Heteroleptic tris-cyclometalated iridium(III) complexes supported by the o-carboranyl-pyridine (CBpy) as a novel C=N chelating ligand were synthesized and characterized. While the CBpy ligand contributes to the electronic stabilization of complexes, their photophysical properties are dominated by 2-arylpyridine ligands.

Cyclometalated iridium(III) complexes have attracted a great deal of interest as phosphorescent emitting materials in organic light-emitting diodes due to their excellent photophysical properties such as good color purity, high quantum efficiency, and relatively short phosphorescence lifetime. The majority of Ir complexes developed to date are based on the C=N-chelating ligands such as 2-phenylpyridine (ppy), which play a crucial role in modulating the energy of the emissive lowest-lying triplet excited states such as MLCT and π-π* (1LC). By the variation of the electronic structure of the C=N ligand, the phosphorescence of the C=N-chelated Ir(III) complexes can be fine-tuned over the entire visible region.

Although homoleptic or heteroleptic tris-C=N-chelate Ir(III) complexes have been investigated with the various C=N ligands, which are primarily based on the prototypical ppy ligand, it is still important to search for a new type of C=N-chelating ligand which may control the energy level of excited states. This led us to consider the use of an o-carborane σ-donor of the C=N-chelate ligand in place of the aryl group. Owing to a highly polarizable σ-aromatic character and electron-deficient nature, o-carborane has recently attracted attention in the field of luminescent materials where the emission properties of luminoaphores are shown to be affected by incorporation of o-carborane. Moreover, it has been well established that o-carborane forms stable M–C bonds with a variety of transition metal ions including Ir(III). However, there have been no reports thus far on the use of the o-carborane as a σ-donor of the C=N-chelate phosphorescent metal complexes. Therefore, it may be intriguing to investigate the effect of the C=N-chelating ligand based on o-carborane on the electronic and photophysical properties of Ir(III)-cyclometalates.

To this end, we prepared and characterized novel heteroleptic tris-cyclometalated iridium(III) complexes 1 and 2 supported by an o-carboranyl-pyridine ligand (CBpy). The impact of the CBpy ligand on the photophysical and electrochemical properties of complexes was investigated with theoretical calculations.

The transmetalation reactions of the lithium salt derived from the 1-(2′-pyridyl)-2-H,1,2-cis-carborane (CBpyH) ligand with the chloro-bridged dimeric Ir(III) complexes, [(C=N)Ir(μ-Cl)]2 (C=N = ppy and dfppy, ppy = 2-phenylpyridinato-C=N, dfppy = 2-(4,6-difluorophenyl)-pyridinato-C=N), in THF afforded the cyclometalated Ir(III) complexes supported by the o-carboranyl-pyridine ligand (1 and 2) in moderate yield (Scheme 1). The 1H NMR spectra show the expected aromatic proton resonances corresponding to the C=N and CBpy ligands, as well as the broad B–H proton signals in the region of δ 1 to 3 ppm. The 11B NMR signals at δ ~5 to 3 ppm confirm the presence of closo-carborane. An X-ray diffraction study unequivocally revealed the molecular structure of 1 and 2 (Fig. 1). The CBpy ligand in both complexes is bound to the Ir atom via bidentate C=N chelation. The two C=N ligands are in a trans disposition of pyridine rings, featuring a mer-like configuration in both complexes. However, the attempt of thermal conversion to the fac-like isomer at 200 °C failed probably due to difficulties in coordinating the β-diketiminate ligands.

![Scheme 1](image-url)
to the steric reason. While the Ir–C(C·N) bond lengths are in a similar range as reported for other complexes with the (C·N)3Ir moiety, including Ir(tpy), (tpy = 2-tolylpyridine) and fac-Ir(tpy),5,16 the Ir–C(CBpy) bond lengths (2.175(11) Å for 1 and 2.178(10) Å for 2) are slightly longer than those of Cp*ClIr complexes (2.099(8) Å).13,14 The Ir–N(CBpy) bond lengths (2.227(8) Å for 1 and 2.191(9) Å for 2) are also longer than those of Ir(C·N)3 (2.09–2.15 Å).13,14 and Cp*Ir–C(C·N) complexes (2.130(8) Å).14 Along with the substantial distortion in the N2–Ir–N3 bond angles (166.2(4), 167.4(4)° for 1 and 167.4(4)° for 2) in comparison with those of other (C·N)3Ir complexes (171.1° for mer-Ir(tpy))5 and 176.3° for (tpy)Ir(acac)),5 the increased Ir–C(CBpy) and Ir–N(CBpy) bond lengths could be attributed to the steric repulsion between the CBpy and the C·N ligands. The Ir–C8 bonds trans to a carboranyl group have lengths (2.055(13) Å for 1 and 2.036(11) Å for 2) slightly shorter than that observed in mer-Ir(tpy),5 (av. 2.08 Å),5 indicating that the trans influence of a carboranyl group should be weaker than that of a phenyl group.

To examine the photophysical properties, UV-vis absorption and PL experiments were carried out with 1 and 2 in degassed THF (Fig. 2 and Table 1). Both complexes feature an intense absorption band at 250–300 nm assignable to the spin-allowed π→π* transition of the C·N(3)Lcigand mixed with the small CBpy transition (Fig. S3 in the ESI†). The lower energy bands at 375–500 nm (ε < 4400 M−1 cm−1) for 1 and 360–470 nm (ε < 4700 M−1 cm−1) for 2 can be majorly assigned to the mixed ML(C·N)CT and ML’(CBpy)CT transitions (see TD-DFT results below).5,8 The blue-shifted absorption band of the difluoro-substituted 2 compared with that of 1 is similar to that observed in the usual C·N-chelate Ir(m) complexes.5,17 The PL spectra of complexes were obtained from both the solution and solid states. Interestingly, both complexes are almost non-emissive in fluidic solution at 298 K, but are luminescent at 77 K and in the solid state, such as a film (5 wt% in PMMA) and a powder. This emission behaviour is in parallel with that observed in the Ir(C·N)3 complexes, in which the mer-isomer displayed very weak emission.5 The emission lifetimes of 0.4 to 0.7 μs for 1 and 0.4 to 0.6 μs for 2, respectively, in the solid state confirm the phosphorescence origin of the emission. Complex 1 shows the emission band centered at 483 nm with the weak shoulder at 517 nm at 77 K, which is slightly blue-shifted (420 cm−1) when compared to that for mer-Ir(tpy)3 (λem = 493 nm at 77 K).5 In contrast, the band position and structured emission feature of 2 (λem = 459, 492 nm at 77 K) are essentially identical to those of mer-Ir(dpppy)3 (λem = 460 nm).5 These results suggest that while the lowest-energy excited state of 1 is mainly 3MLCT in character, 2 has a mixed 3MLCT and 3LC excited state,8,17,18 implying that the phosphorescence is dominated by the (C·N)3Ir moiety. It is notable that in contrast to 2, the powdered sample of 1 exhibits a broad emission band with a large red-shift (ca. 2900 cm−1, 80 nm) in comparison with those obtained at 77 K and in film state. This emission is most likely from intermolecular π–π interactions by aggregation in neat solid state.7,19 Indeed, the addition of water to the THF solution of 1 gradually induced the emission band at the same region (Fig. S4†).

The electrochemical properties of 1 and 2 were examined by cyclic voltammetry (Table 1 and Fig. S6†). While complex 1 undergoes reversible oxidation at 0.62 V, 2 shows quasi-

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**Table 1** Photophysical and electrochemical data for 1 and 2

<table>
<thead>
<tr>
<th>Compound</th>
<th>λabs/nm (ε × 10−3 M−1 cm−1)</th>
<th>λem/nm</th>
<th>τ/μs</th>
<th>Φem (PLQY)</th>
<th>Φem (PMMA)</th>
<th>E1/2 (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>298 K</td>
<td>77 K</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>256 (39.0), 347 (6.4), 396 (4.4), 471 (0.6)</td>
<td>256 (39.0), 347 (6.4), 396 (4.4), 471 (0.6)</td>
<td>483, 517</td>
<td>489, 517</td>
<td>571</td>
<td>0.035</td>
</tr>
<tr>
<td>2</td>
<td>255 (31.6), 306 (12.4), 377 (4.7), 449 (0.3)</td>
<td>255 (31.6), 306 (12.4), 377 (4.7), 449 (0.3)</td>
<td>459, 492</td>
<td>463, 496</td>
<td>496</td>
<td>0.070</td>
</tr>
</tbody>
</table>

*Measured in degassed THF (2 × 10−5 M). ^Spin-coated PMMA film doped with 1 and 2 (5 wt%). †Measured in MeCN (5 × 10−4 M, scan rate = 100 m Vs−1) with reference to an Fe/Fe²⁺ redox couple. ‡Measured in DMF. §Measured in DMF–MeCN (1:2, v/v). ‖Reversible. ‡Quasi-reversible.
 reversible oxidation at 0.94 V. These oxidation potentials are anodically shifted by ca. 0.37 and 0.25 V compared to those of mer-Ir(ppy)$_3$ (0.25 V) and mer-Ir(dfppy)$_3$ (0.69 V), respectively, indicating that the HOMO of 1 and 2 is stabilized by chelation of the CBpy ligand. Since the HOMO is composed of iridium-$\pi$ and phenyl-$\pi$ orbitals (see DFT results below), the stabilization could be related to the less trans influence of a carborene group than a Ph group due to the weak $\pi$-donation of carborene, which in turn strengthens the transient Ir-C(Ph) bonds, as shown in the crystal structure. On the other hand, 1 and 2 display quasi-reversible reduction processes centered at $-2.39$ V for 1 and at $-2.30$ V for 2, which are less negative by ca. 0.24 and 0.20 V than those of mer-Ir(ppy)$_3$ (−2.63 V) and mer-Ir(dfppy)$_3$ (−2.50 V), respectively. Since the LUMO in usual Ir($C^N$)$_3$ complexes is localized in the pyridyl group of the $C^N$ ligand, the lowering of the LUMO level in 1 and 2 may indicate the involvement of the pyridyl group of the CBpy ligand in the reduction. Consequently, the electrochemical HOMO–LUMO band gaps of 1 and 2 increase by ca. 0.13 eV for 1 and 0.05 eV for 2 in comparison with those of mer-Ir($C^N$)$_3$ complexes. The apparent increase in the band gap of 1 compared to that of mer-Ir(ppy)$_3$ is in good agreement with the observed blue shifts in the absorption and emission bands.

To elucidate the photophysical and electrochemical properties, TD-DFT calculations on both the ground state ($S_0$) and the lowest triplet excited state ($T_1$) optimized structures of 1 were performed at the B3LYP/LANL2DZ level (Fig. 3 and ESI†). The lowest energy absorption in 1 is mainly characterized by HOMO $\rightarrow$ LUMO(77.6%) and HOMO $\rightarrow$ LUMO + 1(16.8%) transitions. While the HOMO resides mainly on the Ir(d$_z^2$) (45.8%), the LUMO and LUMO + 1 are localized on the pyridyl rings of CBpy (62.9%) and ppy (47.6%) ligands, respectively. This result suggests that the lowest energy absorption is mainly MLCT/MLCT in character. The significant contribution of the CBpy ligand to LUMO may be responsible for the lowering of the LUMO level, as shown in the electrochemical reduction in 1.

Finally, the TD-DFT calculations at the $T_1$ optimized geometry for 1 show that the lowest energy triplet state is dominated by HOMO $\rightarrow$ LUMO (80.0%) and HOMO $\rightarrow$ 1 $\rightarrow$ LUMO (13.7%) transitions (Fig. 3 and ESI†). Importantly, the CBpy ligand is little involved with the LUMO in both transitions, thus the phosphorescence in 1 is the ($C^N$)$_3$Ir-based $^3$MLCT in character. These results explain the similarity of the phosphorescence properties of 1 and 2 to those observed in usual $C^N$-chelate Ir(III) complexes, such as mer-Ir(ppy)$_3$ and mer-Ir(dfppy)$_3$ discussed above.

In summary, we have synthesized and characterized heteroleptic tris-cyclometalated Ir(u) complexes supported by an o-carboranyl-pyridine (CBpy) ligand as a novel $C^N$-chelate. It was shown from experimental and theoretical studies that while the CBpy ligand contributes to the electronic stabilization of complexes, the photophysical properties are dominated by 2-arylpypyridine ligands, such as ppy and dfppy.

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