Novel Reversible Chlorine-Gas Uptake and Release System with Bis(polypyrazolylborato)ruthenium(II) in the Solid State

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Novel reversible chlorine-gas uptake and release cycles were shown by the bis(polypyrazolylborato)ruthenium(II) complexes in the solid state, with their one-electron [Ru(III)]/[Ru(II)] redox-couples. Formation of ground-state charge-transfer species was also observed for the complexes with some halocarbon solvents.

In the synthetic course of catalytically active (organonitrile)-ruthenium complexes with tridentate polypyrazolylborate ligands ($BRpz_3$) (pz= 1-pyrazolyl),[1-3] the homoleptic bis(polypyrazolyl-borato)ruthenium(II) complexes $[Ru(BRpz_3)_2]$ (**1**, R= H; **2**, R= pz)[3] have been obtained as colorless microcrystals. The present communication describes formation of the ground-state charge-transfer species of the $[Ru(BRpz_3)_2]$ with some halocarbon organic solvents, and also novel reversible chlorine-gas uptake and release cycles on the complexes in the solid state with their one-electron redox-couples of [Ru(III)]/[Ru(II)].

These ruthenium(II) complexes were stable to air in common organic solvents. However, exposure of their chloroform solutions to the sun light for a few days was found to precipitate bloody red crystals, and single-crystal X-ray structural analyses revealed the crystals to be the ruthenium(III) derivatives of $[Ru(BRpz_3)_2]Cl \cdot nCHCl_3$ (**3**, R= H, n= 2; **4**, R= pz, n= 6)[4] (Figure 1). Chloride counter anions were derived from ruthenium-mediated decomposition of solvent chloroform molecules, which did not occur in the dark. Photoirradiation of **2** in chloroform at 313 nm showed the disappearance of its absorption band at 342 nm and the appearance of a new band of **4** at 449 nm, with formation of two isosbestic points at 269 and 377 nm.[5] The quantum photoefficiencies of **1** and **2** in chloroform at 313 nm were determined to be 0.84 and 0.43 at 20 °C, respectively.

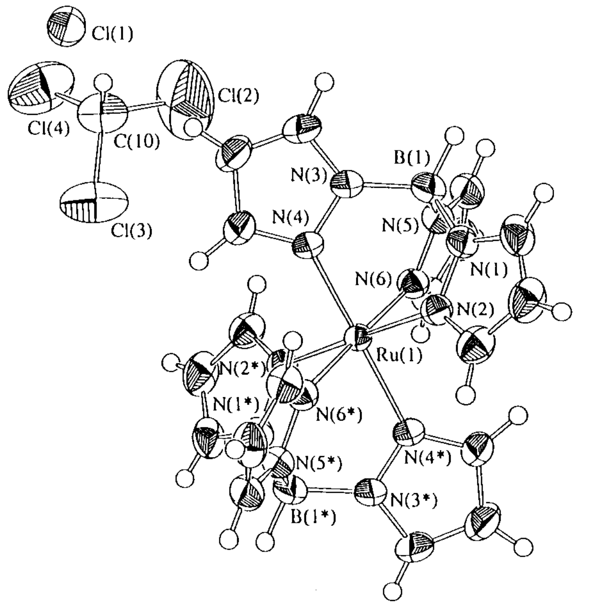

Figure 1. Ortep drawing of **3** showing 50% probability displacement ellipsoids and atom labels for only important atoms. Ru-N(av)= 2.044, B-H= 1.08(3), Ru-B= 3.148(5) Å.

The complexes **1** and **2** in methanol gave the absorption bands at 322 and 328 nm, respectively, which were associated probably with the metal to ligand charge-transfer (MLCT) excitation. On the other hand, these MLCT bands in some halocarbon solutions were found to show significant λ_{max}-shift towards longer wavelength and absorbance increase on their shoulder at the longer wavelength side, and representative was the complex **1** in the halocarbons with comparatively low carbon-halogen dissociation energies, such as chloroform and carbon tetrachloride.[5,6] In addition, pulse laser photoexcitation experiments (YAG, 355 nm, pulse width= 7 ns) were attempted for emission spectrum observations of **1** and **2** in THF and methanol mixtures at room temperature, but significant emission from the photoexcited states with comparatively long lifetimes, in the range of 20 ns to 1 ms, was not detected. These findings on the MLCT bands were attributed to the ground-state charge-transfer complex formation[7] with the halocarbon solvents, rather than to other conceivable solvent-properties, such as coordinating ability and polarity.[6] Therefore, the above-described precipitation of ruthenium(III) derivatives, i.e. photoinduced electron-transfer from the $[Ru(BRpz_3)_2]$ complexes to chloroform molecules was brought about through photoexcitation of their ground-state charge-transfer species formed.

The ruthenium(III) derivatives were fairly stable, but under vacuum (ca. 1 mmHg), their microcrystalline solids faded into pale pink. Column-chromatographic separation confirmed some reductive reconversion to their ruthenium(II) complexes. The reconversion yield of **4** to **2** was 60% for 2 days at 20 °C, whereas at 130 °C, the reconversion proceeded quickly and the yield was ca. 90% for 2 h. In the reduction process, chlorine-gas liberation was also observed. These facts led us to conclude that the reconversion process to the ruthenium(II) complexes became exergonic ($\Delta G<0$) owing to the attendant "spontaneous" evolution of the chlorine gas under vacuum.[8]

As Figure 1 shows, two bulky $BRpz_3$ ligands encapsulated stereochemically the Ru atom in the monocationic $[Ru(BRpz_3)_2]^+$ complexes of the almost same size and structure as those of the uncharged $[Ru(BRpz_3)_2]$, affording electrochemically excellent reversibility of the [Ru(III)]/[Ru(II)] redox couples.[5] In view of the facile reconversion to the ruthenium(II) complexes in the solid state and of the excellent reversibility of the redox, we performed solid-state reactions of the $[Ru(BRpz_3)_2]$ complexes with chlorine gas, and the following novel reversible chlorine-gas uptake and release cycles were observed on these complexes.

$$[Ru(BRpz_3)_2](solid) + \frac{1}{2}Cl_2(gas) \underset{\text{heat, vac.}}{\rightleftharpoons} [Ru(BRpz_3)_2]Cl(solid)$$

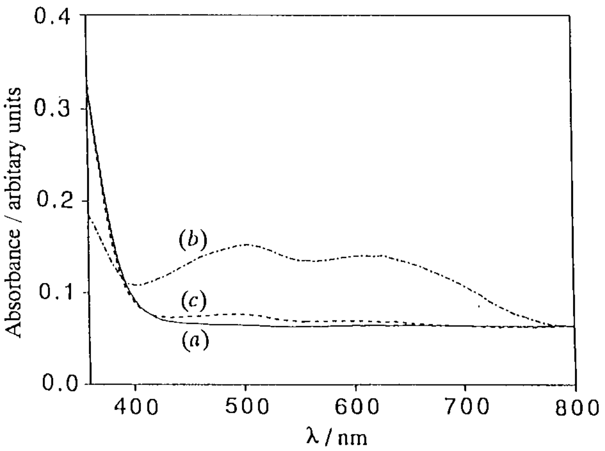

Figure 2. Diffuse reflectance spectra of **5** (1 wt. % / MgO). (*a*), The complex **5**; (*b*), After treatment of **5** with chlorine gas for 30 min; (*c*), Ater heating the sample *b* at 120 °C under vacuum.

When microcrystals of [Ru{B(4-CH_3pz)$_4$}$_2$] (**5**)[9] (4-CH_3pz= 4-methyl-1-pyrazolyl) were exposed to the chlorine gas for 5 and 30 min, the crytals turned reddish brown, and the conversions to the ruthenium(III) derivative, [Ru{B(4-CH_3pz)$_4$}$_2$]Cl were about 4.5 and 31.1%, respectively. Then, the latter highly colored solid was heated at 120 °C for 20 h under vacuum, to give a pale pink solid of the reconverted **5** with only 2.4% contamination of the derivative retained. Diffuse reflectance spectra of Figure 2 exhibit this novel reversible chlorine-gas uptake and release cycle. Photoirradiation was not required in this cycle. To our knowledge, there have been no reports so far, on similar reversible chlorine-gas uptake and release systems with transition-metal compounds, especially those in the solid state, in remarkable contrasts to abundantly described hydrogen-storage metals[10,11] and also to well-known biomimetic oxygen-carriers of cobalt complexes with quadridentate Schiff bases as ligands.[10] Moreover, the present reversible chlorine-gas system showed the clear color-change of the [Ru(III)]/[Ru(II)] redox, and seemed to retain the developable potentiality as a solid-state chlorine-gas sensor.[12] Electrochemical and comparative studies are currently underway for a variety of substituted polypyrazolylborato complexes.

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References and Notes

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4 Crystal data for **1**; ($C_{18}H_{20}B_2N_{12}Ru$, M= 527.1); monoclinic, space group $P2_1/n$ (No.14), a= 9.829(4), b= 17.31(1), c= 13.058(3) Å, β= 96.87(2)°, V= 2206(1) Å^3, Z= 4, D_{calc}= 1.587 g/cm^3, μ(MoKα)= 7.45 cm^{-1}, Data collected at 293 K with a Rigaku AFC-7S diffractometer (Mo radiation, λ= 0.71069 Å; $2\theta_{max}$= 55.0°.); R= 0.036 and R_w= 0.025 for 3661 observations (I>3.00σ(I)). Ru-N(av)=2.061, B-H(av)= 1.14, Ru-B(av)= 3.12 Å.
Crystal data for **3**; {($C_{18}H_{20}B_2ClN_{12}Ru\cdot 2CHCl_3$)/2, M/2= 400.67}; triclinic, space group $P\bar{1}$(No.2), a= 9.349(2), b= 10.177(2), c= 9.156(2) Å, α= 98.83(1)°, β= 100.23(2)°, γ=78.00(1)°, V= 832.4(3) Å^3, Z= 2, D_{calc}= 1.598 g/cm^3, μ(MoKα)= 10.66 cm^{-1}, Data collected at 293 K with a Rigaku AFC-7R diffractometer (Mo radiation, λ= 0.71069 Å; $2\theta_{max}$= 55.0°.); R= 0.048 and R_w= 0.037 for 3204 observations (I>3.00σ(I)). {The Ru(BHpz$_3$)$_2$ structural unit has a crystallographic center of symmetry at the Ru atom.}.
Crystal data for **4**; In spite of some crystallographic orientational disorder of uncoordinated pz groups, preliminary structural analysis was performed with a model giving 0.5 occupancy to each of two rotamers around the axis through B and 1-N atoms in the uncoordinated pz. ($C_{24}H_{24}B_2ClN_{16}Ru\cdot 6CHCl_3$); trigonal, space group $R\bar{3}$ (No.148), a= 13.77(1), c= 26.02(1) Å, V= 4276(5) Å^3, Z= 18; R = R_w= 0.169.

5 λ_{max} ($CHCl_3$) of absorption bands; **1**, 337 (ε 19200); **2**, 342 (ε 19700); **3**, 443 (ε 8400); **4**, 449 nm (ε 10200). The former two bands for **1** and **2** with d^6 electron-configuration were probably associated with the metal to ligand charge-transfer (MLCT) excitation, accompanying some contribution by the metal to solvent charge-transfer one (vide infra). On the other hand, the latter two with the d^5 configuration were associated with the ligand to metal charge-transfer (LMCT) excitation, $E°_{1/2}$ of [Ru(III)]/[Ru(II)], 1 mmol dm^{-3} with 0.1 mol dm^{-3} (Bu_4N)(ClO_4), in CH_2Cl_2; 305 and 435 mV for **1** and **2**, respectively vs. Ag/AgCl/satd. NaCl; {[FeCp$_2$], 510 mV}.

6 Similar λ_{max} shifts and absorbance increase on the longer wavelength side of the MLCT bands were not observed for acetonitrile, methanol, and cyclohexane solutions of the [Ru(BHpz$_3$)$_2$], and absorption spectra in these solvents were almost indistinguishable. Accordingly, solvent polarity and coordinating ability were not key-role-playing parameters in the present absorption-spectrum changes. Halocarbon organic solvents, which showed the spectrum changes, are represented by their small negative values of polarographic half-wave potentials ($E°_{1/2}$ vs. SCE), being associable with low carbon-halogen dissociation energies and with the high capacity to serve as electron acceptors. See, D. Dobos, "Electrochemical Data," Elsevier, Amsterdam (1975), p. 303.

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8 The compounds [Ru(BRpz$_3$)$_2$]PF_6 did not show any color change, i.e. reduction to the ruthenium(II) state, upon similar heating at 130 °C under vacuum.

9 The 4-position on the pz rings, which might have some potential reactivity for halogenation, has been blocked by the CH_3-substituent introduction.

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