INTRODUCTION

Tetradentate dianionic salen ONNO ligands are well known in coordination chemistry, and their metal complexes have found applications in a variety of scientific fields ranging from catalysis to bioorganic and materials chemistry. For example, highly luminescent Pt(II) complexes of salen have been used as dopants in organic light-emitting diodes (OLEDs). The tetradeinate nature of the ligand reduces the possibility of ligand-exchange reactions and benefits both the stability and the luminescence properties of these complexes. Classical salen ligands are easily prepared by the condensation of salicylic aldehyde derivatives with the corresponding diamines. However, the resulting C=N imine bonds are prone to hydrolysis and other degradation pathways. To solve this problem, 6,6′-bis(2-phenoxy)-2,2′-bipyridine (bipyridine bisphenolate, BpyBph) were developed as a more robust system. Indeed, ONNO-type Pt(II) complexes of BpyBph and their phenanthroline analogues (PhenBph) showed strong luminescence in solution at room-temperature, good performance in OLEDs, and excellent thermal stability (Figure 1).

The synthesis of BpyBph ligands is more challenging than that of salen ligands, and there are only a few examples of such ligands described in the literature. The synthesis involves the reaction of 2,2′-bipyridine with 2-methoxyphenyllithium to give 6,6′-bis(2-methoxyphenyl)-2,2′-bipyridine, which is then demethylated to give the target ligand. Because highly nucleophilic reagents are used (n-BuLi), only a limited number of functional groups can be tolerated in the ligand. In this article, we demonstrate a convenient method for the synthesis of BpyBph ligands based on the chemistry of 1,2,4-triazines. This methodology was...
previously employed to prepare a variety of poly(pyridine ligands) as well as their cyclometalated analogues. The key aspect of the methodology is that 1,2,4-triazines can be easily prepared from readily available starting materials and then transformed to their corresponding pyridines by the Boger reaction with enamines. In this way, a variety of substituents can be introduced into the pyridine ring. In this article, we report two synthesis routes employing 3,3′- and 5,5′-bis-triazines as key building blocks in preparing four novel ligands. We then show that the ligands readily form Pt(II) complexes, which are highly luminescent and can successfully be used as dopants in solution-processed OLEDs. In this study, we concentrate exclusively on solution-processed OLEDs and demonstrate that the position of cyclopenteno units plays a key role in increasing the solubility of the complexes.

**RESULTS AND DISCUSSION**

**Synthesis.** The synthesis of the novel salen-type proligands is depicted in Scheme 1. Because the N1 and N2 atoms of the triazine ring are lost during the Boger reaction as dinitrogen, we are limited to using 3,3′- and 5,5′-bis-triazines as key building blocks in preparing four novel ligands. We then show that the ligands readily form Pt(II) complexes, which are highly luminescent and
blocks in the synthesis. 3,3′-Bis-triazines 3a and 3b were prepared in moderate yields by the reaction of corresponding glyoxal derivatives 2a and 2b with ethanedihydrazonamide (1). In order to prepare S,S′-bis-triazine (9a-Et), we started with commercially available 2-ethoxybenzamide (6), which was treated with 1 equiv of hydrazone hydrate to give the corresponding amidrazone.6 The amidrazone was not isolated but was used in situ in the reaction with glyoxal to give 8a-Et in 66% yield. tert-Butyl derivative 8b-Me was synthesized by the desulfurative Suzuki reaction of sulfide 7 with commercially available 3-tert-butyl-5-methoxyphenyl boronic acid.8 The next step involved the dimerization of 1,2,4-triazines 8a-Et and 8b-Me by the action of potassium cyanide. This high-yielding reaction was first reported in 19739 and has already been applied to the synthesis of bipyridines.10 3,3′-Bis-triazines 3a and 3b and S,S′-bis-triazines 9a-Et and 9b-Me were then converted to 2,2′-bipyridines 4a and 4b and 10a-Et and 10b-Me, respectively, by the Böger reaction with 1-morpholincyclopentene. Finally, O-demethylation with pyridinium chloride or boron tribromide under standard conditions gave the desired salen-type pro-ligands 11a, 11b, and 12a. Complexes 12a and 12b, and 13a and 13b were then prepared by the reaction of the corresponding proligands with potassium tetrachloroplatinate in refluxing acetic acid.

It was immediately apparent that 12a is far more soluble than 13a. One explanation for this might be that the cyclopentene units in 12a cause a slight twist of the pyridine rings, reducing the planarity of the molecule and thus minimizing the intramolecular interaction. Indeed, computational data supports this argument and shows that 12a is less planar than 13a (Figure 2).

Interestingly, the introduction of the tert-butyl groups did not significantly improve the solubility in both series of complexes in toluene. Only 12a dissolves well in toluene, while other complexes have very limited solubility. For this reason, all of the solution-processed OLEDs in this work were made using chlorobenzene as the solvent.

Luminescent Properties. The small changes in the ligand structure between 12 and 13 cause noticeable differences in the photophysical properties of the complexes. For example, in toluene solution, 13a, which is an isomer of 12a differing only by the position of the cyclopentene ring, has a more blue-shifted emission spectrum relative to that of 12a. A similar trend is observed in 12b and 13b.

The photoluminescence spectra in solution (Figure 3) are nearly featureless and relatively broad, but when dispersed in a rigid and nonpolar polymer (Zeonex), the spectra show a more resolved vibronic structure. Interestingly, the phosphorescence spectra of each pair of analogues in Zeonex (12a and 12b, 13a and 13b) are nearly identical, although they differ in solution. This indicates that the difference in the emission color of tert-butylated and nonsubstituted analogues is mostly a result of additional vibrational/rotational modes in tert-butylated molecules and the electron-donating effect of this group is less important.

Figure 2. Comparison of optimized structures 12a (gray) and 13a (black).

At 77 K, all four complexes display well-resolved, blue-shifted emission. In all cases, the 0–0 transition is the strongest in the spectrum. Within each group of complexes (12a and 12b, 13a and 13b), the low-temperature phosphorescence spectra show a very similar shape with identical vibronic structure, but the analogues with tert-butyl groups (12b, 13b) give more red-shifted spectra than do their counterparts (12a and 13a). This is, in fact, an indication that the electronic effect of the tert-butyl group is significant. In general, notable rigidochromism is observed in these complexes, showing that the molecules are susceptible to intramolecular motion and interactions at room temperature. In both series, the introduction of the tert-butyl group reduces the luminescence yield, $\Phi_{PL}$, which is probably due to the larger number of vibrational/rotational modes. Molecules with cyclopentene rings on the outer periphery of the bipyridine moiety (13a, 13b) have a larger $\Phi_{PL}$ than do the corresponding isomers (12a, 12b).

This argument is supported by the phosphorescence lifetime measurements. In toluene solution, 13a shows the longest phosphorescence lifetime, whereas 12b shows the shortest. Shorter phosphorescence time constants in 12b and 13b are also found compared to their corresponding analogues (12a and 13a). We attribute the shorter phosphorescence lifetime of 12b and 13b relative to their analogues (12a and 13a) to the increased nonradiative decay. All decay profiles recorded in toluene are perfectly monoeXponential as shown in Figure 3. The physical properties of complexes 12a, 12b, 13a, and 13b are summarized in Table 1.

Electrochemistry. Cyclic voltammetry studies on complexes 12a, 12b, 13a, and 13b show that all compounds behave similarly and show a reversible reduction that involves the NN (bipyridine) ligands. The oxidation of the complexes is, however, irreversible. In this case, the behavior of 12a and 13a is nearly identical, and this is also observed for their tert-butylated analogues, 12b and 13b (Figure 4, Table 2). This indicates that the oxidation of these complexes involves the phenyl rings of the OO ligand, as alkyl substitution of this moity changes the electrooxidation signal pattern. This means that the alkyl- and nonalkyl-substituted complexes undergo different chemical reactions upon oxidation. The complexes have very similar oxidation and reduction potentials, but 13a and 13b have a larger electrochemical energy gap (0.05–0.07 eV), which explains the observed blue shift of their emission in comparison to that of the other two molecules.

Theory and Computational Chemistry. To support the interpretation of the experimental results, we have performed density functional theory (DFT) and time-dependent density functional theory (TDDFT) simulations on 12a and 13a, with the primary focus of rationalizing the structural and emission properties. The structure of the lowest triplet states was optimized using DFT(B3LYP)12 and a def2-SVP basis set as implemented within the ORCA quantum chemistry package.13 The excited-state energies were computed using linear response-time-dependent density functional theory (LR-TDDFT) using the Tamm–Dancoff approximation and the B3LYP exchange and correlation functional as implemented within the Amsterdam Density Functional (ADF) code.14 The SOC matrix elements were computed with the perturbative approach developed by Wang and Ziegler.15 A DZP basis set was used for all atoms, except Pt (TZP), and scalar relativistic effects were accounted for using the zeroth-order relativistic approximation (ZORA).16
the OO to the NN ligands for both complexes. The emission energy (which, following the large phosphorescence and Kasha’s rule, corresponds to the T1 state) for 12a is 629 nm, and that for 13a is 590 nm. The excited-state lifetimes (derived from the radiative rate) of 12a and 13a are 195 and 184 μs, respectively. The large difference between the experimental and calculated lifetimes is that the calculated lifetime does not include non-radiative effects, which are relatively significant in solution, as indicated by the lower quantum yields. For 12a and 13a, the SOC between S1 and T1 states is about ∼350 cm−1 in both cases.

OLED Fabrication and Characterization. Solution-processed devices were fabricated from complexes 12a, 12b, 13a, and 13b using chlorobenzene solutions of mixed host (PVK + PBD) and dopant. (see SI for more details about fabrication of devices.) The dopant concentration was limited in some cases due to the poor solubility of some of the complexes in chlorobenzene. For this reason, toluene could also not be used as a solvent, except for 12a, which was dissolved in toluene to produce a device with a 5% dopant concentration. Devices of 12a in toluene had performances that were similar to those of the presented chlorobenzene-based OLEDs. The poor solubility of complexes 13a and 13b resulted in a limited dopant concentration (1 and 3%, respectively). This is likely to decrease the efficiency of host to dopant energy transfer (due to a limited Forster and Dexter radii) and cause problems with direct charge injection into the dopant, which in turn decreases the efficiency of the device. This is clearly

| solvent | absorption λ_img, nm (ε × 10⁻⁴, M⁻¹ cm⁻¹) | emission λ_img, nm | τ, µs | Φ_pl | emission λ_img, nm | τ, µs |
|---------|------------------------------------------|-------------------|------|-----|------------------------------------------|------|
| toluene | 12a: 541 (0.22), 509 (0.31), 478 (0.27), 417 (0.80), 329 (1.85), 308 (2.12) | 624 | 1.76 ± 0.08 | 0.24 | 580 | 7.6 ± 0.4 |
|         | 13a: 527 (0.17), 489 (0.27), 399 (0.85), 320 (1.80) | 593 | 2.98 ± 0.14 | 0.34 | 564 | 5.5 ± 0.4 |
|         | 12b: 564 (0.30), 523 (0.38), 488 (0.30), 436 (1.02), 335 (2.20), 310 (2.61) | 646 | 0.93 ± 0.04 | 0.12 | 589 | 5.4 ± 0.2 |
|         | 13b: 547 (0.15), 506 (0.26), 470 (0.30), 410 (0.80), 323 (1.57) | 610 | 1.42 ± 0.18 | 0.25 | 572 | 4.8 ± 0.4 |

The absorption band wavelength and absorption coefficient with ± 15% error. aThe emission maxima in toluene. bThe phosphorescence lifetime at room-temperature in degassed solution. cThe photoluminescence quantum yield in degassed solution with ± 15% error. dThe emission maxima in a Zeonex polymer. eThe phosphorescence lifetime in Zeonex in vacuum.
the problem in devices containing 13a. This is also shown in the photophysical study where, in the case of PVK:PBD films with low doping concentrations (complexes 13a and 13b), another, slower mechanism for energy transfer is observed (i.e., limited by hole−electron pair recombination\textsuperscript{17}). When the photophysical data is compared with electroluminescence spectra it becomes clear that in OLEDs direct charge injection to the dopant is the dominant process, while energy transfer from host to guest is less dominant. On the other hand, energy transfer governs the photoluminescence in a PVK:PBD mixed host. For this reason, it is important that the efficiency of the OLED devices is slightly larger than it would be expected to be from photophysics.

The compounds perform well as dopants in OLEDs (Figure 6), giving electroluminescence from yellow-green to orange that is in full agreement with the photophysical results. All dopants except 12b give efficient devices with an EQE of 8.4−10.4% and a satisfactory current efficiency of 22.3−24.9 cd A\textsuperscript{−1}. The brightness of these devices reached 7000 cd m\textsuperscript{−2} in the case of 12a, while the device derived from 12b shows the lowest brightness of 2500 cd m\textsuperscript{−2}. The turn-on voltage is in the typical range for the OLED structure used with a PVK:PBD host.\textsuperscript{18}

Because of the higher photoluminescence quantum yield both in doped film and in solution, the 13a-based OLED was expected to have a higher maximum EQE and in general to outperform the 12a-based OLED. However, the low solubility of the complex imposed limitations in doping concentration, and the device with 13a as the dopant (1%) is therefore less efficient than the device incorporating 12a (5%). The yellowish electroluminescence of devices 1 and 3 is close to that of candlelight, while device 2 has a more green and device 4 a more red electroluminescence. The colorimetric coordinates in the CIE 1931 color space of a typical candle (0.52, 0.42)\textsuperscript{19} and those of presented devices 1 and 3 are close to this value (see Table 3). Interestingly, the candlelight color has been achieved with the use of only one emitter whereas other solutions use 2 to 3 emitters.\textsuperscript{19−21}

Figure 4. Electrochemical oxidation and reduction cycles of the investigated complexes recorded with cyclic voltammetry at a 0.05 V s\textsuperscript{−1} scan rate in 0.1 M Bu\textsubscript{4}NBF\textsubscript{4}/DCM supporting electrolyte. Note that the results for 13b were recorded at a lower concentration due to its limited solubility.

Table 2. Electrochemical Properties of the Investigated Complexes\textsuperscript{a}

| complex | $E_{\text{OX}}$, V\textsuperscript{b} | $E_{\text{RED}}$, V\textsuperscript{b} | $I_{\text{P}}$, eV\textsuperscript{c} | $E_{\text{A}}$, eV | $E_{\text{G}}$, eV\textsuperscript{f} |
|---------|-----------------|-----------------|-----------------|-----------------|-----------------|
| 12a     | 0.40            | −1.92           | 5.50            | 3.18            | 2.32            |
| 13a     | 0.44            | −1.95           | 5.54            | 3.15            | 2.39            |
| 12b     | 0.40            | −1.92           | 5.50            | 3.18            | 2.32            |
| 13b     | 0.40            | −1.97           | 5.50            | 3.13            | 2.37            |

\textsuperscript{a}Note All Potentials Are Relative to the Standard Potential of Ferrocene/Ferrocenium Redox Couple. \textsuperscript{b}Onset oxidation potential was recorded with cyclic voltammetry. \textsuperscript{c}Onset reduction potential was recorded with cyclic voltammetry. \textsuperscript{d}Ionization potential $I_{\text{P}} = E_{\text{OX}} - 5.1$. \textsuperscript{e}Electron affinity $E_{\text{A}} = E_{\text{RED}} + 5.1$. \textsuperscript{f}Electrochemical energy gap $E_{\text{G}} = I_{\text{P}} - E_{\text{A}}$. $I_{\text{P}}$ and $E_{\text{A}}$ correspond to the HOMO and LUMO energy, respectively, and are used as their estimates.

Figure 5. HOMO (a and c) and LUMO (b and d) orbitals of 12a (upper) and 13a (lower).
CONCLUSIONS

The synthesis methodology based on the chemistry of 1,2,4-triazines proved to be efficient and versatile in the synthesis of tetradentate dianionic bipyridine bisphenolate ONNO ligands. The scope of the methodology goes beyond luminescent complexes and is likely to attract attention from scientists in other fields. Many other functional groups can be introduced by the Boger reaction, opening up additional pathways for optimizing and tuning ONNO ligands for different applications. In Pt(II) complexes formed by the new ligands, the introduction of the tert-butyl groups was found not to improve solubility in toluene but reduced the quantum efficiency of the complexes and is thus not a good strategy for optimizing the dopants. However, the 1,2,4-triazine methodology illustrated herein does allow for the synthesis of more soluble isomers by positioning the cyclopentene rings closer together, leading to less-planar structures. This significantly improves the solubility of the complex, but the detrimental effects on the photophysical properties are less profound. This allowed us to obtain the required doping concentration to achieve efficient single-dopant candlelight OLED devices.

EXPERIMENTAL SECTION

The description of the materials and methods and experimental as well as experimental procedures for tert-butyl analogues are described in the Supporting Information.

Table 3. Summary of the Characteristics of the OLED Devices

| device | dopant | turn on at 10 cd m⁻², V | max. at 100 cd m⁻² | max. at 1000 cd m⁻² | max. current efficiency, cd A⁻¹ | max. brightness, cd m⁻² | EL maximum, nm | CIE (x, y) at max brightness |
|--------|--------|-------------------------|-------------------|-------------------|-----------------------------|------------------------|-----------------|--------------------------|
| Dev 1  | 12a    | 7.2                     | 10.0              | 9.7               | 8.2                        | 23.2                   | 7000            | 590                      | 0.54, 0.46             |
| Dev 2  | 13a    | 7.6                     | 8.4               | 6.6               | 8.2                        | 24.9                   | 3500            | 567                      | 0.46, 0.51             |
| Dev 3  | 12b    | 8.7                     | 5.5               | 5.3               | 4.9                        | 9.9                    | 2500            | 603                      | 0.57, 0.42             |
| Dev 4  | 13b    | 6.4                     | 10.4              | 9.3               | 8.0                        | 22.3                   | 5000            | 577                      | 0.52, 0.47             |

Device architecture: ITO/HIL 1.3N (55 nm)/dopant (1–5%) co PVK:PBD (60:40) (80 nm)/TPBi (40 nm)/LiF (0.8 nm)/Al (100 nm). Doping concentration: Dev 1: 12a (5%), Dev 2: 13a (1%), Dev 3: 12b (5%), Dev 4: 13b (3%). "The value was recorded at 118 cd m⁻²."
heated under reflux for 4 h. The mixture was allowed to cool to ambient temperature, and the solid was filtered off, washed with ethanol (20 mL) followed by diethyl ether (40 mL), and allowed to dry in air to afford title compound 3a as a yellow-green solid (1.87 g, 50%). 1H NMR (400.1 MHz, CDCl3, MeSi) δ: 10.12 (s, 2H), 8.38 (dd, J = 7.6, 2H), 7.55 (t, J = 7.6, 2H), 7.16 (t, J = 7.6, 2H), 7.06 (dd, J = 8.8, 2H), 3.99 (s, 6H); 13C NMR (100 MHz, CDCl3, MeSi) δ: 161.9, 158.7, 155.8, 150.1, 134.1, 132.2, 122.3, 121.8, 111.6, 55.8. HRMS (ESI) calc for C28H23N2O2 ([M + H]+): m/z 373.1413. Found: m/z 373.1411.

6.6′-Bis(2-methoxyphenyl)-2,2′-bipyridine (4a). 5,5′-Bis(2-methoxyphenyl)-3,3′-bi-1,2,4-triazine, 3a (2.3 g, 6.18 mmol), was placed in a round-bottomed flask and 1-morpholinocyclopentene (7.54 g, 55 mmol, 10 equiv) was added. The flask was held at 140 °C for 15 min. Acetic acid (30 mL) was added, and the mixture was stirred at reflux for 10 min. Methanol (30 mL) and water (30 mL) were added, and the mixture was allowed to cool to room temperature. The solid was filtered and washed with MeOH (30 mL) to give the desired product (2.1 g, 80%). The product was used without further purification. However, the product can be purified by recrystallization from acetic acid/methanol mixture. 1H NMR (400.1 MHz, CDCl3, MeSi) δ 8.30 (s, 2H), 7.51 (dd, J = 7.6, 1.8, 2H), 7.35 (ddd, J = 8.3, 7.6, 1.8, 2H), 7.07 (br. d, J = 7.6, 2H), 7.12 (br. d, J = 7.6, 2H), 4.02 (q, J = 7.0, 4H), 2.98 (t, J = 7.4, 4H), 2.83 (t, J = 7.4, 4H), 2.04 (quin, J = 7.4, 4H). 12C NMR (100 MHz, CDCl3, MeSi) δ 156.3, 154.9, 154.4, 152.2, 139.6, 131.7, 130.7, 129.4, 120.7, 116.3, 112.3, 64.0, 33.2, 31.5, 95.0. HRMS (ESI) calc for C26H26N2O2 ([M + H]+): m/z 477.2542. Found: m/z 477.2533.

Bpy8ph pphltag (11a). At room temperature, BBr3 (4 mL) was slowly added dropwise to the solution of 10a-Et (500 mg, 1.05 mmol) in CH2Cl2 (20 mL). After the addition was complete, the mixture was stirred at room temperature under argon for 18 h. The reaction was quenched by the slow addition of water. DCM (30 mL) was added, and the organic phase was separated, washed with water, dried, and filtered. The filtrate was filtered through a plug of silica gel. The silica gel was washed with DCM. The solvents were evaporated, and the residue was treated with methanol (5 mL) and water (5 mL). The mixture was allowed to cool to room temperature, and the solid was filtered and washed with water and methanol to give 5a as a yellow solid. Yield: 1.5 g (90%). 1H NMR (400.1 MHz, CDCl3, MeSi) δ: 7.89 (s, 2H), 7.86 (dd, J = 8.4, 1.2, 2H), 7.29 (t, J = 8.4, 2H), 6.99 (dd, J = 8.4, 0.8, 2H), 6.92 (t, J = 8.4, 2H), 3.13 (t, J = 7.6, 4H), 3.08 (t, J = 7.6, 4H); 13C NMR (100 MHz, CDCl3, MeSi) δ: 157.1, 152.6, 153.5, 150.0, 138.0, 131.5, 130.1, 129.7, 120.9, 120.5, 111.5, 55.7, 33.0, 24.2, 25.2. HRMS (ESI) calc for C28H25N2O2 ([M + H]+): m/z 449.2239. Found: m/z 449.2233.

6.6′-Bis(2-hydroxyphenyl)-2,2′-bipyridine (5a). A mixture of 4a (1.8 g, 4.0 mmol) and pyridinium chloride (105 mg, 0.8 mmol) in CDCl3, MeSi) δ: 7.83, 6.72 (m, 2H), 7.05 (t, J = 7.2, 2H), 6.98 (d, J = 7.6, 1.6, 2H), 6.75 (s, 2H), 4.34 (s, 4H), 3.34 (t, J = 7.6, 4H), 2.99 (t, J = 7.6, 4H), 2.11 (quin, J = 7.6, 4H). 13C NMR (100 MHz, CDCl3, MeSi) δ: 157.1, 152.6, 153.5, 150.0, 138.0, 131.5, 130.1, 129.7, 120.9, 120.5, 111.5, 55.7, 33.0, 24.2, 25.2. HRMS (ESI) calc for C26H25N2O2 ([M + H]+): m/z 421.1916. Found: m/z 421.1899.

Platinum Complex (13a). A mixture of the ligand (126 mg, 0.3 mmol) and potassium tetrachloroplatinate (124 mg, 0.3 mmol) in acetic acid (30 mL) was heated under reflux for 14 h. Water (30 mL) was added, and the solid product was filtered off, washed with water, and dried to give 13a as a yellow solid. Yield: 160 mg (87%). 1H NMR (400.1 MHz, CDCl3, MeSi) δ: 8.07 (s, 2H), 7.76 (dd, J = 8.8, 1.6, 2H), 7.33 (dd, J = 8.2, 7.8, 2H, 16.7, 2H), 7.09 (dd, J = 8.2, 1.1, 2H), 6.95 (br. t, J = 8.2, 2H), 3.33 (t, J = 7.4, 4H), 3.09 (t, J = 7.4, 4H), 2.19 (quin, J = 7.4, 4H). HRMS (ESI) calc for C32H33N2O2 ([M + H]+): m/z 613.1386. Found: m/z 613.1395.

ASSOCIATED CONTENT
3 Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.7b03175.

Details of the synthesis of tert-butyl isomers 12b and 13b, copies of NMR and MASS spectra, additional details for photophysical and electrochemical characterization, and OLED device fabrication (PDF)

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Notes
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In response to a reviewer's comments on the unusually high EQE and CE values based on an estimation from the PLQY, the measurements have been repeated and were found to show reproducible values. The detailed mechanism and reasons for these may require further study.