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Communication

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Highly Efficient Blue Phosphorescence from Triarylboron-Functionalized Platinum(II) Complexes of *N*-Heterocyclic Carbenes

Zachary M. Hudson,[†] Christina Sun,[†] Michael G. Helander,[‡] Yi-Lu Chang,[‡] Zheng-Hong Lu,[‡] and Suning Wang*,[†]

[†]Department of Chemistry, Queen's University, Kingston, Ontario, K7L 3N6 Canada

[‡]Department of Materials Science and Engineering, University of Toronto, Ontario, M5S 3E4 Canada

Supporting Information

ABSTRACT: The first examples of $BMes_2$-functionalized NHC chelate ligands have been achieved. Their Pt(II) acetylacetonate complexes have been synthesized and fully characterized. These NHC-chelate Pt(II) compounds display highly efficient blue or blue-green phosphorescence in solution (Φ = 0.41−0.87) and the solid state (Φ = 0.86−0.90). Highly efficient electroluminescent devices based on these new Pt(II) compounds have also been fabricated.

Since the X-ray crystal structure of a stable *N*-heterocyclic carbene (NHC) was first determined by Arduengo in 1991,[1] these compounds have gone from highly specialized ligands to among the most widely used in organometallic chemistry.[2,3] Characterized by exceptionally strong σ-bonding and readily tunable steric and electronic properties, NHCs have found extensive use in both organic and transition-metal catalysis.[3] More recently, the rapid expansion of NHC research has led to their incorporation into a wide variety of functional materials, including antimicrobial agents,[4] liquid crystals,[5] supramolecular structures,[6] and luminescent compounds.[7]

Phosphorescent transition-metal compounds are currently of great interest as biological imaging agents, chemical sensors, and emitters for organic light-emitting diodes (OLEDs).[8] In particular, blue phosphorescent materials represent a considerable challenge, as they often suffer from poor stability and low emission quantum yields. Transition-metal phosphors containing NHC ligands, however, show promise as a solution to this problem. The strong ligand field of the carbene can raise the energy of nonradiative d−d excited states on the metal center, increasing the energy spacing with emissive excited states and improving quantum yields.[7b] Furthermore, the stability of metal−carbene bonds may also increase the operational lifetime of these materials in organic electronic devices. On the basis of these principles, a handful of reports have described the use of NHC complexes of Pt(II) and Ir(III) as phosphorescent emitters for OLEDs.[9]

We and others have recently shown that the phosphorescence of many metal complexes may be dramatically enhanced by functionalization with a triarylboron group.[10−12] This moiety is a powerful π-electron acceptor due to the empty p orbital on boron, facilitating both charge-transfer luminescence and electron transport. When protected from nucleophilic attack by appropriate bulky substituents, highly stable materials may be prepared with impressive quantum yields and charge-transporting properties. As a result, phosphorescent triarylboranes have found use as anion sensors,[10] vapochromic materials,[11] and phosphorescent emitters in OLEDs,[12] including the most efficient Pt(II)-based OLED reported to date.

By combining the emissive and electron-transporting properties of the Lewis acidic triarylboron group with the strong ligand field of *N*-heterocyclic carbenes, triarylboron-functionalized NHCs would be versatile ligands that could find use in both catalysis and advanced materials. Furthermore, in contrast to blue phosphorescent Ir(III) compounds which have been extensively explored, examples of efficient blue-emissive Pt(II) compounds in OLEDs remain rare.[13] Herein we report the synthesis of the first examples of triarylboron-functionalized NHC chelate ligands and their blue and blue-green phosphorescent Pt(II) complexes. These compounds are highly stable to air, moisture, and UV irradiation and have been used as triplet emitters in efficient electrophosphorescent devices.

The synthesis of the boron-functionalized imidazolium salts **1d** and **2d** are readily achieved by Debus/Radziszewski cyclization of the phenylimidazole π-skeleton from the respective triarylboron-functionalized anilines, which were prepared by a modified method of Glogowski and co-workers[14] (Scheme 1). Benzyl protection of the appropriate bromoanilines followed by metal−halogen exchange with *n*-BuLi and substitution with $BMes_2F$ affords the desired amines in good overall yield after deprotection of the benzyl groups. Cyclization with glyoxal, ammonia, and formaldehyde provides the boron-functionalized phenylimidazoles, and upon stirring with CH_3I at room temperature the asymmetric imidazolium salts **1** and **2** may be easily isolated as white precipitates.

The synthesis of the Pt(II) complexes **BC1** and **BC2** is challenging, as literature methods proved incompatible with ligands **1** and **2**. To date only two reports of carbene compounds with the general formula [Pt(C^C)(O^O)] have appeared in literature, prepared by first reacting the imidazolium salts of the NHC ligands with Ag_2O.[9c,f] In these cases, subsequent transmetalation at 80 °C with $[PtCl_2(COD)]$ followed by substitution with acetylacetone in the presence of KO^tBu at 100 °C afforded the desired complexes. Unfortunately, ligands **1** and **2** were found to be unstable to Ag(I) as well as to extended heating at high temperature under basic conditions. However, we

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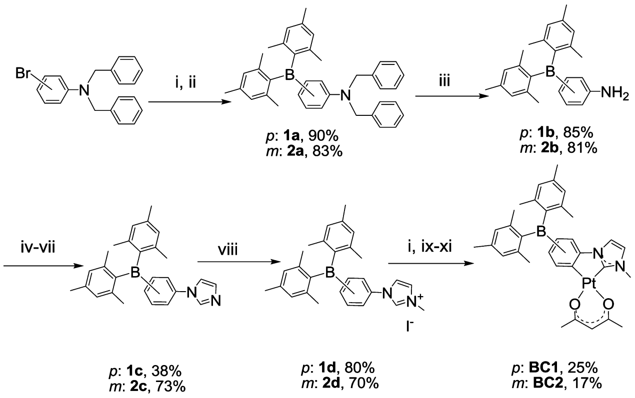
Scheme 1. Synthesis of Boron-Functionalized C^C-chelate Carbene Complexes[a]



[a]Reagents and conditions: i) *n*-BuLi, THF, −78 °C; ii) $FBMes_2$, THF, −78 °C to RT; iii) Pd/C, TsOH, EtOH, 25 °C; iv) glyoxal THF/MeOH, 25 °C; v) H_2CO, NH_4Cl, 25 °C; vi) H_3PO_4, reflux; vii) NaOH(aq), 0 °C; viii) MeI, THF, 25 °C; ix) $[PtMe_2(SMe_2)]_2$, −78 to 55 °C; x) TsOH, 25 °C; xi) Na(acac), THF/MeOH, −78 °C.

recently reported a simple one-pot procedure for the synthesis of N^C- and C^C-chelate Pt(II) *β*-diketonate compounds,[15] which was readily adapted to the synthesis of **BC1** and **BC2**. Deprotonation of the imidazolium salts with *n*-BuLi gives the corresponding free carbenes, which are then coordinated to Pt(II) on the addition of $[PtMe_2(SMe_2)]_2$. Mild heating at 55 °C affords the corresponding Pt(C^C)Me(SMe_2) complexes with irreversible loss of CH_4. Addition of *p*-toluenesulfonic acid (TsOH) induces loss of the remaining methyl group as CH_4, and addition of Na(acac) at low temperature gives the desired complexes which can then be isolated by column chromatography as yellow solids.

The molecular design of these complexes is intended to achieve high-energy blue phosphorescence with maximum quantum yield (Φ_P). The C^C chelate backbone presents a strong ligand field to the Pt(II) center, raising the energy of nonradiative d−d excited states and reducing thermal quenching. The acetylacetonate (acac) ancillary ligand provides good solubility as well as solution and solid-state stability, while its rigid structure and high triplet energy level help to increase Φ_P. The incorporation of a $BMes_2$ group serves to greatly enhance metal-to-ligand charge-transfer phosphorescence.

Single crystals of both **BC1** and **BC2** were successfully obtained and have been examined by X-ray diffraction analyses.[16] (Figure 1) Both molecules display highly planar geometries about the Pt(II) center with minimal strain apparent in either structure, important for the maximization of phosphorescent quantum yields. The strength of the carbene donor is evident in both cases, exhibiting C−Pt bond lengths shorter than those observed between the Pt(II) center and the phenyl ring. The considerable trans influence of the carbene can also be observed, with the Pt−O bond *trans* to the carbene lengthened by as much as 0.05 Å relative to more common nitrogen donors in similar N^C chelate cyclometalated systems.[12b] The crystal structures of both **BC1** and **BC2** show discrete dimeric Pt−Pt stacking, with Pt−Pt distances of 3.389(2) and 3.505(2) Å, respectively (see Supporting Information [SI]).

Both **BC1** and **BC2** display weak absorption bands around 375 nm (Figure 2), which are absent in the nonborylated phenylimidazole Pt(II) complex.[9f] TD-DFT calculations at the B3LYP level of theory demonstrate that the lowest triplet state involves mainly HOMO to LUMO character (see SI). The HOMO levels include significant electron density on the Pt(II) centers, whereas the LUMO levels show large contributions from the empty p orbital on boron, with significant participation of the *π*-backbone of the ligands in both orbitals. The lowest-energy electronic transitions are thus of mixed MLCT/LC character, and it can be seen that the $BMes_2$ group significantly enhances MLCT in these C^C chelate systems. The enhancement in MLCT is accompanied by a large increase in phosphorescent quantum yield for both complexes, relative to the parent nonborylated Pt(C^C)(acac) complex. Doped PMMA films (10 wt %) of **BC1** and **BC2** exhibit impressive quantum yields of 90 and 86%, respectively, compared to only 13% for an analogous control compound lacking the $BMes_2$ group. Despite the difficulty in developing blue-emissive Pt complexes, the research groups of Strassner[9h] and Chi[13g] respectively have recently reported blue-emissive complexes with quantum yields of 50% and 56% in the solid state, although higher values are known for blue-green emitters.[9f,13f] The solid-state quantum yield of **BC2** thus represents the highest observed to date for a blue phosphorescent Pt(II) complex.[13] **BC1** exhibits blue-green phosphorescence in the solid state and solution, with an emission maximum of 478 nm in CH_2Cl_2. This emission is blue-shifted by 20 nm in **BC2**, resulting in sky-blue emission from the complex at λ_{max} = 462 nm (Figure 2, Table 1).

DFT results indicate that the 5-position of the phenyl ring makes a large atomic orbital contribution to the HOMO of the

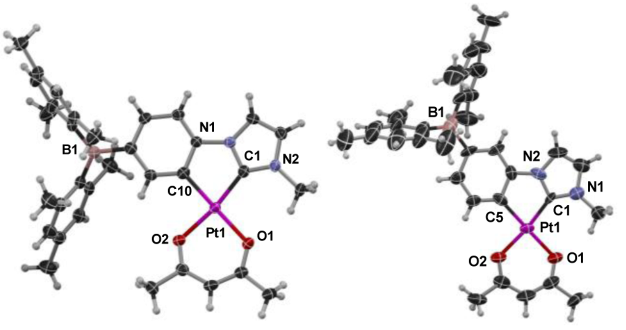


Figure 1. The crystal structures of **BC1** (left) and **BC2** (right) with 50% thermal ellipsoids and labeling schemes for key atoms. Important bond lengths (Å) and angles (deg), **BC1**: Pt(1)−C(1) 1.947(4), Pt(1)−C(10) 1.989(4), Pt(1)−O(1) 2.095(3), Pt(1)−O(2) 2.040(3); C(1)−Pt(1)−O(2) 170.68(13), C(10)−Pt(1)−O(1) 176.53(12). **BC2**: Pt(1)−C(1) 1.912(8), Pt(1)−C(5) 1.983(13), Pt(1)−O(1) 2.068(7), Pt(1)−O(2) 2.030(8); C(1)−Pt(1)−O(2) 172.5(4), C(5)−Pt(1)−O(1) 175.6(4).

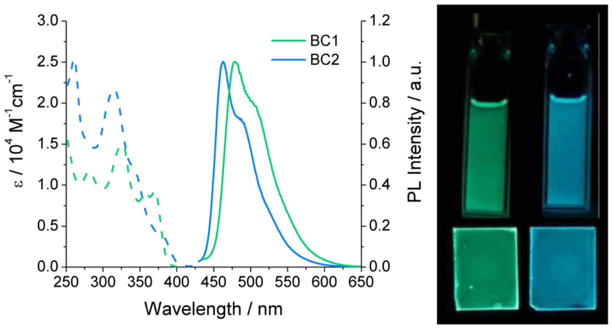


Figure 2. (Left) Absorption (dashed) and emission (solid) spectra of **BC1** and **BC2** at 10^{-5} M in CH_2Cl_2. (Right) Phosphorescence color of 10^{-5} M solutions of **BC1** (green-blue) and **BC2** (blue) in CH_2Cl_2 (top) and thin films of **BC1** and **BC2** on quartz substrates doped at 10 wt % in PMMA (bottom), λ_{ex} = 365 nm.

Table 1. Photophysical Properties of BC1 and BC2

	$\lambda_{\text{max, abs}}$ (nm), (ε [10^4 $M^{-1}cm^{-1}$])^a	$\lambda_{\text{max, EM}}$ (nm) solution^a/solid^b	$\tau_P{}^a$ (μs)	$\Phi_P{}^c$ solution^a/solid^b	$E_{1/2}{}^{\text{red}}$ (V)^d	HOMO (eV)^e	LUMO (eV)^f
BC1	381 (0.38), 344 (1.16), 316 (2.15)	478/482	6.9	0.87/0.90	−2.50	−5.73	−2.64
BC2	371 (0.76), 356 (0.80), 324 (1.48)	462/464	3.4	0.41/0.86	−2.49	−5.86	−2.65

[a] Measured in degassed CH_2Cl_2 at 1×10^{-5} M. [b] Doped into PMMA at 10 wt %. [c] Solution quantum efficiencies were measured in CH_2Cl_2 relative to $Ir(ppy)_3$ = 0.97.[17] Solid state quantum yields were measured using an integration sphere. All QYs are ±10%. [d] In DMF relative to $FeCp_2{}^{0/+}$. [e] Measured by UV photoelectron spectroscopy. [f] Calculated from the HOMO level and the optical energy gap.

phenylimidazole π-skeleton, whereas the 4-position makes a large contribution to the LUMO (see SI). Functionalization at either position with the electron-withdrawing $BMes_2$ thus decreases the energy of the corresponding orbital, resulting in a wider optical band gap and blue-shifted phosphorescence for **BC2** compared to those for **BC1**. In both cases the emission shows some vibronic character, indicative of phosphorescence from an excited state of both ligand-centered and MLCT character. Both **BC1** and **BC2** also undergo reversible reduction, indicative of electron-transporting functionality imparted by the $BMes_2$ group.

Because of the impressive quantum yields, both **BC1** and **BC2** were evaluated as phosphorescent emitters for OLEDs fabricated by vacuum vapor deposition on ITO-coated glass substrates. Due to the wide band gaps of these materials, care was taken to ensure that the HOMO and LUMO energy levels of both emitters were confined within the band gap of the host material, to facilitate efficient trapping of both holes and electrons. Furthermore, it was necessary to employ a host material with a sufficiently high triplet level to ensure that excitons within the device were confined to the dopant. On the basis of these considerations, preliminary devices were fabricated using 4,4′-*N*,*N*′-dicarbazolylbiphenyl (CBP) as the hole-transport layer, 1,3,5-tris(*N*-phenylbenzimidazole-2-yl)-benzene (TPBI) as the electron-transport layer, and *N*,*N*′-dicarbazolyl-3,5-benzene (mCP) as host. These devices have a structure of ITO/MoO_3 (1 nm)/CBP (35 nm)/mCP (5 nm)/mCP:Pt-emitter (12%, 15 nm)/TPBI (65 nm)/LiF (1 nm)/Al, (see SI). The performance of both devices is shown in Figure 3.

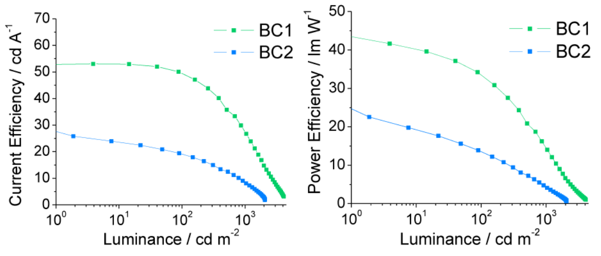


Figure 3. Current and power efficiencies for OLEDs based on **BC1** and **BC2**.

The device incorporating **BC1** as an emitter shows peak current and power efficiencies of 53.0 cd/A and 41.6 lm/W, remaining as high as 49.6 cd/A and 33.6 lm/W at the display-relevant brightness of 100 cd/m^2. Devices based on the blue-emitting **BC2** also show impressive performance, with peak efficiencies of 25.8 cd/A and 22.5 lm/W, remaining at 19.2 cd/A and 13.6 lm/W at 100 cd/m^2. Although research on platinum−NHCs in OLEDs has been limited, Strassner et al. have recently reported blue-green devices with external quantum efficiencies (EQEs) reaching 6.2%.[9f] More recently, Li and co-workers have achieved up to 14.8% EQE in an OLED based on a Pt−NHC complex.[13b] To our knowledge, the value of 17.9% EQE for the device based on **BC1** is the highest reported to date for a Pt(II)−carbene complex. The EL spectra of both devices, however, are broadened relative to the PL spectra, an indication that excitons are likely not fully confined to the dopant. As such, future studies will focus on optimization of the device structures and the design of new host materials to further improve device performance.

In summary, we have developed a synthetic route to the first triarylboron-functionalized metal−carbene complexes, and have shown that the presence of the boron moiety greatly increases the phosphorescent quantum yield of these systems. Furthermore, the strong ligand field exerted by the carbene enables the preparation of Pt(II) complexes with efficient high-energy blue phosphorescence. The utility of these complexes has been further demonstrated in a series of preliminary electroluminescent devices with high efficiencies (see Table 2.)

Table 2. Electroluminescent Device Data

device	BC1	BC2
V_{on}/V	4.0	3.6
L_{max}/cd m^{-2}	4165	2098
current efficiency, max./cd A^{-1}	53.0	25.8
power efficiency, max./lm W^{1-}	41.6	22.5
EQE_{max}/%	17.9	9.8
CIE/(*x*,*y*)	(0.34, 0.53)	(0.27, 0.50)

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Synthetic details and characterization data for all precursor compounds and the Pt(II) compounds, crystal structural data, CV, and EL data. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

wangs@chem.queensu.ca

Notes

The authors declare no competing financial interest.

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