

Molecule-Bridged Mixed-Valent Intermediates Involving the Ru^I Oxidation State

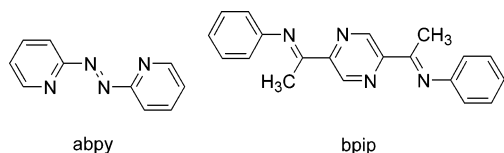
Biprajit Sarkar,[†] Wolfgang Kaim,^{*,†} Jan Fiedler,[‡] and Carole Duboc[§]

Institut für Anorganische Chemie, Universität Stuttgart, Pfaffenwaldring 55, D-70550 Stuttgart, Germany, J. Heyrovský Institute of Physical Chemistry, Dolejškova 3, CZ-182 23 Prague 8, Czech Republic, and Grenoble High Magnetic Field Laboratory, MPI-CNRS, 25, Avenue des Martyrs, BP 166, F-38042 Grenoble Cedex 9, France

Received June 18, 2004; E-mail: kaim@iac.uni-stuttgart.de

In contrast to the vast number of diruthenium(II,III) compounds¹ and to several diruthenium(III,IV) species,² there has been a conspicuous absence of molecule-bridged mixed-valent intermediates with lower oxidation number combinations, such as Ru^IRu^{II} (d⁷/d⁶) or Ru⁰Ru^I (d⁸/d⁷). Metal–metal bonded Ru^IRu^{II} species were reported,³ and the d⁸/d⁷ combination has been detected for ligand-bridged systems involving organometallic Rh^IRh^{II},⁴ Ir^IIr^{II},⁴ and Pt^{II}Pt^{III} arrangements.⁵ The latter three showed only small splittings, $\Delta E < 0.15$ V, of corresponding redox potentials, translating to comproportionation constants $K_c < 10^{2.5}$ ($RT \ln K_c = nF(\Delta E)$).^{4,5} Using areneruthenium(II) complex fragments as precursors,⁶ we report observations made during the reduction of the Ru^{II}Ru^{II} complexes $\{(\mu\text{-L})[\text{RuCl}(\text{Cym})]_2\}(\text{PF}_6)_n$ (Cym = *p*-cymene) with bridging L = 2,2'-azobispyridine = abpy and $n = 1$, or L = 2,5-bis(1-phenyliminoethyl)pyrazine = bpip and $n = 2$. The abpy⁷ and bpip⁸ π acceptor ligands are well characterized, including their different capacity to mediate metal–metal interaction, e.g., in diruthenium(II,III) complexes.^{7–9} The stepwise reduction of the complexes was monitored via cyclic voltammetry, UV–vis–NIR spectroelectrochemistry, and EPR spectroscopy.

The precursor complexes were isolated as the diamagnetic $\{(\mu\text{-bpip})[\text{RuCl}(\text{Cym})]_2\}(\text{PF}_6)_2$ containing only one of two possible (syn or anti) isomers⁴ and as the paramagnetic $\{(\mu\text{-abpy})[\text{RuCl}(\text{Cym})]_2\}(\text{PF}_6)$. The first high-frequency (285 GHz) EPR spectrum of a



ruthenium radical complex was obtained for the latter species at 5 K; the small *g* anisotropy ($g_1 = 1.9990$, $g_2 = 1.9886$, $g_3 = 1.9780$) confirms that an abpy anion radical ligand binds two Ru^{II} centers.

Starting from the dications, cyclic voltammetry reveals an overall reversible E₁EC₁EC₂E sequence for the reduction which has similarly been found for some dirhodium and diiridium complexes (C = reversible Cl[−] dissociation).⁴ The cyclovoltammograms could be simulated as shown in Figure 1.

After the initial E process, the second reduction causes one chloride to dissociate to form a formally Ru^{II}Ru⁰ mixed-valent species as a consequence of ligand-mediated coupling between reaction centers.⁴ The electrochemical analysis of the third (EC) and fourth (E) reduction steps yields potential differences $\Delta E = E_3' - E_3''$ of 120 and 130 mV, respectively, corresponding to K_c values of $10^{2.0}$ and $10^{2.2}$ for the intermediates $\{(\mu\text{-L})[\text{Ru}(\text{Cym})]_2\}^+$,

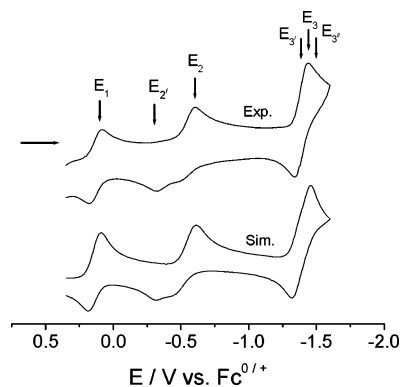


Figure 1. Cyclic voltammogram of the preoxidized complex $\{(\mu\text{-abpy})[\text{RuCl}(\text{Cym})]_2\}(\text{PF}_6)_2$ in $\text{CH}_3\text{CN}/0.1$ M Bu_4NPF_6 at 100 mV/s scan rate (top) with simulation (bottom) involving the following steps (cf. Supporting Information): $\{(\mu\text{-L})[\text{RuCl}(\text{Cym})]_2\}^{2+} \rightarrow \{(\mu\text{-L})[\text{RuCl}(\text{Cym})]_2\}^{+}$ (E₁), $\{(\mu\text{-L})[\text{RuCl}(\text{Cym})]_2\}^{+} \rightarrow \{(\text{Cym})\text{Ru}(\mu\text{-L})\text{RuCl}(\text{Cym})\}^{+} + \text{Cl}^-$ (E₂), $\{(\text{Cym})\text{Ru}(\mu\text{-L})\text{RuCl}(\text{Cym})\}^{+} \rightarrow \{(\mu\text{-L})[\text{Ru}(\text{Cym})]_2\}^{+} + \text{Cl}^-$ (E₃), $\{(\mu\text{-L})[\text{Ru}(\text{Cym})]_2\}^{+} \rightarrow \{(\mu\text{-L})[\text{Ru}(\text{Cym})]_2\}$ (E₃'').

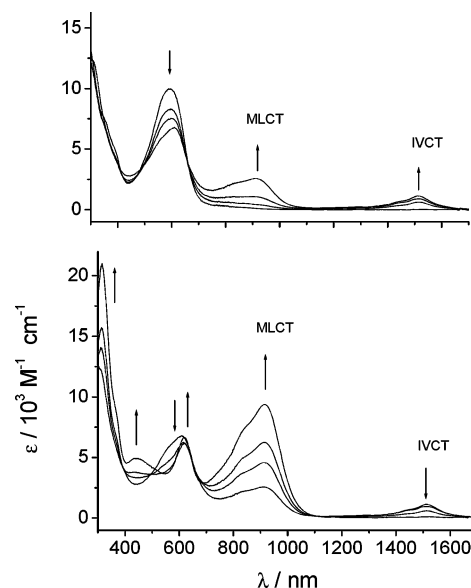


Figure 2. UV–vis–NIR spectroelectrochemical reduction of electrogenerated $\{(\text{Cym})\text{Ru}(\mu\text{-L})\text{RuCl}(\text{Cym})\}^{2+}$ to $\{(\mu\text{-L})[\text{Ru}(\text{Cym})]_2\}^{+}$ and Cl[−] (top), and of $\{(\mu\text{-L})[\text{Ru}(\text{Cym})]_2\}^{+}$ to $\{(\mu\text{-L})[\text{Ru}(\text{Cym})]_2\}$ (bottom) in $\text{CH}_3\text{CN}/0.1$ M Bu_4NPF_6 (L = abpy).

L = abpy or bpip. Typical K_c values for diruthenium(III,II) species with π -accepting bridges are significantly higher; for instance, the related $\{(\mu\text{-abpy})[\text{Ru}(\text{bpy})]_2\}^{3+}$ has $K_c \approx 10^{8.5,9}$.

Spectroelectrochemical monitoring (Figure 2) reveals the emergence of bands in the near-infrared for $\{(\mu\text{-L})[\text{Ru}(\text{Cym})]_2\}^{+}$. Such

[†] University Stuttgart.

[‡] Heyrovsky Institute.

[§] HMFL Grenoble.

absorptions are typical for intervalence charge-transfer (IVCT) transitions.^{1,4,9} We therefore attribute these intense ($\epsilon \approx 1200 \text{ M}^{-1} \text{ cm}^{-1}$) and rather narrow bands ($\Delta\nu_{1/2} \approx 700 \text{ cm}^{-1}$) to a mixed-valent situation, either $[\text{Ru}^{\text{I}}(\mu\text{-L})\text{Ru}^{\text{0}}]^+$ or $[\text{Ru}^{\text{I}}(\mu\text{-L}^{2-})\text{Ru}^{\text{II}}]^+$. While the latter formulation is most likely with the easily reducible L = abpy,⁷ the former description is favored for the complex of bpip.

EPR spectroscopy confirms the predominant metal localization of the spin in paramagnetic $\{(\mu\text{-L})[\text{Ru}(\text{Cym})_2]^+\}$ through large g anisotropies:³ $g_1 = 2.155$, $g_2 = 1.988$, and $g_3 = 1.9585$ (L = abpy) or $g_1 = 2.210$, $g_2 = 2.027$, and $g_3 = 1.958$ (L = bpip).

The stark disagreement between the experimental (ca. 750 cm^{-1}) and the calculated line widths, $\Delta\nu_{1/2}(\text{calc}) = (2310\nu_{\text{IVCT}})^{1/2} \approx 4000 \text{ cm}^{-1}$, according to Hush,¹⁰ suggests a valence-averaged situation.^{1,3}

We attribute the unusually small K_c values and ligand effects to the partial occupation of metal d_σ orbitals³ from the e_g set for d^7 configurations in an approximately octahedral symmetry. In contrast to the efficient acceptor ligand-mediated $d_\pi/\pi^*(\text{L})/d_\pi$ interaction for Ru^{III} ($4d^5$)-containing mixed-valent species, the interaction between d_σ orbitals has to occur through the σ framework of the organic ligand, which apparently does not show great variations. Nevertheless, the observation of the “normal” IVCT features in the near-infrared region illustrates that mixed-valent diruthenium compounds can occur in unconventional configurations, e.g., in low oxidation states involving an organometallic ligand setting.

Acknowledgment. The authors acknowledge support from the DFG, FCI, the European Union, the Grant Agency, and the Ministry of Education of the Czech Republic.

Supporting Information Available: Spectroscopic characterization; tables of electrochemical and absorption data; cyclic voltammograms; EPR and absorption spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) (a) Creutz, C. *Prog. Inorg. Chem.* **1983**, *30*, 1–73. (b) Richardson, D. E.; Taube, H. *Coord. Chem. Rev.* **1984**, *60*, 107–129. (c) Crutchley, R. J. *Adv. Inorg. Chem.* **1994**, *41*, 273–325. (d) Kaim, W.; Klein, A.; Glöckle, M. *Acc. Chem. Res.* **2000**, *33*, 755–763. (e) Demadis, K. D.; Hartshorn, C. M.; Meyer, T. J. *Chem. Rev.* **2001**, *101*, 2655–2686.
- (2) (a) Baumann, J. A.; Meyer, T. J. *Inorg. Chem.* **1980**, *19*, 345–350. (b) Naklicki, M. L.; White, C. A.; Kondratiev, V. V.; Crutchley, R. J. *Inorg. Chim. Acta* **1996**, *242*, 63–69. (c) Hoshino, Y.; Higuchi, S.; Fiedler, J.; Su, C.-Y.; Knödler, A.; Schwederski, B.; Sarkar, B.; Hartmann, H.; Kaim, W. *Angew. Chem., Int. Ed.* **2003**, *42*, 674–677.
- (3) Heck, J.; Lange, G.; Malessa, M.; Boese, R.; Bläser, D. *Chem. Eur. J.* **1999**, *5*, 659–668.
- (4) (a) Kaim, W.; Reinhardt, R.; Fiedler, J. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2493–2495. (b) Berger, S.; Klein, A.; Wanner, M.; Fiedler, J.; Kaim, W. *Inorg. Chem.* **2000**, *39*, 2516–2521.
- (5) Klein, A.; Hasenzahl, S.; Kaim, W.; Fiedler, J. *Organometallics* **1998**, *17*, 3532–3538.
- (6) (a) Kaim, W.; Reinhardt, R.; Sieger, M. *Inorg. Chem.* **1994**, *33*, 4453–4459. (b) Kölle, U.; Görissen, R.; Hörmig, A. *Inorg. Chim. Acta* **1994**, *218*, 33–39.
- (7) Kaim, W. *Coord. Chem. Rev.* **2001**, *219–221*, 463–488.
- (8) Klein, A.; Kasack, V.; Reinhardt, R.; Sixt, T.; Scheiring, T.; Zalis, S.; Fiedler, J.; Kaim, W. *J. Chem. Soc., Dalton Trans.* **1999**, 575–582.
- (9) (a) Kelso, L.-S.; Reitsma, D. A.; Keene, F. R. *Inorg. Chem.* **1996**, *35*, 5144–5153. (b) Ernst, S.; Kasack, V.; Kaim, W. *Inorg. Chem.* **1988**, *27*, 1146–1148. (c) Krejčík, M.; Zalis, S.; Klima, J.; Sykora, D.; Matheis, W.; Klein, A.; Kaim, W. *Inorg. Chem.* **1993**, *32*, 3362–3368.
- (10) Hush, N. S. *Prog. Inorg. Chem.* **1967**, *8*, 391–444.

JA046397E