

Mononuclear Rhodium(II) and Iridium(II) Complexes Supported by Tetradentate Pyridinophane Ligands

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Supporting Information

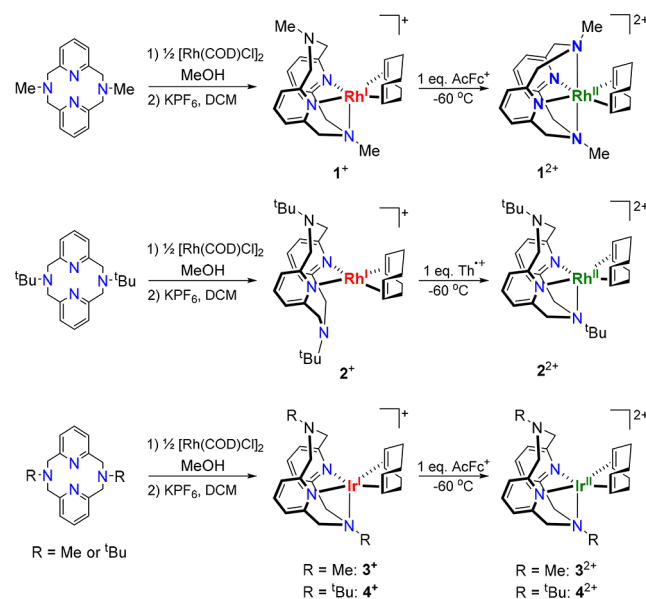
ABSTRACT: The tetradentate ligands *N,N'*-dialkyl-2,11-diaza[3,3](2,6)pyridinophane (^RN₄, where R = Me or *t*Bu) were employed to synthesize and fully characterize [(^RN₄)M^I(COD)]⁺ complexes (M = Rh or Ir; COD = cyclooctadiene). Interestingly, these complexes exhibit accessible oxidation potentials and can generate detectable [(^RN₄)M^{II}(COD)]²⁺ complexes, which were characterized by electron paramagnetic resonance and high-resolution electrospray ionization mass spectrometry. Moreover, a rare mononuclear [(^{Me}N₄)Rh^{II}(COD)]²⁺ complex was isolated and crystallographically characterized, allowing for a direct comparison with its rhodium(I) analogue. The detailed characterization of such paramagnetic rhodium(II) and iridium(II) complexes enables further investigation of their redox reactivity.

Rhodium and iridium complexes have received much attention for their use in a wide range of chemical transformations, including C–C^{1,2} and C–H^{3–11} bond activation and hydrogen-atom-transfer reactions.^{12,13} In these reactions, paramagnetic Rh and Ir centers could play an important role; however, isolated and well-characterized monomeric species in the 2+ oxidation state are rare compared to their 1+ and 3+ counterparts. Multidentate ligands have been found to successfully stabilize these less accessible rhodium(II) and iridium(II) species.^{14–24} While rhodium(II) complexes are more often encountered as bimetallic species with bridging ligands and metal–metal bonds,²⁵ various ligands such as porphyrin-based ligands,^{26,27} a *N,N*-bis(2-pyridylmethyl)amine ligand, and pincer ligands have been used to stabilize mononuclear rhodium(II) species.^{2,13,17,22,28–31} Within this list of complexes, it is rare to find an octahedral monomeric rhodium(II) complex chelated by a tetradentate ligand.^{19,20} Herein we report the use of ^{Me}N₄ and ^{tBu}N₄ pyridinophane ligands to isolate and full characterize mononuclear Rh^I/Ir^I(COD) complexes, as well as a rare mononuclear (^{Me}N₄)Rh^{II} complex. The isolation of these complexes allows a direct structural and spectroscopic comparison of group 9 complexes that possess similar geometries and ancillary ligands.

The ^{Me}N₄ and ^{tBu}N₄ ligands were synthesized using previously reported procedures.³² The addition of [M(COD)Cl]₂ (M = Rh or Ir) to ^RN₄ (R = Me or *t*Bu) led to the isolation of yellow [^{Me}N₄Rh(COD)]PF₆ (**1**⁺),³³ [^{tBu}N₄Rh(COD)]PF₆ (**2**⁺), [^{Me}N₄Ir(COD)]PF₆ (**3**⁺), and [^{tBu}N₄Ir(COD)]PF₆ (**4**⁺) in

88%, 82%, 91%, and 85% yield, respectively (Scheme 1). Complexes **2**⁺–**4**⁺ were structurally characterized by X-ray

Scheme 1. Synthesis of (^RN₄)Ir(COD) and (^RN₄)Rh(COD) Complexes (Th^{•+} = Thianthrenyl)



crystallography, while **1**⁺ has been previously characterized by Gal et al. to reveal a square-pyramidal geometry at the Rh center.³³ By comparison, the X-ray structure of **2**⁺ reveals a square-planar geometry of the Rh center, which is bound to the two pyridyl N atoms and the COD ligand (Figure 1). The structures of **3**⁺ and **4**⁺ both reveal a distorted square-pyramidal geometry of the Ir centers, which are bound to two pyridyl N atoms and the COD ligand in the equatorial plane and one amine N donor in the axial position.

When compared to the iridium complex **3**⁺, the square-pyramidal rhodium complex **1**⁺ exhibits increased M–N bond lengths. This can be attributed to the increase in the coordination number, leading to increased steric effects from a four-coordinate geometry to a five-coordinate geometry (Figure 1). Contrary to the other five-coordinate complexes, the rhodium(I) complex **2**⁺ is forced into its square-planar geometry because of the presence

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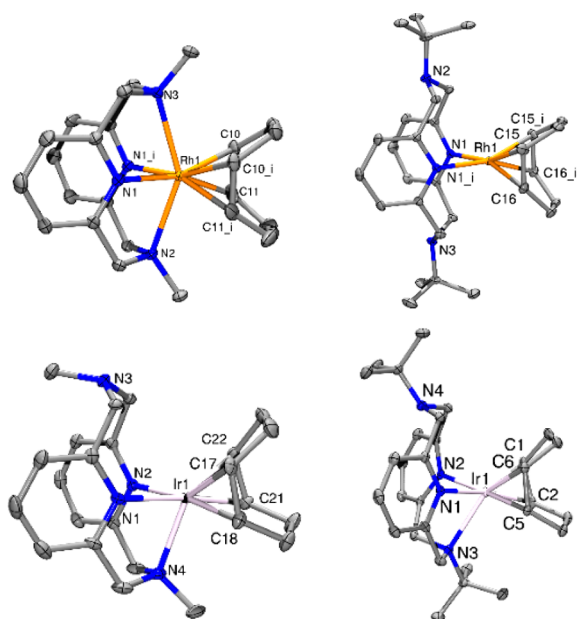


Figure 1. ORTEP representation (50% probability ellipsoids) of the cations of $[1^{2+}](\text{BF}_4)_2$ (top left), $[2^+]\text{PF}_6$ (top right), $[3^+]\text{PF}_6$ (bottom left), and $[4^+]\text{PF}_6$ (bottom right). Selected bond distances (Å) and angles (deg): 1^{2+} , Rh1–C10i 2.189(2), Rh1–C11i 2.199(3), Rh1–N1 2.091(2), Rh1–N2 2.447(3), Rh1–N3 2.459(3), N1–Rh1–N3 76.46(7), N1–Rh1–N2 77.11(7), N1i–Rh1–N1 78.48(1); 2^+ , Rh1–C16 2.142(2), Rh1–C15 2.148(2), Rh1–N1 2.123(1), N1–Rh1–C16 160.67(6), N1–Rh1–N1i 76.91(7); 3^+ , Ir1–C18 2.083(4), Ir1–C17 2.104(4), Ir1–N2 2.146(3), Ir1–N1 2.162(3), Ir1–N4 2.286(3), N2–Ir1–N4 77.93(12), N1–Ir1–N4 78.36(12), N1–Ir1–N2 76.50(11); 4^+ , Ir1–C5 2.091(2), Ir1–C6 2.097(2), Ir1–C1 2.130(2), Ir1–C2 2.148(2), Ir1–N1 2.1023(2), Ir1–N2 2.203(2), Ir1–N3 2.461(2), N1–Ir1–N3 75.05(5), N2–Ir1–N3 75.44(5), N1–Ir1–N2 82.99(5).

of the bulky *t*Bu N-substituents and the COD ligand, as well as the decrease in the ionic radius from iridium to rhodium. Interestingly, similar five-coordinate iridium complexes are more commonly chelated by phosphorus-based ligands, such as PNP, PCP, POCOP, PBP, or PSiP pincer ligands,^{34–43} and are rarely stabilized by N-donor ligands.^{44,45}

Both iridium complexes 3^+ and 4^+ have square-pyramidal geometry, but there are structural variances due to differences in alkyl N-substituents. The increased steric bulk of the *t*BuN4 ligand leads to the Ir–N_{axial} bond being elongated by 0.175 Å from 3^+ to 4^+ . There is also a greater bending of the alkyl substituent from 3^+ to 4^+ , with the N2–Ir1–N4–C16 dihedral angle for 3^+ being greater than the N2–Ir1–N3–C23 angle for 4^+ by 27.9°, a change that is apparent in the side view of 4^+ .³² This bending of the alkyl substituent also minimizes the distance between the *t*Bu group and the COD ligand, leading to a skewed orientation of the COD ligand in 4^+ compared to the more symmetric COD in 3^+ .³² In addition, the four-coordinate 2^+ shows minimal distortion of the COD ligand, while the five-coordinate structure of 1^+ reveals that the binding of a single axial N causes a distortion in the COD ligand.^{32,33}

The cyclic voltammograms (CVs) of 1^+ and 2^+ in 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6)/acetonitrile (MeCN) exhibit irreversible oxidation waves at $E_{\text{pa}} \approx 0.08$ V versus ferrocene/ferrocenium (Fc^+/Fc) for 1^+ and $E_{\text{pa}} \approx 0.43$ V versus Fc^+/Fc for 2^+ , which are tentatively assigned to the $\text{Rh}^{\text{I/II}}$ redox couples (Figures 2 and S6).³² As predicted for 2^+ , we observe higher oxidation potentials with an increase in steric bulk

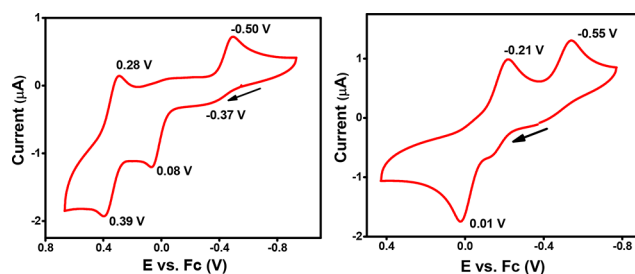


Figure 2. CVs of 1^+ (left) and 3^+ (right) in 0.1 M $\text{Bu}_4\text{NClO}_4/\text{MeCN}$ (100 mV/s).

from MeCN_4 to tBuN_4 , as seen previously with $(^R\text{N}_4)\text{PdMe}_2$ and $(^R\text{N}_4)\text{PdMeCl}$ complexes.⁴⁶ Interestingly, 1^+ exhibits two oxidation processes at -0.37 and $+0.08$ V versus Fc^+/Fc , and both are tentatively assigned to $\text{Rh}^{\text{I/II}}$ couples that correspond to two different conformations of 1^+ in which the MeCN_4 ligand can adopt either a κ^4 or κ^3 binding mode, respectively.⁴⁷ This assignment was confirmed by variable-scan-rate CVs, where, upon an increase in the scan rate from 10 mV/s to 2 V/s, the ratio of the peak currents I_{pa} for the oxidation waves at -0.37 V decreased and at $+0.08$ V increased significantly. This observation, in addition to the presence of a single cathodic potential, supports our assignment of the anodic potential at -0.37 V as the oxidation of the minor conformer $[(\kappa^4\text{-MeCN}_4)\text{-Rh}(\text{COD})]^+$ that is expected to exhibit a lower oxidation potential, similar to what was observed previously for $(^R\text{N}_4)\text{Pd}$ complexes.⁴⁶

The mononuclear rhodium(II) complex 1^{2+} was isolated in 67% yield following the addition of 1 equiv of $(^A\text{Fc}^+)\text{BF}_4$ to 1^+ in MeCN at -60 °C. Structural characterization of $[1^+](\text{BF}_4)_2$ confirms the presence of a Rh^{II} center with a distorted octahedral geometry (Figure 1), with the axial Rh–N bonds tilted toward the ligand. Compared to the rhodium(I) analogue 1^+ ,³³ the equatorial Rh–N and axial Rh–N bonds in 1^{2+} are shortened by 0.276 and 0.245 Å, respectively. Further evidence for a monomeric rhodium(II) complex was obtained using the Evans method, which revealed a magnetic moment of $1.896 \mu_{\text{B}}$ for 1^{2+} . This value suggests a complex with a single unpaired electron and is comparable to those reported for monomeric $(\text{PNP})\text{Rh}^{\text{II}}$ complexes.^{17,18} Moreover, the electron paramagnetic resonance (EPR) spectrum for 1^{2+} reveals an anisotropic signal with $g_{\text{ave}} = 2.100$ corresponding to a $\text{Rh}^{\text{II}} d^7$ metal center with a d_z^2 ground state. The quintet superhyperfine coupling in the g_z region ($A_{2\text{N}} = 20.8$ G) is attributed to interaction with the two axial N donors ($I = 1$), suggesting that the octahedral geometry of 1^{2+} is maintained in solution (Figure 3).

Because of the higher $\text{Rh}^{\text{I/II}}$ oxidation potential observed for 2^+ , the use of a stronger one-electron oxidant, thianthrenyl tetrafluoroborate (Th^+BF_4), was needed to generate the rhodium(II) species $[(^t\text{BuN}_4)\text{Rh}^{\text{II}}(\text{COD})]^{2+}$ (2^{2+}), which can be characterized by EPR. The spectrum reveals a rhombic signal with $g_{\text{ave}} = 2.411$, hyperfine coupling to the Rh metal center ($A_{\text{Rh}} = 16$ G; $I = 1/2$), and superhyperfine coupling to the single axial N donor ($A_{\text{N}} = 23$ G; $I = 1$) in the z direction, suggesting a square-pyramidal $\text{Rh}^{\text{II}} d^7$ center in a d_z^2 ground state (Figure 3). However, 2^{2+} is temperature-sensitive, and its EPR signal disappears within seconds at room temperature likely due to a disproportionation reaction.³² A similar spectrum exhibiting (super)hyperfine couplings to the metal and the axial N donor was observed for $[(\text{Bn-dla})\text{Rh}(\text{COD})]^{2+}$ [$\text{Bn-dla} = N$ -benzyl- N,N -bis(6-methyl-2-pyridylmethyl)amine] by de Bruin et al.¹³

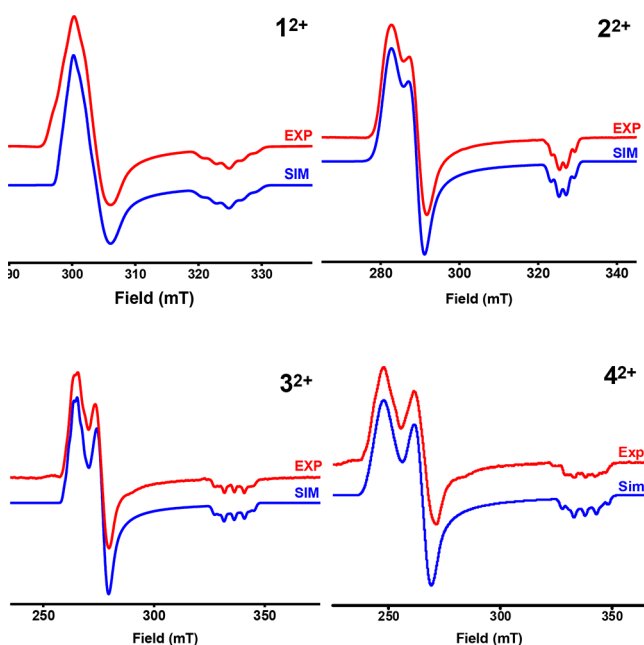


Figure 3. Experimental (1:3 MeCN:PrCN glass, 77K) and simulated EPR spectra of 1^{2+} (top, left), 2^{2+} (top, right), 3^{2+} (bottom, left), and 4^{2+} (bottom, right). The following parameters were used for simulations: 1^{2+} , $g_x = 2.165$ ($A_{2N} = 9.2$ G, $A_{Rh} = 4.5$ G); $g_y = 2.136$ ($A_{2N} = 10.5$ G, $A_{Rh} = 3$ G); $g_z = 2.000$ ($A_{2N} = 20.8$ G, $A_{Rh} = 7$ G); 2^{2+} , $g_x = 2.998$ ($A_N = 11$ G, $A_{Rh} = 14$ G); $g_y = 2.243$ ($A_N = 9$ G, $A_{Rh} = 20$ G); $g_z = 1.990$ ($A_N = 20$ G, $A_{Rh} = 14$ G); 3^{2+} , $g_x = 2.456$ ($A_{2N} = 19$ G, $A_{Ir} = 8$ G); $g_y = 2.346$ ($A_N = 13$ G, $A_{Ir} = 6$ G); $g_z = 1.933$ ($A_N = 21$ G, $A_{Ir} = 46$ G); 4^{2+} , $g_x = 2.604$ ($A_{2N} = 27$ G, $A_{Ir} = 10$ G); $g_y = 2.429$ ($A_{2N} = 19$ G, $A_{Ir} = 19$ G); $g_z = 1.911$ ($A_{1N} = 28$ G, $A_{Ir} = 50$ G).

Similar to complexes 1^+ and 2^+ , the CVs of 3^+ and 4^+ in 0.1 M $Bu_4NPF_6/MeCN$ exhibit an increase in the oxidation potential with increasing steric bulk.³² The CVs of 3^+ and 4^+ in 0.1 M $Bu_4NPF_6/MeCN$ exhibit irreversible oxidation waves at $E_{pa} \approx 0.01$ and 0.26 V versus Fc^+/Fc for the $Ir^{I/II}$ redox couple, respectively (Figures S7 and S8). In addition, these CVs exhibit similar trends, where the intensity of the $Ir^{I/II}$ oxidation and corresponding reductive waves may suggest a disproportionation reaction. For complex 3^+ , the reductions at $E_{pc} \approx -0.21$ and -0.55 V are likely $Ir^{III/II}$ and $Ir^{II/I}$ reductive waves, respectively, and both waves are half the intensity of the oxidative wave at $E_{pa} \approx 0.01$ V, suggesting that the iridium(II) complex may disproportionate to form a 1:1 ratio of iridium(I)/iridium(II) species in solution.³² Given this observed behavior, the isolation of such iridium(II) species was attempted but proved difficult possibly because of a rapid disproportionation reaction.

One-electron oxidation of complexes 3^+ and 4^+ with 1 equiv of $(^AcFc^+)BF_4$ generates the iridium(II) species $[(^{Me}N_4)Ir(COD)]^{2+}$ (3^{2+}) and $[(^{tBu}N_4)Ir(COD)]^{2+}$ (4^{2+}). The EPR spectra of 3^{2+} and 4^{2+} reveal rhombic signals corresponding to a $Ir^{II} d^7$ metal center with a d_{z^2} ground state and $g_{ave} = 2.245$ – 2.315 (Figure 3),³² along with strong hyperfine coupling to the Ir metal center ($A_{Ir} = 46$ – 50 G; $I = 3/2$) and superhyperfine coupling to the single axial N donor ($A_{1N} = 21$ – 28 G; $I = 1$) in the z direction, which suggests a square-pyramidal geometry for the iridium(II) species. This coupling pattern has also been observed for iridium(II) complexes with similar geometry, as reported by de Bruin et al.^{13,28} The reason that the iridium complex 3^{2+} has a square-pyramidal geometry while the rhodium complex 1^{2+} has an octahedral geometry may be due to the larger ligand-field-

splitting parameter for iridium versus rhodium, which leads to a more preferred square-pyramidal geometry for iridium and thus a lower d_{z^2} orbital. The EPR signals for both 3^{2+} and 4^{2+} disappear within minutes at room temperature, proving that it is difficult to isolate these paramagnetic species for structural characterization.

Preliminary reactivity studies have focused on the aerobic oxidation of complexes 1^+ – 4^+ in O_2 -saturated CD_3OD solutions; however, no reactions were observed by 1H NMR or EPR after 24 h. The reactivity of 3^+ was also studied by Gal et al., which showed that, upon reaction with excess H_2O_2 in the presence of 1 equiv of acid, an oxocyclooctenyl complex, $[^{Me}N_4Ir^{III}(C_8H_{11}O)]^{2+}$, was formed.³³ However, no reaction was observed when either 1^+ , 2^+ , or 4^+ was reacted with excess H_2O_2 in the absence or presence of acid, with only the corresponding protonated ligand being observed instead under acidic conditions. Overall, the COD ligand seems to stabilize to a great extent these Rh^I/Ir^I centers toward oxidation, and thus it is expected that the use of a more labile ligand (such as cyclooctene or even solvent molecules) could enable further reactivity studies of such rhodium/iridium complexes.

In conclusion, we have isolated and characterized $Ir^I(COD)$ and $Rh^I(COD)$ complexes stabilized by the tetradentate ligands $^{Me}N_4$ and $^{tBu}N_4$. The isolation of these complexes allowed for a direct structural comparison between the two different ligands, as well as between the Rh and Ir centers. CV and EPR studies provided evidence for the formation of paramagnetic rhodium(II) and iridium(II) species. Moreover, a rare mononuclear rhodium(II) complex 1^{2+} was accessible in high yields and was further characterized by X-ray diffraction. Our current research efforts are focused on probing in more detail the reactivity of such rhodium(II)/iridium(II) complexes, including their organometallic chemistry and their potential catalytic applications.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.7b01619.

Text, tables, and figures giving crystallographic, experimental, and spectroscopic data (PDF)

Accession Codes

CCDC 1558232–1558235 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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