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Denial of Tris(*C*,*N*-cyclometalated) Ruthenacycle: Nine-Membered η^6-*N*,*N*-*trans* or η^2-*N*,*N*-*cis* Ru^{II} Chelates of 2,2′-Bis(2-pyridinyl)-1,1′-biphenyl

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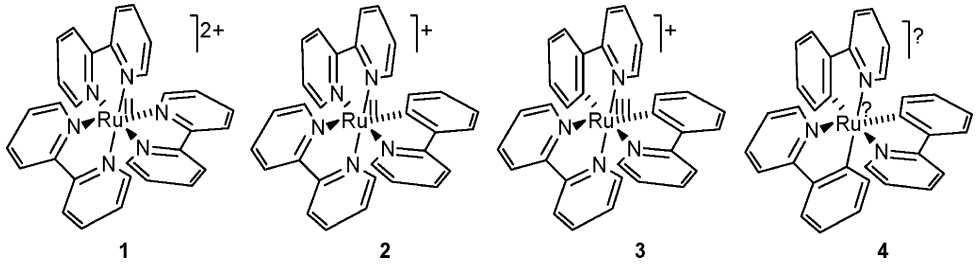
In the attempt to prepare the tris(cyclometalated) ruthenium derivative of 2-phenylpyridine, [Ru(η^6-C_6H_6)(phpy)Cl] was treated with Hg(phpy)$_2$. The anticipated [Ru(phpy)$_3$]$^{n+}$ species was not formed. Instead, the product of oxidative coupling of two 2-(2-pyridinyl)phenyl ligands to form octahedral [Ru^{II}(phpy)(pbp)]PF_6 with pbp = 2,2′-bis(2-pyridinyl)-1,1′-biphenyl was isolated; pbp forms a nine-membered chelate with two N and two η^2-C=C donor centers. The binding of η^2-C=C donor units is weak as they are readily replaced by CO.

Tris(2,2′-bipyridine)ruthenium(II) (**1**, 6*N*/0*C*) was described in 1936.[1] In water, its reduction potential for the $Ru^{III/II}$ transition is 1.24 V vs. NHE.[2] Compound **2**, the 5*N*/1*C* structural analog of **1** with one N-donor replaced by one σ-bound sp^2-carbon atom of 2-phenylpyridine, was prepared in 1986.[3] Its reduction potential in water is 0.524 V.[4] Reported in 2006,[5] the 4*N*/2*C* compound **3** with two sp^2-carbon donors and four bpy-like nitrogen atoms has a potential of ca. 0.0 V vs. NHE, and therefore **3** is an Ru^{III} derivative, though **1** and **2** are Ru^{II} species. Compounds **1**–**3** have numerous applications; those of type **1** species have been reviewed.[6,7] Complexes like **2** and **3** are promising as electron shuttles for mediated enzymatic redox bio-processes.[4,5,8–12] Recently, we became intrigued by the idea of preparing and studying a so far unknown fourth member in the series shown in Scheme 1, i.e. tris(3*N*/3*C*-cyclometalated) compound **4**, which was once postulated and its properties hypothesized.[13]

There were several objectives for this study. The central metal atom of **4** could have an oxidation state as high as 4+, if the above-mentioned trend in changing the reduction potential with composition persists. Tris(cyclometalated) compounds of iridium[14] and rhodium,[15] but not ruthenium, have been known for decades. A series of related molecules such as **1**–**4** is always interesting for fundamental, applied, and/or theoretical investigations. This was an extra stimulus for the attempted synthesis of **4**. The results reported here suggest that a transient compound of type **4** could have been present. We hypothesize that, if formed, the central metal atom could stabilize itself by pushing the "intramolecular" reductive elimination of a pair of cyclometalated *C*,*N*-2-(2-pyridinyl)phenyl ligands to afford complexes **7** incorporating recently reported 2,2′-bis(2-pyridinyl)-1,1′-biphenyl (pbp),[16–18] but this time coordinated to



Scheme 1. A series of structurally similar real (**1**–**3**) and hypothetical (**4**) ruthenium complexes of the [Ru(bpy)$_3$]$^{2+}$ type.

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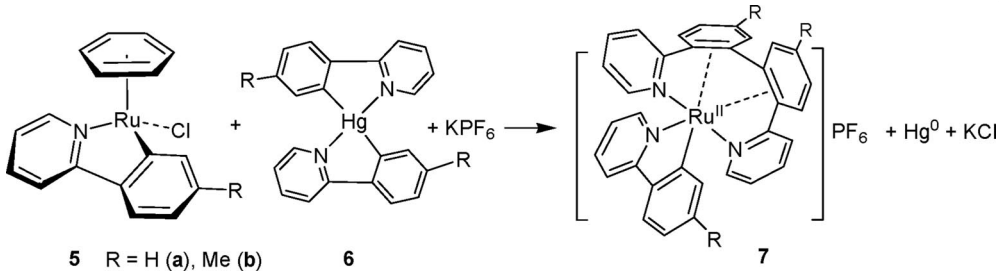
Supporting information for this article is available on the WWW under http://www.eurjic.org or from the author.



Scheme 2. Synthesis of pbp complexes **7**.

Ru^{II} (Scheme 2). The pbp ligand forms a nine-membered cycle and reveals an unusual η^6-tetradentate N/η^2-C=C/η^2-C=C/N coordination with the nitrogen atoms in the *trans* position. The tetradentate coordination transforms readily into the η^2-bidentate *cis*-*N*/*N* binding mode by treating **7b** with CO to give **8**.

The synthesis was based on the symmetrical organomercury compound **6** as a source of the 2-(2-pyridinyl)phenyl anion.[19] The reaction with $RuCl_3$ gave a mixture of complexes that could not be separated. The neutral complex **5**, the benzene ring of which is a good leaving ligand,[4] proved to be the most appropriate. Complexes **5** and **6** react cleanly in methanol to afford red species **7a**,**b** in 64 and 50% yield, respectively.

The analytical and mass-spectrometric data could not rule out the formulation of new compounds as complexes of type **4**, though the ^{1}H NMR spectra indicated products of lower symmetry. Therefore, the structures of **7a**,**b** were established by X-ray crystallography [Figure S1 (Supporting Information) and Figure 1, respectively].[20] Both **7a**,**b** contain coordinated pbp, likely a product of reductive elimination of two 2-(2-pyridinyl)phenyl ligands presumably via an Ru^{IV} precursor of type **4**. The Ru^{II} compounds **7a**,**b** crystallize with a molecule of CH_2Cl_2. The geometry of both complexes could be approximated by a strongly distorted octahedron. The central atom is surrounded by three meridional pyridine nitrogen atoms and one η^1-bound sp^2-carbon atom. The remaining *cis* sites are occupied by two η^2-bound pseudo-alkene C=C units of pbp, the nitrogen atoms of which are in a mutual *trans* position. The η^2-C=C units have slightly elongated C–C bonds (1.406 and 1.413 Å in **7a**). They occupy *trans* positions relative to the N- and C-donor centers of the 2-(2-pyridinyl)phenyl ligand. Hence, the Ru–C=C centroid distances (Ru–C19/C20 and Ru–C32/C33 in **7b**, Figure 1) are different, i.e. 2.443/2.289 Å in **7a** and 2.427/2.285 Å in **7b**, respectively, in accordance with the diverse *trans* influence of the N- and C-donor centers. For instance, the centroid distance in the undistorted octahedral d^6 complex $[Ru^{II}Cl_2(CO)(C_2H_4)(PMe_2Ph)_2]$ is 2.104 Å.[21] The pseudo-alkene fragments in red compound **7** are thus weakly bound to Ru^{II} and are readily replaced by CO in CH_2Cl_2 to form colorless **8**. Coordinated pbp in **8** is an N,N-bidentate ligand producing a nine-membered cycle (Figure 1). Interestingly, this pseudo-substitution of alkene moieties by CO is accompanied by a *trans*-to-*cis* isomerization of the pbp nitrogen atoms.

Studies of the new compounds by cyclic voltammetry in MeCN support that complexes **7** contain ruthenium(II). There are quasi-reversible Ru^{II}/Ru^{III} waves at 582 and 538 mV (vs. Ag/AgCl in 0.1 M nBu$_4$NPF$_6$) for **7a**,**b** respectively [Figure S2 (Supporting Information)]. The behavior of **7** is similar to that of the Ru^{II} complex **2**, the reduction potential of which is 531 mV under the same conditions. A small anodic shift of 51 mV for **7a** is likely due to stronger π-acceptor properties of the η^2-C=C units compared to the pyridine nitrogen atoms in **2**.

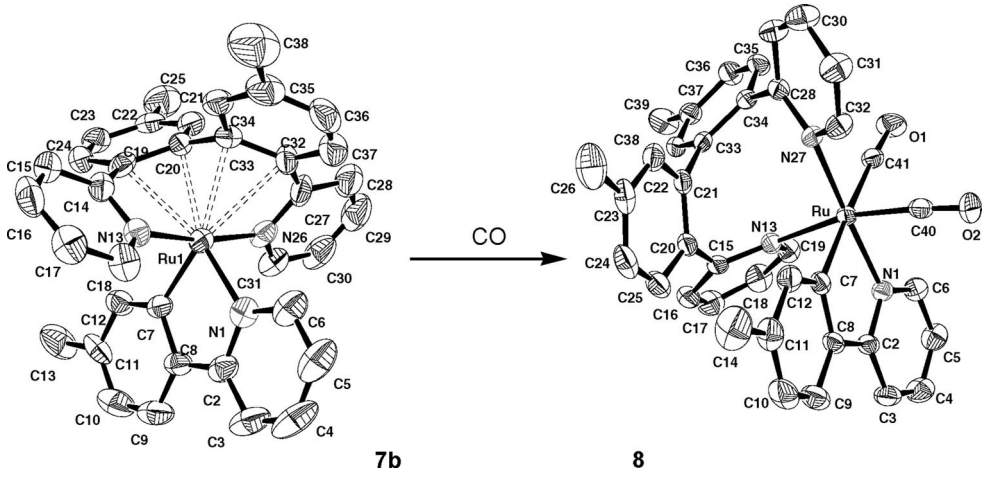


Figure 1. ORTEP views of compounds **7b** (left) and **8** (right). Hydrogen atoms and PF_6 anions are omitted for clarity.

We believe that that compounds **7** may be formed by the "intramolecular" reductive elimination of two 2-(2-pyridinyl)phenyl ligands from an intermediate similar to **4**. Strictly speaking, reductive elimination is always intramolecular. The quotation marks emphasize that pbp, a postulated product of reductive elimination, remains in the metal coordination sphere. Perhaps non-dissociative reductive elimination could be a better term to describe this chemistry. The reductive elimination of 2-(2-pyridinyl)-phenyl ligands from an octahedral Pd^{IV} complex affords free pbp in a pyridine solvent.[18] Therefore, the reaction described here could also involve an M^{IV} precursor. If a variation trend in the reduction potentials described above for **1**–**3** holds for **4**, the $Ru^{III/II}$ reduction potential for **4** could be around –0.65 V [Figure S3 (Supporting Information)]. Hence, the oxidation state of 4+ seems reasonable for the intermediate. If so, the electron count of 16 for the octahedral species such as **4** violates the 18-electron rule. Therefore, the Ru^{IV} complex may not be stable and attains the 18e count by acquiring two missing electrons through the intramolecular reductive elimination. Furthermore, ruthenium(IV) species have recently been proposed as intermediates in the catalytic coupling of aromatic compounds.[22,23] There are few reasons why pbp remains bound to Ru^{II} but dissociates from Pd^{II}. Palladium(II) complexes are square-planar, and pbp, if bound to Pd^{II}, should be constrained and distorted. Ruthenium(II) complexes are by a factor of about 10^4 substitutionally less labile compared to those of Pd^{II}.[24] Therefore, pbp is more prone to be bound to Ru^{II} than to Pd^{II}. The reductive elimination of pbp from Pd^{IV} occurs readily in a coordinating pyridine solvent,[18] which should also favor the substitution of pbp from Pd^{II}.

In conclusion, compound **4** is difficult to prepare due to its chemical controversy. We postulate that three 2-(2-pyridinyl)phenyl ligands reduce the reduction potential of the complex significantly, and this could make species such as **4** unstable. Instead, the coupled pbp product is formed that stays bound to Ru^{II} in a unique tetradentate *trans-N,N* N/η^2-C=C/η^2-C=C/N manner, the biphenyl fragment being a source of two alkene donor centers.

Experimental Section

7a,b: A mixture of **5** (0.20 mmol), **6** (0.20 mmol), and KPF_6 (0.42 mmol) in MeOH (20 mL) was refluxed for 4 h. The solvent was evaporated, the dark residue was extracted with CH_2Cl_2 (3 mL), and the solution was filtered through Al_2O_3 with CH_2Cl_2 as eluent. A red fraction was collected and concentrated to ca. 2 mL. Addition of Et_2O induced crystallization of a red solid, which was washed with Et_2O and dried under vacuum.

8: Carbon monoxide was bubbled through a CH_2Cl_2 solution of **7b** (0.05 mmol) for 15 min. The product was purified as above. A pale yellow fraction was collected, and the solvents were evaporated to dryness. Crystallization from CH_2Cl_2/pentane gave colorless crystals, which were washed with pentane and dried under vacuum.

Supporting Information (see footnote on the first page of this article): Preparation of **5a**,**b**, analytical, spectral, and structural data for **7** and **8**.

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[1] F. H. Burstall, *J. Chem. Soc.* **1936**, 173–175.
[2] D. R. Lide, *CRC Handbook of Chemistry and Physics*, Taylor & Francis, New York, **2006**–**2007**.
[3] E. C. Constable, J. M. Holmes, *J. Organomet. Chem.* **1986**, *301*, 203–208.
[4] A. D. Ryabov, V. S. Sukharev, L. Alexandrova, R. Le Lagadec, M. Pfeffer, *Inorg. Chem.* **2001**, *40*, 6529–6532.
[5] R. Le Lagadec, L. Alexandrova, H. Estevez, M. Pfeffer, V. Laurinavicius, J. Razumiene, A. D. Ryabov, *Eur. J. Inorg. Chem.* **2006**, 2735–2738.
[6] E. A. Seddon, K. R. Seddon, *The Chemistry of Ruthenium*, Elsevier, New York, **1984**.
[7] J. G. Vos, J. M. Kelly, *Dalton Trans.* **2006**, 4869–4883.
[8] I. S. Alpeeva, V. S. Soukharev, L. Alexandrova, N. V. Shilova, N. V. Bovin, E. Csöregi, A. D. Ryabov, I. Y. Sakharov, *J. Biol. Inorg. Chem.* **2003**, *8*, 683–688.
[9] A. D. Ryabov, V. S. Kurova, E. V. Ivanova, R. Le Lagadec, L. Alexandrova, *Anal. Chem.* **2005**, *77*, 1132–1139.
[10] E. V. Ivanova, I. V. Kurnikov, A. Fischer, L. Alexandrova, A. D. Ryabov, *J. Mol. Catal. B* **2006**, *41*, 110–116.
[11] V. S. Soukharev, A. D. Ryabov, E. J. Csöregi, *J. Organomet. Chem.* **2003**, *668*, 75–81.
[12] R. Le Lagadec, L. Rubio, L. Alexandrova, R. A. Toscano, E. V. Ivanova, R. Meskys, V. Laurinavicius, M. Pfeffer, A. D. Ryabov, *J. Organomet. Chem.* **2004**, *689*, 4820–4832.
[13] E. C. Constable, C. E. Housecroft, *Polyhedron* **1990**, *9*, 1939–1947.
[14] K. A. King, P. J. Spellane, R. J. Watts, *J. Am. Chem. Soc.* **1985**, *107*, 1431–1432.
[15] M. G. Colombo, T. C. Brunold, T. Riedener, H. U. Guedel, M. Fortsch, H.-B. Buergi, *Inorg. Chem.* **1994**, *33*, 545–550.
[16] X. Chen, X.-S. Hao, C. E. Goodhue, J.-Q. Yu, *J. Am. Chem. Soc.* **2006**, *128*, 6790–6791.
[17] K. L. Hull, E. L. Lanni, M. S. Sanford, *J. Am. Chem. Soc.* **2006**, *128*, 14047–14049.
[18] S. R. Whitfield, M. S. Sanford, *J. Am. Chem. Soc.* **2007**, *129*, 15142–15143.
[19] A. M. Clark, C. E. F. Rickard, W. R. Roper, L. J. Wright, *Organometallics* **1999**, *18*, 2813–2820.
[20] Crystal-structure data. **7b**·CH_2Cl_2: $C_{37}H_{32}Cl_2F_6N_3PRu$, M_r = 835.60, 0.31 × 0.06 × 0.03 mm, orthorhombic, $P2_12_12_1$, a = 9.0366(6), b = 13.4029(9), c = 29.4067(19) Å, V = 3561.6(4) Å^3, Z = 4, $\rho_{calcd.}$ = 1.558 Mg/m^3, μ = 0.698 mm^{-1}, graphite-monochromated Mo-K_α radiation (0.71073 Å), T = 298(2) K, $2\theta_{max}$ = 50.74°, 29733 reflections collected, 6520 independent reflections, R(int) = 0.1098, $R1$ = 0.0612, $wR2$ = 0.0946, Largest diff. peak/hole 0.781/–0.454 e Å^{-3}. **8**: $C_{38}H_{30}F_6N_3O_2PRu$, M_r = 806.69, 0.33 × 0.08 × 0.07 mm, monoclinic, $P2_1/n$, a = 14.599(2) Å, α = 90, b = 10.812(1), β = 101.516(2), c = 22.875(2) Å, γ = 90°, V = 3538.0(7) Å^3, Z = 4, $\rho_{calcd.}$ = 1.514 mg/m^3, μ = 0.558 mm^{-1}, graphite-monochromated Mo-K_α radiation (0.71073 Å), T = 298(2) K, $2\theta_{max}$ = 50.72, 28636 reflections collected, 6464 independent reflections, R(int) = 0.0807, $R1$ = 0.0453, $wR2$ = 0.0702, Largest diff. peak/hole 0.804/–0.453 e Å^{-3}. Diffraction intensities data were collected with a Bruker SMART Apex diffractometer.The structures were solved by Patterson methods using the SHELXS-97 program and refined by full-matrix least-squares procedures on F^2. Hydrogen atoms were input at calculated positions and

allowed to ride on the atoms to which they are attached. CCDC-687664 (**7a**), -687665 (**7b**), and -687666 (**8**) contain the crystallographic data and are avalaible free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[21] L. D. Brown, C. F. J. Barnard, J. A. Daniels, R. J. Mawby, J. A. Ibers, *Inorg. Chem.* **1978**, *17*, 2932–2935.

[22] S. Oi, H. Sato, S. Sugarawa, Y. Inoue, *Org. Lett.* **2008**, *10*, 1823–1826.

[23] I. Özdemir, S. Demir, B. Çetinkaya, C. Gourlaouen, F. Maseras, C. Bruneau, P. H. Dixneuf, *J. Am. Chem. Soc.* **2008**, *130*, 1156–1157.

[24] A. Cusanelli, U. Frey, D. T. Richens, A. E. Merbach, *J. Am. Chem. Soc.* **1996**, *118*, 5265–5271.

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