

Strongly Phosphorescent Transition Metal π Complexes of Boron-Boron Triple Bonds

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KEYWORDS: boron, copper complex, diboryne, luminescence, intersystem crossing

ABSTRACT: Herein are reported the first π complexes of compounds with boron-boron triple bonds to transition metals, in this case Cu^I. Three different compounds were isolated that differ in the number of copper atoms bound to the BB unit. Metallation of the B-B triple bonds causes lengthening of the B-B and B-C^{NHC} bonds, as well as large upfield shifts of the ¹¹B NMR signals, suggesting greater orbital interactions between the boron and transition metal atoms than those observed with recently published diboryne / alkali metal cation complexes. In contrast to previously-reported fluorescent copper(I) π complexes of boron-boron double bonds, the Cu_n- π -diboryne compounds (n = 2, 3) show intense phosphorescence in the red to near-IR region from their triplet excited states, according to their microsecond lifetimes, with quantum yields of up to 58%. While the Cu diborene bond is dominated by electrostatic interactions, giving rise to S₁ and T₁ states of pure IL(π - π^*) nature, DFT studies show that the Cu^I π complexes of diborynes reported herein exhibit enhanced metal d orbital contributions to HOMO and HOMO-1, which results in S₁ and T₁ having significant MLCT character, enabling strong spin-orbit coupling for highly efficient intersystem-crossing S₁→T_n and phosphorescence T₁→S₀.

INTRODUCTION

Transition metal (TM)-alkyne π complexes are key compounds in organic synthesis and catalysis. Such complexes form during catalytic processes and are important intermediates in many metal-catalyzed reactions involving alkynes, the most well-known being heteroatom-hydrogen additions (hydro-X-ation),¹ cycloadditions including [2+2+2] alkyne cyclotrimerizations,² the azide-alkyne Huisgen (click) cycloaddition,³ annulation reactions⁴ and the Pauson-Khand reaction.⁵ While many catalytically-relevant π complexes exist only as transient intermediates, a large number of room-temperature-stable and fully characterized TM-alkyne π complexes also exist.⁶ Some of these display intense luminescence and are thus of great interest for opto-electronic applications.⁷ Among the subset of photoactive TM-alkyne π complexes, the majority comprise clusters in which σ -acetylide ligands are additionally bound to coinage metals in an η^2 fashion.^{7a,b,e-j} However, a number of emissive Pt^{II}- σ -alkynyl complexes with group 11 cations bound side-on (η^2) to their alkynyl ligands have also been reported.^{7a,b,k}

Due to the inherent rarity of non-carbon alkyne analogues, far fewer π complexes between TMs and molecules containing element-element (E-E) triple bonds are known. Of these, the tendency for many elements to resist forming E-E multiple bonds, exemplified by their often strongly *trans*-bent structures, leads to unusual bonding situations with the bound metal fragments. A salient example is Iwamoto's reaction of a dis-

ilyne (RSiSiR) with [M(PCy₃)₂] (M = Pd, Pt), which led to the formation of stable side-on-bound complexes (**I**) with non-planar Si atoms (Figure 1).⁸

One year later, Robinson and coworkers presented a copper(I) chloride complex of a carbene-stabilized disilicon(0) fragment, which, similar to the disilyne complex **I**, avoids true π -complex formation by binding the copper fragment in an η^1 fashion.⁹ Nevertheless, both computational studies and VT NMR spectroscopy suggested that there exists a dynamic equilibrium whereby the copper fragment switches between the two silicon atoms through a π -bound intermediate (**IIa**). A number of non-carbon TM/E \equiv E π complexes also exist with other main-group elements, such as complexes of group 15 diatomics (N₂,¹⁰ P₂,¹¹ As₂,¹² Bi₂¹³), a digermine,¹⁴ a diplumbyne dianion (Pb₂²⁻),¹⁵ and iminoboranes (RBNR).¹⁶

Thus far, only a couple of compounds with multiple bonds between group 13 elements¹⁷ have shown the tendency to form π complexes with metals. The first example was prepared in our laboratories in 2012, and took the form of a π complex between AgCl and a doubly NHC-stabilized diborene (LRB=BRL) (**III**, Figure 1), with a copper analogue (**IV**) being presented in 2015.¹⁸ An unexpected property of these compounds is their bright fluorescence with exceptionally high quantum yields, hinting at their potential application for use as emissive materials, in stark contrast to TM-alkene complexes, which are not generally known to be emissive. In 2013 we presented the isolation of a π complex between a zeroval-

lent platinum fragment $[\text{Pt}(\text{PCy}_3)_2]$ and an in-situ-generated base-free diborene ($\text{RB}=\text{BR}$, **V**),¹⁹ while in 2016 we reported the synthesis of a complex containing the same diborene ligand and bound across one Pt-Pt bond of the trimetallic fragment $[\text{Pt}_3(\text{PCy}_3)_3]$.²⁰

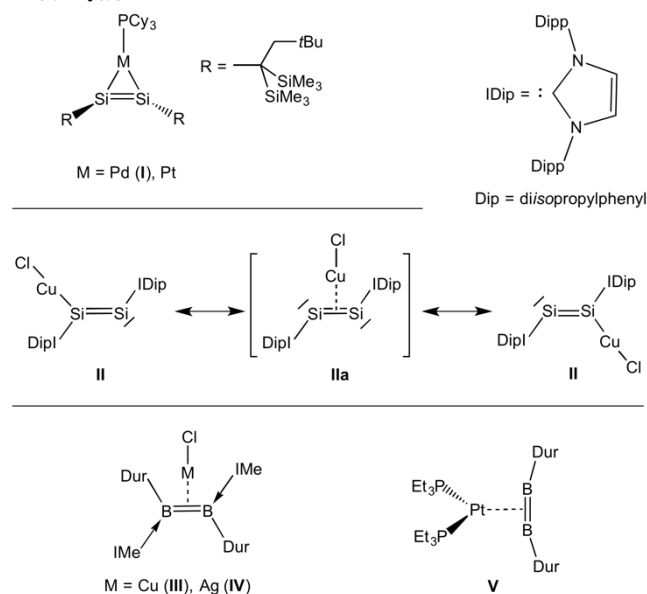


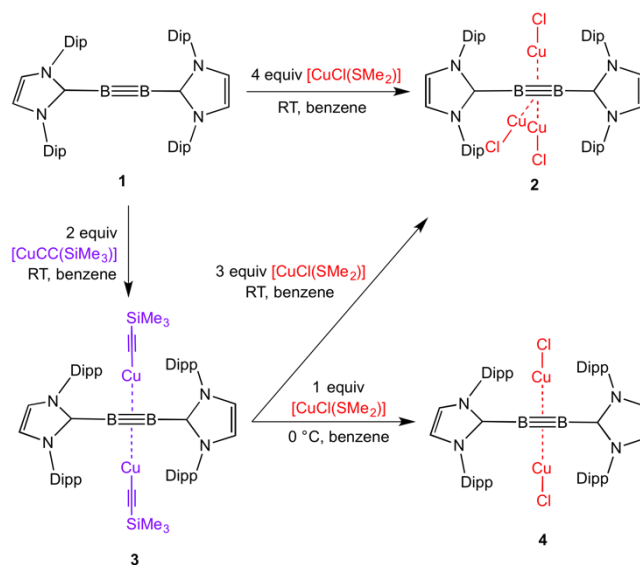
Figure 1. Selected transition metal π complexes of disilyne and diborene compounds (top and bottom). Dynamic complexation equilibrium of a Cu^{I} disilicon(0) complex (middle).

The diboryne B_2IDip_2 (**1**; IDip = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene), the first reported example of a stable compound with a boron-boron triple bond,²¹ has also recently shown the ability to bind electron-deficient (non-transition) metal centers, with the isolation of complexes in which naked alkali metal cations are encapsulated by the BB triple bond and the pendant aryl groups of the diboryne unit.^{21d} However, a computational study of these complexes indicated that very little of the bonding interactions between the alkali metal cations and the BB triple bond can be ascribed to orbital interactions, and thus the binding of the metal cations is dependent on strong electrostatic interactions. This work inspired us to turn to neutral transition metal fragments as potential coordination partners for diborynes, in the hopes of constructing stronger $M\text{-B}_2$ π bonds with significant covalent character. Herein we describe the first isolation and characterization of transition metal π complexes of boron-boron triple bonds – including di- and trinuclear π complexes – and uncover their luminescent properties.

RESULTS AND DISCUSSION

Synthesis and structural characterization of Cu^{I} diboryne π complexes. Our first attempt at binding transition metal fragments to boron-boron triple bonds was the addition of varying amounts of $[\text{CuCl}(\text{SMe}_2)]$ to diboryne **1** (Scheme 1). The only pure compound we could isolate was obtained using a Cu-to-**1** molar ratio of 4:1; higher and lower ratios led to intractable mixtures and/or the decomposition of **1**. Over the course of the 4:1 reaction a color change from green to orange was observed, as well as an upfield shift of the ^{11}B NMR signal from 39 to -7.3 ppm. After filtration of the elemental copper formed during the reaction, and repeated recrystalliza-

tion, a small amount of a pure orange solid was obtained (**2**; 8% yield based on the derived formula). Crystallization from a mixture of dichloromethane/hexane provided crystals suitable for X-ray diffraction (Figure 2). Compound **2** crystallizes in Pccn symmetry with a C_2 rotation center between the two boron atoms. Its solid-state structure shows the complexation of three copper chloride units arranged in a T-shape around the BB bond, with the two acute Cu -centroid(BB)- Cu angles of 88.39° . The BB bond of tris(copper) complex **2** ($1.526(4)$ Å) is longer than that of the metal-free precursor **1** ($1.449(3)$ Å); the same is true for the B-C bonds which are significantly lengthened upon copper coordination (**1**: $1.487(3)$, $1.495(5)$ Å; **2**: $1.562(3)$ Å). The NHC units of **2** are coplanar, with the central copper sandwiched between one Dipp group of each NHC. However, this arrangement appeared not to persist in solution, as NMR spectroscopy showed only one sharp set of signals for the Dipp groups, indicating that the three CuCl moieties rotate around the BB unit without any significant energy barrier.



Scheme 1. Reactions of **1** with Cu^{I} complexes, leading to the di- and trinuclear π -diboryne complexes **2**, **3** and **4**.

The low yield of complex **2** and apparent formation of elemental Cu during the reaction led us to assume the operation of competing redox reactions ($\text{Cu}^{\text{I}} \rightarrow \text{Cu}^0$) induced by the strongly reductive diboryne **1**.^{21b,c,e} In an attempt to suppress this reaction pathway, we turned to the more redox-inactive copper complex $[\text{Cu}(\text{C}\equiv\text{CSiMe}_3)]$,²² which, when treated with 0.5 equiv. of **1**, provided full conversion to a new complex (**3**). Equimolar addition of $[\text{Cu}(\text{C}\equiv\text{CSiMe}_3)]$ to **1** also led to **3** according to ^{11}B NMR spectroscopy, albeit with ca. 50% conversion. Addition of greater than two equivalents of $[\text{Cu}(\text{C}\equiv\text{CSiMe}_3)]$ to **1** provides only **3** (and presumed excess $[\text{Cu}(\text{C}\equiv\text{CSiMe}_3)]$). Complex **3** was obtained as (diffraction-quality) red crystals in 86% yield. ^1H NMR spectroscopy indicated the presence of two SiMe_3 units per diboryne, suggesting that the complex contained only two copper fragments bound to the BB triple bond (Scheme 1). The ^{11}B NMR spectrum of **3** shows a signal at -1.7 ppm, a less-pronounced upfield shift than that observed in the synthesis of **2**. The solid-state molecular structure of **3** confirmed the presence of two $[\text{Cu}(\text{C}\equiv\text{CSiMe}_3)]$ units bound to the B-B bond, however, these are somewhat splayed compared to those of **2**, with a Cu -BB(centroid)- Cu angle of 115.23° (Figure 2). The B-B dis-

tance of **3** (1.478(3) Å) sits between those of **1** and **2**, as do the B–C distances (1.535(2) Å and 1.531(2) Å). Again, the structure found in the single-crystal appears to deviate from the species present in solution, as the sharp signals in the ¹H NMR spectrum suggest a highly symmetrical arrangement with a 180° angle between the Cu–TMSA groups. Free rotation of the copper moieties is unlikely, as the bulky TMSA groups should lead to a significant barrier due to steric interactions with the Dipp substituents of the NHCs.

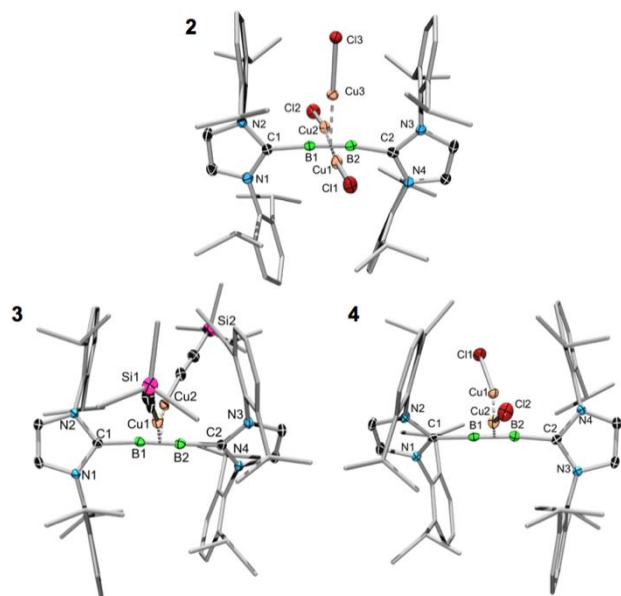


Figure 2. Molecular structures of **2**, **3** and **4** in the solid state. Thermal ellipsoids are shown at 50% probability. H atoms and the ellipsoids of the diisopropylphenyl rings are omitted for clarity. Selected bond lengths (Å) and angles (°) for **2**: B1–B1' 1.526(4), B1–Cu1 2.056(2), B1'–Cu1 2.068(2), B1–Cu2 2.107(2), Cu1–B1–Cu2 81.03(8), Cu1–Cu2–Cu1' 90.13(2). For **3**: B1–B2 1.478(3), B1–Cu1 2.087(2), B1–Cu2 2.087(2), B2–Cu2 2.085(2), B2–Cu1 2.087(2), Cu1–B1–Cu2 104.53(8), Cu1–B2–Cu2 104.15(8). For **4**: B1–B2 1.486(4), B1–Cu1 2.087(3), B1–Cu2 2.079(3), B2–Cu2 2.078(3), B2–Cu1 2.075(3); Cu1–B1–Cu2 102.6(1), Cu1–B2–Cu2 103.0(1).

Given the binding of only two copper units in compound **3**, we envisaged the possibility of adding a third, smaller, copper fragment to form a trinuclear complex akin to **2**. However, reaction of **3** with one equivalent of [CuCl(SMe₂)] led not to incorporation of a third copper unit but instead to the complete substitution of the [Cu(CCSiMe₃)] units by [CuCl], providing the dinuclear complex **4** in 48% yield as a yellow solid. Alternatively, reaction of **3** with two or more equivalents of [CuCl(SMe₂)] led to the formation of trinuclear complex **2** (Scheme 1). A single-crystal X-ray diffraction study indicated that compound **4** possesses a very similar geometry to compound **3**, with only very minor or statistically insignificant differences in the B–B (1.486(4) Å) and the B–C distances (1.545(4), 1.547(4) Å). The Cu1–BB(centroid)–Cu2 angle (113.59°) is in the same range as that in compound **3**. According to NMR spectroscopic studies, the orthogonal conformation is prone to free rotation of the CuCl moieties as found for compound **2**.

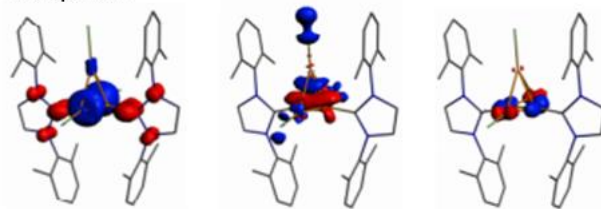
Overall, the solid-state structures of **2–4** suggest that increasing metallation of the B≡B unit not only weakens this

bond but the B–C bonds as well. The B–Cu distances, averaging 2.077 Å (**2**), 2.087 Å (**3**) and 2.080 Å (**4**), are comparable to one another, but significantly shorter than those of diborene–CuCl analogue **III** (2.149(3), 2.146(3) Å).¹⁸ Known copper boryl complexes containing Cu–B σ bonds²³ (2.002(3) Å,^{23a} 1.973(6) Å,^{23b} 1.995(4) Å^{23c}) show shorter distances than **2–4**, a contrast to be expected given the established differences between σ and π bonding. It should also be noted that, while there are over a thousand crystallographically-characterized complexes containing more than two metal centers π-bound to alkynes, only a handful do not contain secondary interactions tethering the metals together, e.g. direct M–M bonds, bridging ligands or metal centers.²⁴ Thus, **2** represents a very rare example of a π complex with more than two independent metal units bound to a triple bond.

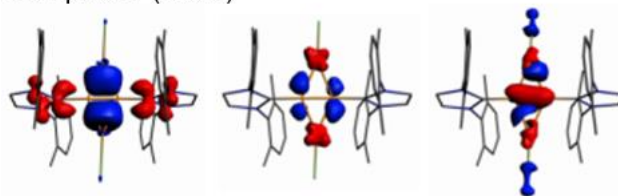
Table 1. The energy decomposition (in kcal mol⁻¹) for compounds **2'** and **4'** calculated via ETS-NOCV at the B3LYP*/TZP level.

	ΔE_{Pauli}	$\Delta E_{\text{Orb. Int}}$	ΔE_{Elsta}
2'	449.01	-212.65	-432.16
4' (linear)	271.72	-127.56	-283.32
4' (orthogonal)	283.14	-130.32	-289.68

Complex 2'



Complex 4' (linear)



Complex 4' (orthogonal)

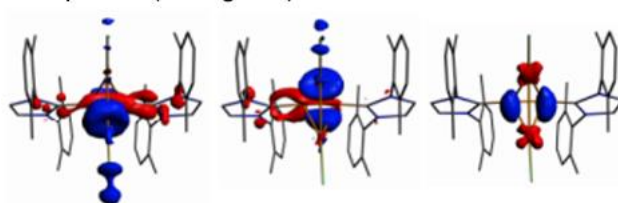


Figure 3. First three deformation densities of **2'**, linear and orthogonal **4'** calculated at the B3LYP*/TZP level. Isovalues set to 0.003 except the far right, middle deformation density (set to 0.002). Charge flow from red to blue.

DFT Calculations. Calculations provided support for the observed experimental results. Ground-state energy minimization at the B3LYP*/TZP level and analysis of the charge flow between the diboryne and the copper units using the ETS-NOCV method were carried out on simplified model compounds **2'** and **4'**, which differ from **2** and **4** by the replacement of the eight *i*Pr groups with methyl groups. For the pur-

poses of analysis, compound **4'** was also partially optimized in its orthogonal conformation where the CuCl units are perpendicular to each other. The Cu-B-B-Cu dihedral angle was set to 90° (see Supporting Information). The bonding between the diboryne and the CuCl units can be decomposed into several interactions, namely orbital and electrostatic interactions, and Pauli repulsion (see SI). Table 1 shows the different energetic components of the bonding in compounds **2'** and **4'**. Charge flow between the diboryne and the CuCl units can be depicted by so-called deformation densities, as shown in Figure 3 for compounds **2'** and **4'**. The energy decomposition analysis shows that for both compounds **2'** and the two conformations of **4'**, the attractive electrostatic interaction is more dominant than the orbital interaction, although the repulsive Pauli interaction also contributes to a considerable extent (further discussion on the nature of interaction based on the so called Natural Bonding Orbitals is given in the SI). The non-negligible contribution from the orbital and Pauli interactions, together with the obvious back-bonding to the boron centres (seen in the second deformation density plot of linear **4'**, and the third deformation density plot of orthogonal **4'**, Figure 3), suggest the presence of covalent character in the diboryne-copper interaction. Furthermore, calculations show that the linear conformation of compound **4'** is more stable than the orthogonal conformation by $4.77 \text{ kcal mol}^{-1}$, resulting from the substantially reduced Pauli repulsion component. The deformation densities show a greater flow of electrons from the B-B bond to the metal centers in the orthogonal conformation, hence the increased stability of the linear conformation is due

to the lower amount of Pauli repulsion compared to the orthogonal conformation. Thus it is likely that where crystal packing forces within the solid can overcome the destabilizing interactions, compound **4** will adopt the orthogonal conformation to garner improved orbital overlap.

Finally, the frontier molecular orbitals (MOs) of **2'** and **4'** have been compared with those of the previously published d^{10} coinage metal π complexes of diborenes (Figure 4). Within the unoccupied MOs there are strong similarities between all compounds, in that the LUMO possesses strong BB π^* character, while the LUMO+1 is located at the NHC. Interestingly, the HOMO of the diborene complex **III** has very little Cu d orbital contribution, while the BB unit barely participates in the HOMO-1 and HOMO-2. In contrast, the HOMOs of **2'** and **4'** show a much larger degree of contribution from the metal centres in line with the increased covalent nature, which has a profound effect on the photophysical properties (*vide infra*). The dynamics and characterization of the low-lying excited states in different spin manifolds, both in the gas and condensed phases, will be investigated and published at a later date.

Photophysical studies. The successful synthesis and investigation of copper π -diborene complexes in 2014, which turned out to be highly luminescent boron analogues of otherwise non-emissive TM alkene π -complexes, indicated the potential of boron-based π -chromophores,¹⁸ prompting us to study the photophysical properties of the copper π -diboryne complexes

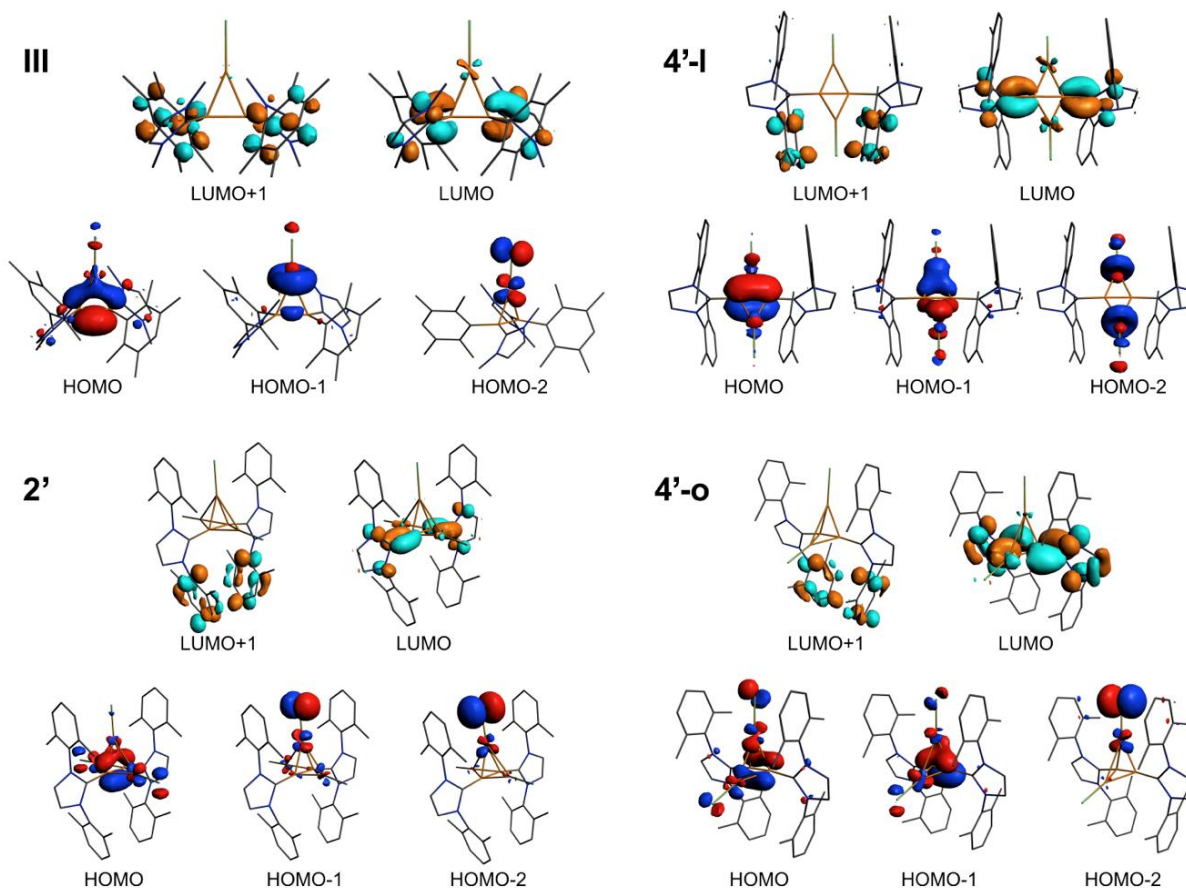


Figure 4. Selected frontier molecular orbitals of the copper diborene π complex **III**, and the tricopper π -diboryne complex **2'** and the dicopper π -diboryne complex **4'** in its linear (l) and orthogonal (o) conformations calculated at the B3LYP*/TZP level.

in some depth. Compounds **1-4** were characterized by UV/vis absorption, emission and excitation spectroscopy in solution and in the solid state. Selected photophysical data are given in Table 2. Complexes **2-4** show very strong absorption bands with maxima between $\lambda_{\text{abs}} = 335$ and 385 nm, and additional weak bands between 400-500 nm, which are most pronounced for [(CuCl)₃{ μ_3 : η^2 -B₂IDip₂}] (**2**) with an additional maximum at $\lambda_{\text{abs}} = 420$ nm (Figure 5). Upon excitation at $\lambda_{\text{ex}} = 420$ nm of **2** in toluene solution, an intense orange-red luminescence ($\lambda_{\text{max}} = 637$ nm) with a quantum yield of $\Phi = 0.29$ is observed, the long lifetime of which ($\tau = 26.45$ μ s) confirms its assignment as phosphorescence from the triplet excited state T₁. In the solid state, the emission is even more efficient ($\Phi = 0.58$). The excitation spectra, both in solution and in the solid state, are in agreement with the absorption spectrum (Figure 5, bottom). In contrast, the dicopper(I) diboryne complexes **3** and **4** show much weaker luminescence in the solid state, reaching only $\Phi = 0.03$ for [(CuCl)₂{ μ_2 : η^2 -B₂IDip₂}] (**4**), the band of which is bathochromically shifted into the near-IR region by ca. 160 nm and exceptionally broad, spanning the range between 620-1150 nm. While [(CuC≡CSiMe₃)₂{ μ_2 : η^2 -B₂IDip₂}] (**3**) does not emit in solution, compound **4** exhibits weak phosphorescence in solution, being blue-shifted relative to its solid-state emission to $\lambda_{\text{max}}(\text{em}) = 674$ nm.

Table 2. Selected Photophysical Data for Diboryne **1 and its Copper(I) Complexes **2-4** Recorded at Room Temperature under Argon in the Solid State and in Toluene Solution (in Brackets).**

	$\lambda_{\text{max}} / \text{nm}^a$	$\lambda_{\text{em}} / \text{nm}$	Φ	$\tau / \mu\text{s}$
1	335, 385, 600	- ^b	- ^b	- ^b
2	336, 352, 420	628 (637)	0.58 (0.29)	52 (26)
3	384, 458	805 (- ^b)	- ^b	- ^b
4	378, 450	805 (674)	0.03 (0.01)	25 (2.0 ^c)

^a In toluene. ^b Emission too weak. ^c Average lifetime; solution of multi-exponential decay: $\tau = 0.7(75\%)$, $3.3(21\%)$, $19(4\%)$ μ s.

We note that the excitation spectra of **3** and **4** do not match their absorption spectra, in that the high intensity absorption at $\lambda_{\text{max}}(\text{abs}) \approx 380$ nm represents a minimum. Thus, excitation in that particular band leads to less population of the emissive triplet states than one would expect. This indicates that these two complexes do not obey Kasha's Rule, which states that ISC, photochemistry or fluorescence occur from the S₁ state because the internal conversion S_n → S₁ is much faster than any competing processes.²⁵ Presumably, this high-energy absorption is of intra-ligand (IL) (π - π^*) nature, localized at the Dipp substituents of the NHC, and does not couple well with the S₁ geometry that undergoes ISC. Although this absorption is also present in **2**, its specific structural and electronic characteristics seem to allow for good coupling between the IL(π - π^*) state and the S₁ state, allowing for efficient ISC S₁ → T_n.

The differing luminescence properties of the dicopper(I) complexes (**3/4**) and the tricopper(I) compound **2** are likely to be related to the specific orientation of the Cu^I centers and due to structural changes in the excited state. The orthogonal arrangement in **3** and **4** found in the single crystals gives rise to the low-energy solid-state emission at $\lambda_{\text{max}}(\text{em}) = 805$ nm. However, a flattening distortion of the two copper(I) units to a

linear arrangement in the excited state in toluene appears to occur in **4**, which is not possible to this extent in the solid state, and leads to a hypsochromic shift of the emission as a result of a more stabilized ground state with a linear geometry. This is in line with our DFT studies showing the linear coordination to be stabilized by 4.77 kcal mol⁻¹ compared to the geometry found in the single crystals (*vide supra*). The same is not observed for **3**, as the TMSA groups lead to enhanced non-radiative decay and thus no emission is detected in solution.

The threefold coordination of CuCl to diboryne **1** provides a permanent linear arrangement of two copper(I) units in **2**, and thus gives phosphorescence in both solution and in the solid state, which is similar to the emission profile of **4** in toluene solution. The third CuCl unit of **4**, orthogonal to the other two units, does not greatly influence the energy of the emitting T₁ state.

The previously-reported d¹⁰ coinage metal π complexes of diborenes fluoresce efficiently from their S₁ state despite the strong spin-orbit coupling (SOC) of the heavy atom.¹⁸ This was rationalized by S₁ and T₁ being of pure IL(π - π^*) nature, as the HOMO and the LUMO are localized at the diborene (Figure 4), a consequence of the largely electrostatic bonding situation. The Cu^I π complexes of diborynes **2-4** reported herein show intense phosphorescence from T₁, with no emission detected from S₁. This difference between diborene and diboryne π complexes is due to enhanced metal d orbital contributions to HOMO and HOMO-1 in compounds **2-4** (*vide supra*), which results in S₁ and T₁ having significant MLCT character and enables strong SOC that facilitates highly efficient ISC S₁ → T_n and phosphorescence T₁ → S₀ transitions.²⁶

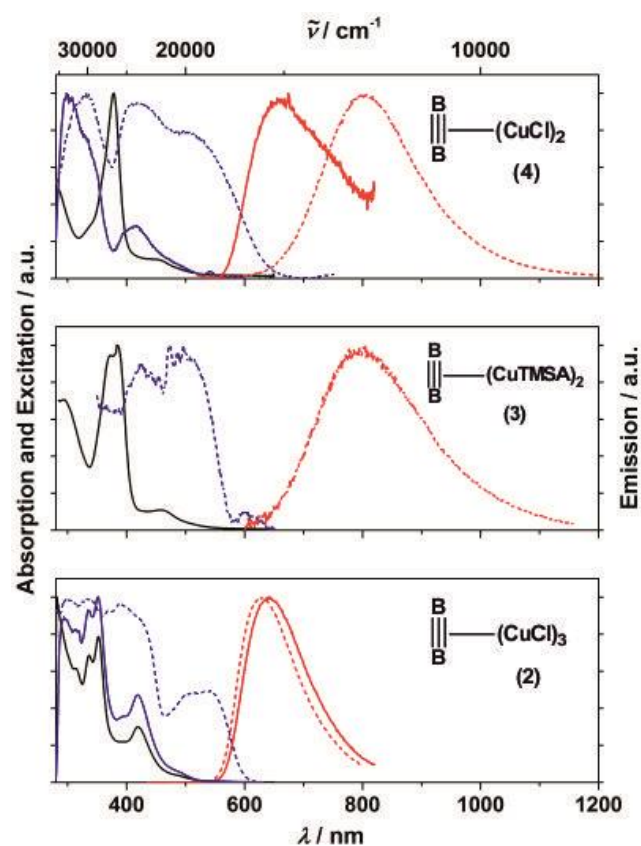


Figure 5. Absorption (black), excitation (blue) and emission (red) spectra of **2-4** in degassed toluene solution (solid line) and in the solid state (dashed line) under argon at 297 K.

CONCLUSIONS

With the isolation of three copper π -diboryne complexes, this work has resulted in the first syntheses of boron analogues of transition metal alkyne π complexes. Whereas two $\text{CuC}\equiv\text{CSiMe}_3$ units can be coordinated in an orthogonal geometry to the boron-boron triple bond, di- and tri-coordination can be achieved by using CuCl . Structural characterization and DFT studies indicate a weakening of the $\text{B}\equiv\text{B}$ bond upon metalation due to enhanced orbital interactions between the transition metal atoms and the diboryne compared to previously reported diboryne / alkali metal cation complexes and d^{10} coinage metal diborene complexes. The higher degree of metal d orbital participation in the occupied frontier orbitals (HOMO and HOMO+1) also results in photophysical properties that are vastly different from the diborene complexes. Whereas the latter show fluorescence from their S_1 states, due to their pure $\text{IL}(\pi-\pi^*)$ nature located at the $\text{B}=\text{B}$ unit, the copper(I) π -diboryne π complexes exhibit quantitative $S_1\rightarrow T_n$ ISC and very efficient red to near-IR phosphorescence with quantum yields of up to 0.58. Thus, the bonding situation of the BB unit, *i.e.* $\text{B}=\text{B}$ double vs. $\text{B}\equiv\text{B}$ triple bond, and the degree of metalation, allows control of the excited state behavior, paving the road to new boron-based luminescent materials.

ASSOCIATED CONTENT

Supporting Information. Experimental and spectroscopic data, DFT and TD-DFT results, crystallographic details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

A.S. and H.B. thank the Deutsche Forschungsgemeinschaft (DFG) for financial support (grant nos. STE1834/5-1 and BR1149/16-1). A.V. thanks the University of Sussex for financial support.

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