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# *p*-Carborane: A New Cage Spacer for Photoactive Metal Polypyridine Dyads

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The first example of a binuclear ruthenium complex involving the *p*-carborane framework in the bridging ligand is reported. The bridging ligand is a symmetric linear array comprising a central *p*-carborane unit, two *p*-phenylene spacers, and two 5-yl-2,2′-bipyridine coordinating units. A homobinuclear $Ru^{II}$ complex, with 2,2′-bipyridine as peripheral ligands, was synthesized and characterized. The $Ru^{II}$–$Ru^{III}$ mixed-valence species, obtained by partial oxidation, has been investigated with steady-state and time-resolved techniques in $CH_3CN$. The rate of photoinduced electron transfer is $2.3 \times 10^8$ $s^{-1}$.

Oligonuclear complexes based on ruthenium(II) and osmium(II) polypyridine components are interesting systems for photochemical energy conversion and photonic devices.[1] In the design of these systems, the bridging ligands are crucial not only for their structural role but also for providing electronic coupling between the linked units, thus permitting intercomponent processes. Rigid rodlike molecules[2] are attractive building blocks for the construction of supramolecular arrays. Among these units, 1,12-dicarba-*closo*-dodecaborane (1,12-$C_2B_{10}H_{12}$, known as *p*-carborane) is particularly interesting.[3] The thermal stability, general chemical inertness, and UV transparency of these units, together with their ability to form extended rodlike structures (*carborods*),[4] have raised considerable interest in the synthesis[2,4,5] of novel systems containing *p*-carborane as a structural motif. Notably, Hawthorne and co-workers synthesized a variety of supramolecular species containing carborane derivatives assembled through appropriate metal centers.[6,7]

The *p*-carborane unit has recently attracted special attention in relation to electron-transfer processes. Wade et al. studied the transmission of the electronic effect through *p*-carborane substituted with aryl electron-donor and -acceptor moieties, monitoring the $^{13}C$ NMR chemical shifts and the UV−vis spectra.[8] With electrochemical experiments on a series of $\eta$-$CpFe(CO)_2$-substituited *p*-carborane derivatives, Hawthorne measured the extent of electronic communication through the carborane bridge.[9,10] Analogous electrochemical results were obtained by Low and co-workers on *p*-carborane functionalized at the carbon vertexes by cobalt clusters.[11] It has recently been suggested that $\sigma$-bonded carbon cage structures may be used as electron tunnel barriers in molecular electronic circuits.[12−14] In this context, the matrix element relevant to electron tunneling through *p*-carborane has been calculated.[15]

We have focused our effort in the construction of polynuclear complexes in which photoactive and redox-active

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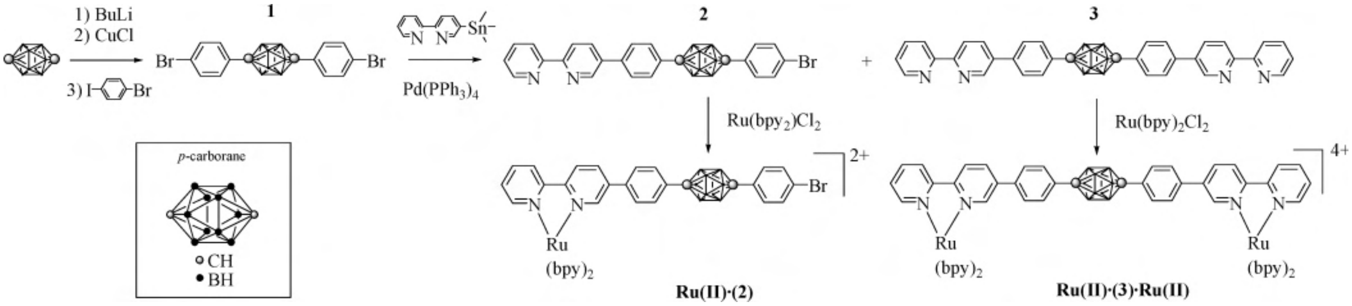
**Scheme 1**



metal polypyridine units are linked by bridges based on *p*-carborane units. For this purpose, we have made use of the known reactivity of carboranes,[3,7,16,17] which can be functionalized at the C−H vertexes via metalation. Herein, we report the synthesis of the homonuclear Ru$^{II}$ dimer, **Ru$^{II}$·3·Ru$^{II}$** (Scheme 1). The *p*-carborane reacts with 2.2 equiv of 4-bromoiodobenzene,[18] giving the bis-substitution product **1**[19] (80% yield). The ligands **2** and **3** were synthesized by a Pd(PPh$_3$)$_4$-catalyzed Stille cross-coupling protocol: the reaction between the dibromo intermediate **1** and 2.2 equiv of the trimethyltin derivative of the 5-bromobipyridine[20] in *m*-xylene gave a mixture of the bridging ligand **3** (yield ca. 20%) and the ligand **2** (yield ca. 10%).[21] The Ru$^{II}$ complexes were prepared by reacting **2** and **3** with 1.1 and 2.2 equiv, respectively, of Ru(bpy)$_2$Cl$_2$ in refluxing methanol/chloroform (1:1). The mononuclear complex **Ru$^{II}$·2** and the homonuclear dyad **Ru$^{II}$·3·Ru$^{II}$** were purified by size-exclusion chromatography (Sephadex LH20, methanol as the eluent).[22]

Cyclic voltammetry of **Ru$^{II}$·3·Ru$^{II}$** in acetonitrile showed a single reversible oxidative wave with $E_{1/2} = 1.28$ V vs SCE ($\Delta E_p = 140$ mV).[23] In the reductive region, a single reversible wave $E_{1/2} = -1.24$ V vs SCE ($\Delta E_p = 90$ mV) and two irreversible[24] reductive waves with $E_{p,c} = -1.45$ and $-1.82$ V were detected. The oxidative wave involves metal center oxidation and is bielectronic in nature.[25] In analogy with the assignments for similar compounds,[26] the first reduction is thought to be based on the bridging ligand whereas the following irreversible reduction waves are based on the peripheral bipyridine ligands. The bridging ligand reduction has the same wave amplitude as the metal oxidation and is thus a two-electron process as well. Altogether, the electrochemical results are consistent with a very weak degree of electronic communication between the ruthenium centers and between the two halves of the bridging ligand through the *p*-carborane group.[27−29]

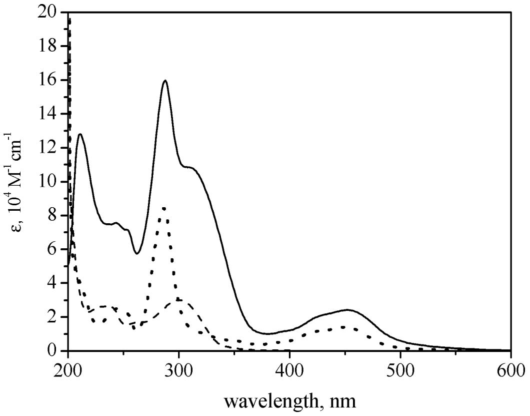


**Figure 1.** Absorption spectra of **Ru$^{II}$·3·Ru$^{II}$** (straight line), Ru(bpy)$_3^{2+}$ (dotted line), and the bridging ligand **3** (dashed line) in acetonitrile.

The absorption spectra of ligand **3** and **Ru$^{II}$·3·Ru$^{II}$** are shown in Figure 1, together with that of Ru(bpy)$_3^{2+}$ (for purposes of comparison). The absorption spectrum of **Ru$^{II}$·3·Ru$^{II}$** is typical for a ruthenium(II) polypyridine complex.

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(18) We have tested two synthetic ways: without catalyst[16] and with Pd catalyst.[17] The two methods gave equivalent results. We choose the way without the catalyst for practical reasons.

(19) The product is purified by sublimation from the *p*-carborane unreacted and monosubstituted product. **1**: $^1$H NMR (CDCl$_3$) δ 7.30 (dd, 4H), 7.10 (dd, 4H), 1.2−3 (10H, BH$_{Cb}$); $^{11}$B NMR (CDCl$_3$) δ 12.320 (s, 10B).

(20) This reagent was made with a stoichiometric amount of BuLi and a slight excess of Me$_3$SnCl in dichloromethane at −78 °C, as described by: Pugliesi, A.; et al. *Eur. J. Org. Chem.* **2003**, 1552.

(21) Bridging ligand **3** precipitated as a white solid. The ligand **2** was isolated from the reaction mixture by preparative thin-layer chromatography on aluminium oxide (100:2:1 cyclohexane/ethyl acetate/triethylamine as the eluent). **2**: $^1$H NMR (CDCl$_3$) δ 8.85 (s, H$_{6'}$), 8.70 (d, H$_6$), 8.40 (t, H$_3$, H$_{3'}$), 7.95 (d, H$_{4'}$), 7.85 (t, H$_4$), 7.50 (d, 2H$_{ph}$), 7.35 (m, 4H$_{ph}$, H$_5$), 7.10 (d, 2H$_{ph}$); $^{11}$B NMR (CDCl$_3$) δ 12.170 (s, 10B). **3**: $^1$H NMR (CDCl$_3$) δ 8.90 (s, 2H$_{6'}$), 8.70 (d, 2H$_6$), 8.50 (m, 2H$_3$, 2H$_{3'}$), 8.00 (d, 2H$_{4'}$), 7.85 (t, 2H$_4$), 7.55 (d, 4H$_{ph}$), 7.35 (d, 4H$_{ph}$), 7.30 (m, 2H$_5$); $^{11}$B NMR (CDCl$_3$) δ 12.170 (s, 10B).

(22) **Ru$^{II}$·2**: $^1$H NMR (CD$_3$OD) δ 8.70 (m, 6H$_{3,3'}$), 8.40 (d, 1H$_{4'}$), 8.20 (m, 5H$_4$), 7.90−7.70 (m, 6H$_{6,6'}$), 7.60−7.20 (m, 5H$_{5,5'}$ 8H$_{ph}$); $^{11}$B NMR (CD$_3$OD) δ 8.37 (s, 10B); ESI-MS *m*/*z* 472 (M − 2PF$_6$)$^{2+}$ (main peak). **Ru$^{II}$·3·Ru$^{II}$**: $^1$H NMR (CD$_3$OD) δ 8.70 (m, 12H$_{3,3'}$), 8.34 (d, 2H$_{4'}$), 8.12 (m, 10H$_4$), 7.90−7.70 (m, 12H$_{6,6'}$), 7.50 (m, 10H$_{5,5'}$), 7.32 (m, 8H$_{ph}$); $^{11}$B NMR (CD$_3$OD) δ 8.37 (s, 10B); ESI-MS *m*/*z* 358 (M − 4PF$_6$)$^{4+}$ (main peak).

(23) Cyclic voltammetry was performed in argon-deaerated acetonitrile at 298 K with TBAPF$_6$ as the electrolyte (0.1 M), scan rate 100 mV s$^{-1}$, SCE as the reference electrode, and glassy carbon as the working electrode. Identical results were obtained with Pt as the working electrode.

(24) The irreversible behavior is likely caused by electrode adsorption.

(25) Comparative experiments with, e.g., (bpy)$_2$Ru(bbpe)(bpy)$_2^{4+}$ (bbpe = 1,2-bis[4-(4′-methyl-2,2′-bipyridinyl)]ethane), yield identical wave amplitudes.

(26) In a related binuclear complex, where the bipyridine moieties of the bridging ligand also carry a phenyl substituent in the 5 position, the first reduction wave occurs at −1.19 V (Warnmark, K.; Baxter, P. N. W.; Lehn, J.-M. *Chem. Commun.* **1998**, 993).

(27) The separation of oxidation waves is usually taken as a measure (among other factors) of the degree of electronic communication between the redox centers.[28] It has been pointed out, however, that for some strongly coupled systems such a correlation may not be valid.[29]

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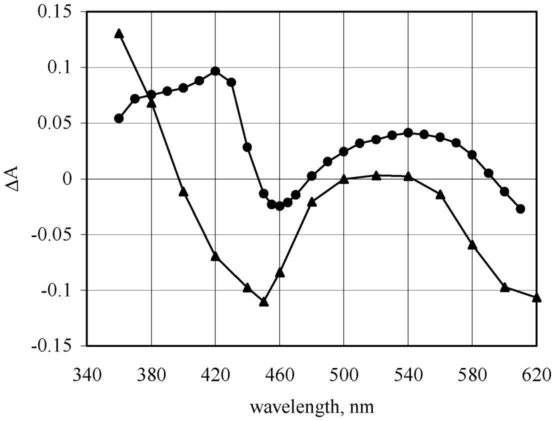

**Figure 2.** Transient absorption spectra in acetonitrile of $\mathbf{Ru^{II}{\cdot}3{\cdot}Ru^{II}}$ (●) and $Ru(bpy)_3^{2+}$ (▲) taken immediately after the laser pulse ($\lambda_{exc} = 355$ nm; half-width = 10 ns).

Intense ligand-centered bands dominate the UV region. The $\pi-\pi^*$ transitions corresponding to the peripheral bipyridine ligands appear at 288 nm, while an additional shoulder is around 310 nm (see, for comparison, the spectrum of **3**). The visible region is dominated by moderately intense metal-to-ligand charge-transfer (MLCT) bands, with a maximum at 450 nm. The similarity between the MLCT energies of $\mathbf{Ru^{II}{\cdot}3{\cdot}Ru^{II}}$ and $Ru(bpy)_3^{2+}$ confirms again the absence of extensive delocalization through the bridging ligand. The spectrum of $\mathbf{Ru^{II}{\cdot}2}$ is virtually identical with that of $\mathbf{Ru^{II}{\cdot}3{\cdot}Ru^{II}}$, except for the smaller (by a factor of ca. 2) molar absorptivities.

The complexes $\mathbf{Ru^{II}{\cdot}3{\cdot}Ru^{II}}$ and $\mathbf{Ru^{II}{\cdot}2}$ are photoluminescent upon excitation at 450 nm in a methanol solution at room temperature ($\lambda_{max}^{em} = 625$ nm) as well as in a 1:1 ethanol/methanol rigid matrix at 77 K ($\lambda_{max}^{em} = 580$ nm). In both cases, the emission is slightly but significantly red-shifted (ca. 20 and 10 nm, respectively) with respect to that of $Ru(bpy)_3^{2+}$. This suggests that the lowest, emitting MLCT state involves the bridging ligand rather than the terminal ones. In both cases, the emission decayed exponentially with a lifetime of ca. 1 $\mu$s in deaerated acetonitrile.

The transient spectrum obtained upon nanosecond laser flash photolysis of $\mathbf{Ru^{II}{\cdot}3{\cdot}Ru^{II}}$ (methanol, 10 ns after 355-nm excitation) is compared in Figure 2 with that of $Ru(bpy)_3^{2+}$. As usual for ruthenium(II) polypyridine complexes,[30] the positive absorption bands in the transient spectra are principally due to $\pi-\pi^*$ transitions of the ligand radical anion (formally present in the MLCT excited state). The transient bleaching at ca. 450 nm results from loss of ground-state absorption. The apparent bleach in the red portion of the spectrum is due to MLCT emission. When compared to $Ru(bpy)_3^{2+}$, the main difference is that the high-energy positive absorption bands of $\mathbf{Ru^{II}{\cdot}3{\cdot}Ru^{II}}$ are substantially red-shifted and somewhat intensified, so as to almost hide the ground-state bleach. These differences confirm the notion that the lowest MLCT state monitored in transient absorption involves the bridging ligand rather than the terminal ones. Very similar results are obtained for the mononuclear compound, $\mathbf{Ru^{II}{\cdot}2}$. In both cases, the transient absorption decayed with the same lifetime as emission.

Finally, the homonuclear $\mathbf{Ru^{II}{\cdot}3{\cdot}Ru^{II}}$ was partially oxidized to obtain the mixed-valence compound $\mathbf{Ru^{II}{\cdot}3{\cdot}Ru^{III}}$. This reaction was performed using $Ce^{IV}$ as the oxidant[31] in acidified acetonitrile (0.1 M trifluoroacetic acid). The oxidation was monitored by the decrease in the MLCT band intensity at 450 nm and was stopped when the $Ru^{II}$ concentration was reduced to half of the initial value. Because the two metal units have the same oxidation potential, the process yields a 1:2:1 distribution of the $\mathbf{Ru^{II}{\cdot}3{\cdot}Ru^{II}}$, $\mathbf{Ru^{III}{\cdot}3{\cdot}Ru^{II}}$, and $\mathbf{Ru^{III}{\cdot}3{\cdot}Ru^{III}}$ species. Of these species, $\mathbf{Ru^{III}{\cdot}3{\cdot}Ru^{III}}$ is nonluminescent, and $\mathbf{Ru^{II}{\cdot}3{\cdot}Ru^{II}}$ should exhibit long-lived emission (see above), while for $\mathbf{Ru^{III}{\cdot}3{\cdot}Ru^{II}}$ the emission of the $Ru^{II}$ unit is expected to be quenched by electron transfer to the $Ru^{III}$ center.[31] Single-photon-counting experiments carried out on the semioxidized solutions show, besides the expected long-lived emission, an intense component of 4.4-ns lifetime. Thus, the rate constant of photoinduced electron transfer across the carborane-based bridging ligand is $2.3 \times 10^8$ $s^{-1}$. This rate constant can be compared with the value $1.1 \times 10^9$ $s^{-1}$ obtained by De Cola and coworkers[31] on a related $Ru^{II}-Ru^{III}$ binuclear complex, where the conjugation is effectively interrupted by the rigid saturated bicyclo[2.2.2]octane spacer. The comparison suggests an analogous insulating role for the two cage spacers, although a precise evaluation is prevented by other differences (vinylene instead of *p*-phenylene additional spacers) between the two bridges. According to the calculations of Pati et al., the electron-transfer coupling matrix element is larger for *p*-carborane[15] than for bicyclo[2.2.2]octane.[12] In the comparison between the two systems, the difference in electronic coupling through the cage spacer is offset by the difference in the extent of conjugation through the intermediate groups.

In conclusion, the electrochemical and spectroscopic behavior of the new *p*-carborane-bridged $Ru^{II}$ binuclear species indicate little delocalization through this bridge. The relatively slow rate obtained for photoinduced electron transfer in the mixed-valence species confirms the low “conducting” ability of the *p*-carborane spacer. Further work will be directed, in particular, toward the synthesis of modular bridges and of heteronuclear complexes.

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