π-Diborene Complexes

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Unexpected Luminescence Behavior of Coinage Metal π-Diborene Complexes**

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Abstract: *A number of unprecedented photophysical phenomena were observed in the study of luminescent π-diborene complexes of Cu and Ag. These observations included unusually high fluorescence quantum yields (up to 100%) in solution for complexes of these metals. This result indicates that very little or no intersystem crossing between S_1 and T_n occurs in the complexes, despite the strong spin–orbit coupling of the metal atoms. The replacement of carbon with boron thus yields luminescent isolobal analogues of otherwise non-emissive olefin complexes of Cu and Ag.*

Early work on the reduction of diboranes(4) by the groups of Berndt (**A**, Figure 1),[1] Power (**B**),[2] and later Nöth,[3] uncovered a number of charged species with boron–boron multiple bond character and formal bond orders of 1.5 or 2. These results paved the way to Robinson's reduction/hydrogen abstraction synthesis of the first neutral compounds with definitive boron–boron double bonds in 2007: base-stabilized diborenes (**C**).[4] These diborenes, being isoelectronic, isosteric, and isolobal to conventional olefins, were an exciting addition to the field of main-group multiple bonding.[5] Recently our group has extended this concept by developing rational and high-yield reductive routes to diaryl- and dibromodiborenes stabilized by Lewis donors such as N-heterocyclic carbenes (NHCs) and phosphines (**D**).[6]

Given the isoelectronic and isolobal relationship of base-stabilized diborenes to conventional olefins, the π coordination of the former to transition metals was a particularly enticing possibility. Side-on-bound π-olefin complexes are ubiquitous in organometallic chemistry and appear as key intermediates in widely-used catalytic reactions, notably transition-metal-catalyzed olefin polymerization processes.[7]

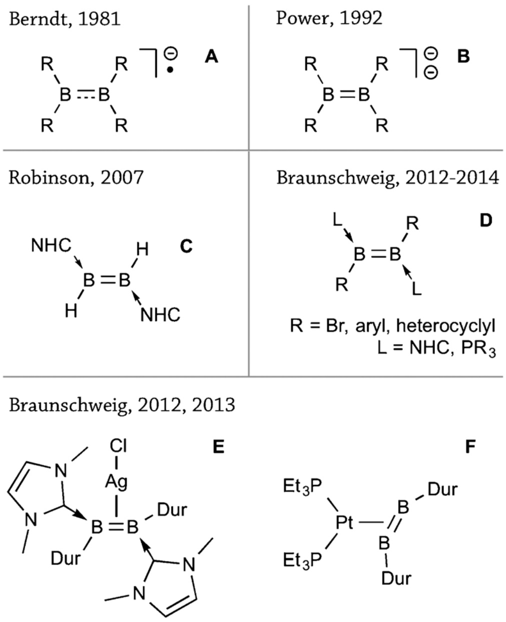

Figure 1. Known classes of compounds with boron–boron double bonds (**A**–**D**) and transition-metal complexes thereof (**E**, **F**).

As a consequence, non-carbon main-group analogues of π-olefin complexes represent a fascinating line of research. Transition-metal homoatomic π-ene complexes of the form $M(\eta^2\text{-}R_nE{=}ER_n)$ have been structurally authenticated only in cases where E represents carbon, silicon, oxygen, or the elements of Group 15.[8,9] In fact, outside of traditional π-alkene complexes, only a handful of such π-ene complexes exist. In our first communication on diborenes, we reported the synthesis of the first transition-metal π-diborene complex through the addition of silver(I) chloride (**E**, Figure 1). Later, a complex of a non-base-stabilized diborene (DurB=BDur) with the zerovalent fragment $[Pt(PEt_3)_2]$ was prepared (**F**), however this species is structurally and electronically more reminiscent of a π-alkyne complex.[10]

We recognized that these free and base-stabilized π-diborene complexes offer a unique opportunity to study the properties of π-olefin complex analogues containing elements to the left of carbon on the periodic table. Furthermore, we were interested in the photophysical properties of diborenes and their metal π-complexes since these compounds, despite their outward similarity to olefins, are vastly different in terms of electronics, reactivity, and stability. Consequently, we prepared a new π-diborene complex of copper chloride (see below), and together with its previously-reported silver π-

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diborene congener **E** (Figure 1),[6b] set out to investigate the photophysical properties of these unusual π-olefin complex mimics. During qualitative tests under a UV lamp, we were immediately struck by the strong visible luminescence of the complexes, and quantitative studies of their luminescence uncovered highly unusual photophysical phenomena. These effects can be summarized as follows: 1) π-olefin complexes do not usually show luminescence but analogous π-diborene complexes are strongly luminescent; 2) the compounds exhibit the seemingly contradictory properties of large Stokes shifts (usually indicative of phosphorescence) and very short lifetimes (indicative of fluorescence); 3) the compounds show exceptionally high fluorescence quantum yields for coinage-metal complexes, particularly for complexes of copper; and 4) counterintuitively, the addition of polar solvents increases the luminescence quantum yield in the case of the silver complex. This communication aims to describe and provide explanations for these unprecedented properties.

Complex **2** was isolated as a yellow solid in 56% yield upon treating a slight excess of CuCl with **1** in benzene (Figure 2).[11] The ^{11}B NMR signal for **2** ($\delta = 18.3$ ppm, C_6D_6) is located slightly upfield with respect to that of the free ligand (**1**: $\delta = 24.7$ ppm) and is in the same range as that of the silver complex **E** ($\delta = 18.1$ ppm). The close relationship between **2** and **E** is also apparent in the solid-state structure: the overall geometry of **2** resembles that observed for the silver complex **E**. The Cu−Cl fragment adopts a perpendicular orientation to the diborene ligand and this leads to a slight elongation of the B1−B2 bond [**2**: 1.633(4); **1**: 1.590(5) Å].

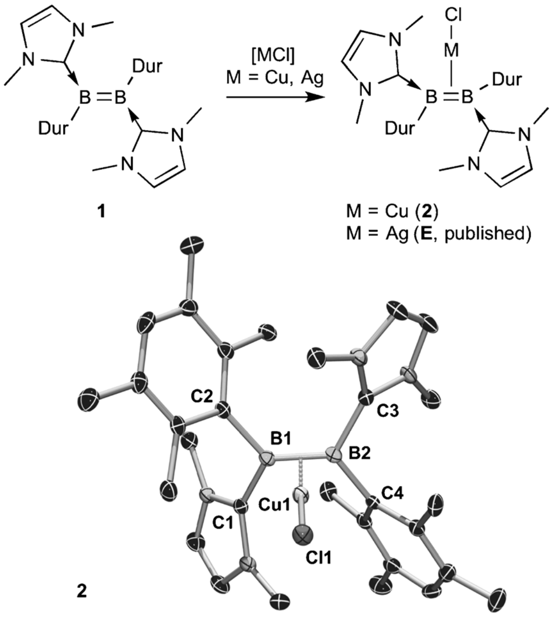

Figure 2. Top: Synthesis of the π-diborene complexes **2** (new) and **E** (previously published[6b]). Bottom: Molecular structure of **2**. Thermal ellipsoids shown at 50% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [deg]: B1–B2 1.633(4), B1–C1 1.593(4), B1–C2 1.628(4), B2–C3 1.591(4), B2–C4 1.622(4), B1–Cu1 2.149(3), B2–Cu1 2.146(3), Cu1–Cl1 2.1730(9); B1-Cu1-Cl1 156.16(8), Cl1-Cu1-B2 158.39(8), B1-Cu1-B2 44.7(1).

The ligand **1**, as well as the complexes **2** and **E**, were studied by UV/Vis absorption, emission, and excitation spectroscopy in solution in order to examine the changes in the optical properties and the excited-state behavior of diborenes upon coinage-metal coordination. Selected photophysical data are given in Table 1, while the absorption and emission spectra recorded in toluene are shown in Figure 3.

Table 1: Selected photophysical data for **1**, **2**, and **E** (recorded at room temperature unless otherwise stated).

	Solvent	λ_{max} [nm]	λ_{em} [nm]	Φ_{fluo}	Stokes shift [cm^{-1}]	τ_f [ns]
1	Toluene	541	657	–[a]	3300	–[a]
2	Toluene	417	578	0.18	6700	2.47
2	THF	413	578	0.11	6900	1.11
2	MTHF (77 K)	411[b]	569	–[a]	6800	5.22 (9%) 11.6 (91%)[c]
E	Toluene	417	519	0.77	4700	6.18
E	THF	413	519	0.95	4900	6.96

[a] Not determined. [b] Excitation maximum. [c] $\tau_{av} = 11.05$ ns.

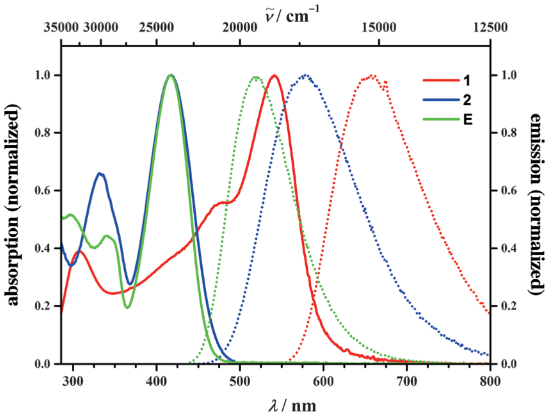

Figure 3. Absorption (solid lines) and emission (dotted lines) spectra of **1** (red), **2** (blue), and **E** (green) recorded in toluene at room temperature.

The free diborene **1** shows a very intense absorption band with a maximum at $\lambda_{abs} = 541$ nm and weaker, broad and overlapping bands at higher energy, similar to their previously reported behavior in Et_2O.[6b] For the copper species **2**, the absorption profile measured in toluene shows two distinct bands at $\lambda_{abs} = 332$ and 417 nm. An identical absorption at 417 nm was also found in the spectrum of **E**, but at higher energy, two distinct bands at $\lambda_{abs} = 342$ and 297 nm are also observed. Interestingly, the lowest-energy absorption band of the diborene **1** appears to shift dramatically to higher energy upon coordination to Cu or Ag. The diborene **1** is only very weakly emissive ($\lambda_{em} = 657$ nm) and determination of the quantum yield and lifetime was thus not possible, however, its small Stokes shift of ca. 3300 cm^{-1} is indicative of fluorescence. Upon excitation at 420 nm, the copper complex **2** shows a strong yellow luminescence at $\lambda_{em} = 578$ nm with a large Stokes shift of 6700 cm^{-1}. The heavy-atom effect, also mediated by the strong spin–orbit coupling (SOC) of the metal d electrons in Cu^I d^{10} complexes, usually quenches the fluorescence from the singlet excited state S_1 by efficient intersystem crossing (ISC) to the triplet excited state T_1. One would thus expect low-energy phosphorescence to predominate in the π-diborene complexes prepared herein.[12] Surprisingly, the quantum yield ($\phi = 0.18$) and lifetime ($\tau = 2.47$ ns) of **2** clearly indicate that this emission is a fluorescence process ($S_1 \rightarrow S_0$). Even at 77 K in a glassy matrix of 2-methyltetrahydrofuran (MTHF), we did not observe any phosphorescence for **2** between 500 and 1350 nm (see the Supporting Information). Instead, the emission lifetime of $\tau_{av} = 11.05$ ns (the average lifetime of the recorded biexponential decay) is very close to the intrinsic lifetime of the S_1 state ($\tau_0 = \tau_f/\Phi = 13.7$ and 10.0 ns in toluene and THF, respectively), thus pointing to a fluorescence quantum yield near unity. The large Stokes shift therefore appears to be a result of a pronounced charge-transfer (CT) character or a significant geometrical change in the emitting singlet excited state S_1, and not due to phosphorescence from T_1 (see below).

Similar behavior is found for **E**, the fluorescence band of which ($\lambda_{em} = 519$ nm) is found at higher energy than that of **2**. Most striking are the quantum yield ($\phi_{fluo} = 0.77$) and the fluorescence lifetime ($\tau_{fluo} = 6.18$ ns) of **E**, which are both distinctly higher than those of **2**. Upon switching from toluene to the more polar solvent THF, neither the bands of the absorption nor the emission spectra of **2** and **E** undergo a considerable change (Table 1), thus indicating that a geometrical change in the excited state is mainly responsible for the large Stokes shift, although there is a significant difference in quantum yields and lifetimes. For the copper species **2**, these values drop to $\phi_{fluo} = 0.11$ and $\tau_{fluo} = 1.11$ ns when the spectrum is recorded in THF rather than toluene. In contrast, the quantum yield of silver complex **E** ($\phi_{fluo} = 0.95$) is significantly higher in THF and nearly reaches unity.

It is important to note that the emission maxima of both complexes are shifted to higher energy compared to the free ligand **1**. Coordination of a chromophore ligand to a transition-metal center usually leads to a significant bathochromic shift owing to an enhanced (metal-to-ligand) charge transfer admixture of the emitting excited state.[12] As mentioned above, the observation of efficient fluorescence in Cu^I complexes is also highly unusual and, to the best of our knowledge, unprecedented.[12b,13] The same is true for silver(I) complexes, for which residual fluorescence besides the expected phosphorescence has been reported in only a very few cases.[14]

DFT and TD-DFT calculations were carried out (see the Supporting Information) in order to rationalize the photophysical behavior of the Cu (**2**) and Ag (**E**) complexes in comparison to: 1) the free diborene **1**, that is, the observed high-energy-shifted absorption and emission, and more importantly, 2) other M^I d^{10} transition-metal complexes, which usually show phosphorescence instead of fluorescence as a result of ISC processes ($S_1 \rightarrow T_1$).

It was found that coordination of diborene **1** to Cu or Ag mainly occurs through electrostatic interactions ($E_{el} = -145$ (**2**) and -133 kcal mol^{-1} (**E**)), with significantly smaller covalent contributions ($E_{orb} = -68$ and -54 kcal mol^{-1}, respectively; see the Supporting Information). The HOMO of the diborene is partially polarized towards the metal atom (Figure 4), thus leading to the formation of a metallacycle-like structure, which accounts for the weakening of the B=B double bond, as apparent from its observed lengthening upon metallation (1.590(5) (**1**) versus 1.645(6) (**E**) and 1.633(4) Å (**2**)). The LUMO remains mainly centered on the NHC groups in the metal complexes; owing to the nearly pure dative binding of **1** to Cu and Ag, the stabilization of the HOMO of **1** is much more pronounced than for the LUMO in **2** and **E**.

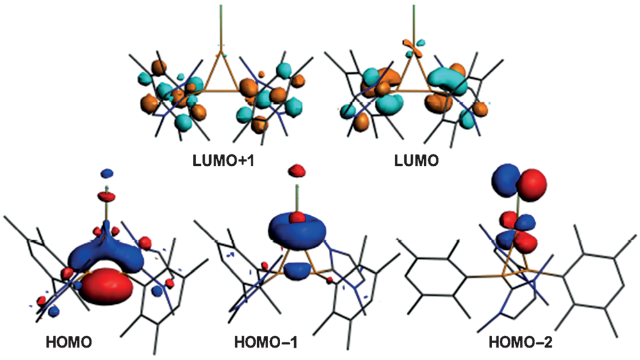

Figure 4. Selected frontier molecular orbitals of **2**.

The larger HOMO–LUMO gap in **2** and **E** compared to that of the free diborene **1** is responsible for the observed hypsochromic shifts of the lowest energy absorptions $S_0 \rightarrow S_1$ (calculated to be at 531 (**1**), 426 (**2**), and 434 (**E**) nm), since these bands originate mainly from a HOMO→LUMO transition for all three compounds (Figure 5). The S_1 states indeed exhibit a significant intraligand charge transfer (ILCT) character, thus leading to a large Stokes shift in the emission experiments of **2** and **E** (see above).

The question of why we detect highly efficient fluorescence rather than phosphorescence in **2** and **E** can now also be answered. Although diborene **1** is coordinated to transition metals with reasonable SOCs, the Cu and Ag atoms barely participate in the CT of the S_1 state owing to the nearly pure ligand nature of the frontier orbitals. The ILCT nature is maintained in the lowest excited triplet states T_1, which are also composed of HOMO→LUMO transitions and optimized at much lower energy (1275 (**1**), 764 (**2**), and 741 nm (**E**), respectively) than the experimental values for the S_1 states. The low degree of metal participation in the excited states, and thus the "weakly active" SOC, seems to be responsible for the low efficiency of the ISC processes.[13] Even if, in the case of **2**, triplet states are formed to a small extent, the sizeable energy gap between S_1 and T_1 would hamper the efficiency of spin-forbidden phosphorescence.

These findings show that incorporation of boron in the place of carbon can successfully lead to the construction of highly luminescent isolobal analogues of otherwise non-emissive coinage-metal olefin complexes. The results also constitute the first forays into the materials properties of compounds containing B=B multiple bonds, which, although appearing outwardly analogous to conventional olefins, in reality show vast electronic differences. These differences,

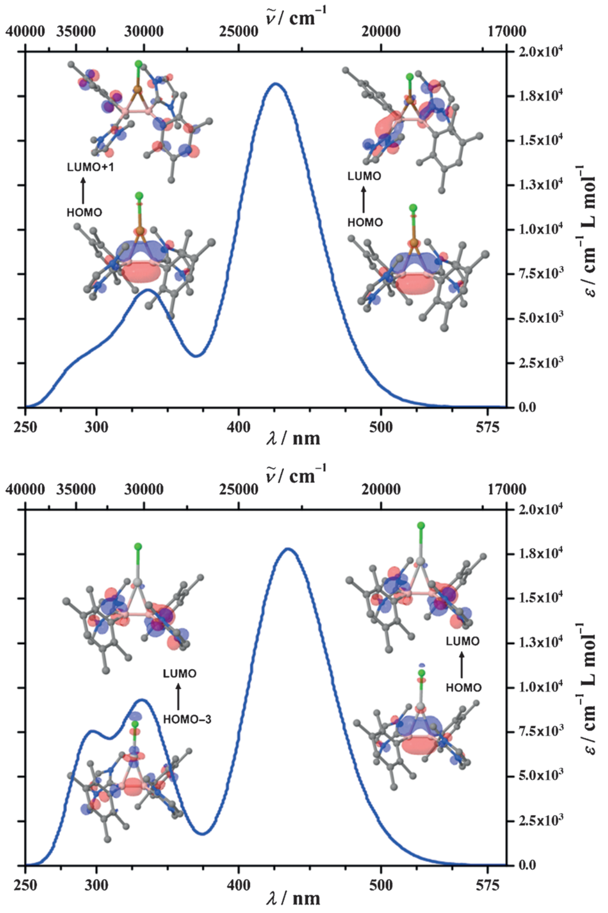

Figure 5. Calculated absorption spectra and main transitions of **2** (top) and **E** (bottom).

primarily the exceedingly energetic HOMO level of diborenes, are largely responsible for the phenomena we observe in this study. For instance, although there is some degree of σ donation and π backdonation in these complexes, the major contributor to the $M{-}B_2$ binding energy is electrostatic (owing to the high negative charge on the boron atoms). The ISC processes that one would normally expect from these metals, and the resulting phosphorescence, is thus suppressed. Similarly, the high-lying HOMO of the free diborene is significantly stabilized by coordination to the metal, thus explaining the large hypsochromic shift of the absoption upon metal coordination. We are currently investigating the scope and limitations of the synthesis and photophysical properties of these unusual new boron-based compounds. In particular, great potential can be envisaged for these complexes in the area of photoactive materials.

Keywords: boron · coinage metals · diborenes · fluorescence · intersystem crossing

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[11] See the Supporting Information section for full experimental, analytical, and crystallographic data, as well as computational details. CCDC 949591 (**2**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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