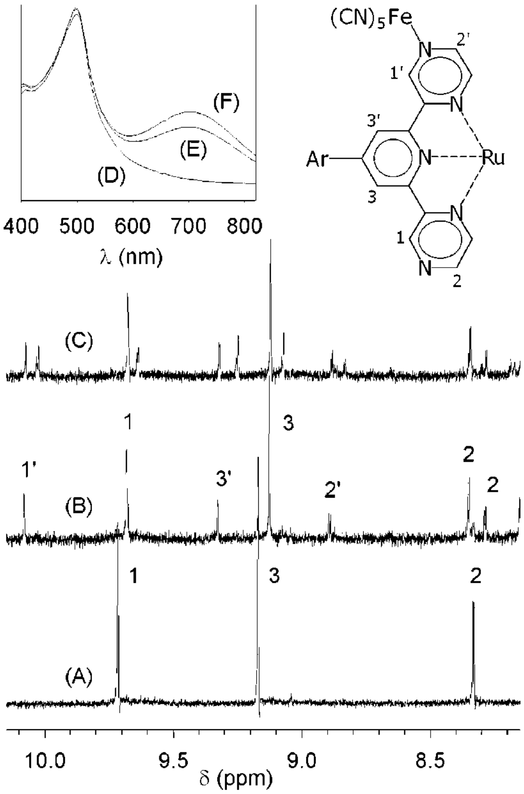

Figure 4. ^1H NMR spectra (600 MHz, 1:1 CD_3CN-D_2O) of $[RuL_2](PF_6)_2$ titrated with (A) 0, (B) 0.9, and (C) 2.7 equiv of $Na_3[Fe(CN)_5NH_3]$. Inset: UV−visible spectra (1:1 CH_3CN-H_2O) using (D) 0, (E) 1, and (F) 3 equiv of Fe.

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Supporting Information Available: Crystallographic data in CIF format for L and $[RuL_2](PF_6)_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) $C_{40}H_{30}F_{12}N_{10}P_2Ru{\cdot}2CH_3CN$, M 1123.86, tetragonal, $a = b = 12.1640(2)$ Å, $c = 61.5970(12)$ Å, $\alpha = \beta = \gamma = 90°$, $V = 9114.1(3)$ Å^3, $T = 293(2)$ K, space group $I4_1/a$:2 (No. 88), $Z = 8$, μ(Mo K$_\alpha$) = 0.513 mm^{-1}; 5204 unique reflections [$R_{int} = 0.0457$]; $R_w(F^2) = 0.2224$ (all data), $R = 0.1699$ (all data), 0.0916 ($I > 2\sigma(I)$).

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