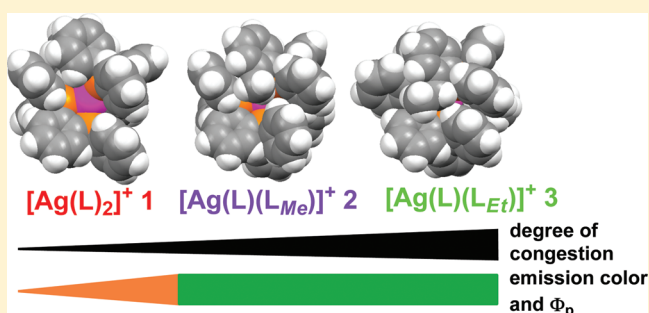


## Photoluminescence Properties, Molecular Structures, and Theoretical Study of Heteroleptic Silver(I) Complexes Containing Diphosphine Ligands

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## S Supporting Information

**ABSTRACT:** The homoleptic complex  $[\text{Ag}(\text{L})_2]\text{PF}_6$  (**1**) and heteroleptic complexes  $[\text{Ag}(\text{L})(\text{L}_{\text{Me}})]\text{BF}_4$  (**2**) and  $[\text{Ag}(\text{L})(\text{L}_{\text{Et}})]\text{BF}_4$  (**3**) [ $\text{L}$  = 1,2-bis(diphenylphosphino)benzene,  $\text{L}_{\text{Me}}$  = 1,2-bis[bis(2-methylphenyl)phosphino]benzene, and  $\text{L}_{\text{Et}}$  = 1,2-bis[bis(2-ethylphenyl)phosphino]benzene] were synthesized and characterized. X-ray crystallography demonstrated that **1–3** possess tetrahedral structures. Photophysical studies and time-dependent density functional theory calculations of **1–3** revealed that alkyl substituents at the ortho positions of peripheral phenyl groups in the diphosphine ligands have a significant influence on the energy and intensity of phosphorescence of the complex in solution at room temperature. The results can be interpreted in terms of the geometric preferences of each complex in the ground and excited states. The homoleptic complex **1** exhibits weak orange phosphorescence in solution arising from its flat structure in the triplet state, while heteroleptic complexes **2** and **3** show strong green phosphorescence from triplet states with tetrahedral structure. Larger interligand steric interactions in **2** and **3** caused by their bulkier ligands probably inhibit geometric relaxation within the excited-state lifetimes, leading to higher energy phosphorescence than that observed for **1**. NMR experiments revealed that **2** and **3** in solution possess structures that are much more immobilized than that of **1**; fluxional motion is completely suppressed in **2** and **3**. Accordingly, conformational changes of **2** and **3** are expected to be suppressed by the alkyl substituents not only in the ground state but also in excited states. Consequently, nonradiative decay of the excited states of **2** and **3** occurs less efficiently than in **1**. As a result, the quantum yields of phosphorescence for **2** and **3** are 6 times larger than that for the homoleptic complex **1**.



## ■ INTRODUCTION

A number of  $d^{10}$  coinage metal complexes that exhibit interesting luminescence properties have been synthesized.<sup>1</sup> With regard to silver complexes, most reported to date are multinuclear complexes that have argentophilic bonding, an analogue of aurophilic bonding known as “closed-shell ( $d^{10}-d^{10}$ ) interactions”.<sup>2</sup> Luminous mononuclear silver complexes, however, had rarely been reported until recently.<sup>3</sup> In previous papers, we reported luminescence from the tetrahedral silver complex  $[\text{Ag}(\text{dppb})_2]\text{PF}_6$  [**1**;  $\text{dppb}$  = 1,2-bis(diphenylphosphino)benzene ( $\text{L}$ )].<sup>3a</sup> This complex exhibits an efficient phosphorescence performance in frozen 2-methyltetrahydrofuran (2-MeTHF) at 77 K: the maximum wavelength of phosphorescence  $\lambda_{\text{max}} = 441$  nm, and the phosphorescence quantum yield  $\Phi_p = 0.88$ . However, this complex shows weakened phosphorescence in solution at room temperature, resulting from structural distortion in the excited state from tetrahedral to planar geometry because of the metal-

to-ligand charge-transfer (MLCT) character of the excited state. While the  $d^{10}$  ground state possesses  $D_{2d}$  symmetry, the MLCT excited state favors  $D_2$  symmetry. The change in the structure of the triplet state results in both a red shift of  $\lambda_{\text{max}}$  and a decrease in  $\Phi_p$ , with  $\lambda_{\text{max}} = 670$  nm and  $\Phi_p = 0.05$  in 2-MeTHF at ambient temperature. This phenomenon can be explained by the rigidochromic effect,<sup>4,5</sup> as is frequently seen in some copper(I) complexes.<sup>5</sup>

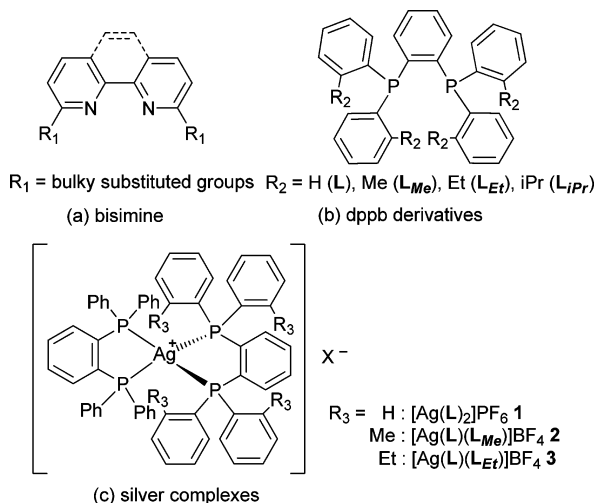
According to the extensive chemistry of tetrahedral copper(I) complexes with two diimine ligands,<sup>6</sup> the incorporation of bulky substituents into diimine ligands on the side of the metal center is an effective means to prevent structural relaxation and maintain a good phosphorescence performance even in solution at room temperature. For instance, sterically congested alkyl substituents are generally introduced at the 2 and 9

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positions of phenanthroline (or the 6 and 6' positions of 2,2'-bipyridine) to attain high  $\Phi_{\text{P}}$ , as shown in Chart 1a.

Chart 1. Ligands and Silver Complexes



In line with this approach used for copper(I) diimine complexes, we have prepared diphosphine ligands in the form of dppb derivatives with substituents [Me (**L<sub>Me</sub>**), Et (**L<sub>Et</sub>**), and iPr (**L<sub>iPr</sub>**)] at the ortho positions of four peripheral phenyl groups to afford rigid environments around the metal center in their silver(I) complexes (Chart 1b). Heteroleptic silver(I) complexes [Ag(**L**)(**L<sub>Me</sub>**)]BF<sub>4</sub> (**2**) and [Ag(**L**)(**L<sub>Et</sub>**)]BF<sub>4</sub> (**3**) were readily synthesized using dppb derivatives (Chart 1c). The steric effects of bulky substituents at the ortho positions have been briefly described in a previous paper on three-coordinate copper(I) complexes with **L<sub>Me</sub>**.<sup>7</sup> <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR experiments confirmed that heteroleptic silver(I) complexes **2** and **3** were stable and did not show ligands scrambling in solution.

The photophysical properties of the dppb derivatives **2** and **3** are discussed on the basis of molecular orbital (MO) calculations, and the ability of the dppb derivatives to prevent flattening distortion through steric protection is described in detail.

## EXPERIMENTAL SECTION

**Chemicals.** 1,2-Bis(dichlorophosphino)benzene and magnesium were obtained from Wako Pure Chemical Industries, Ltd. (2-Methylphenyl)magnesium bromide was purchased from Sigma-Aldrich. Silver(I) tetrafluoroborate, silver(I) hexafluorophosphate, (2-bromoethyl)benzene, and (2-isopropylphenyl)benzene were obtained from TCI Co., Ltd. Iodine and magnesium were purchased from Kanto Chemical Co., Inc.

**General Information.** All synthetic reactions were carried out under an atmosphere of argon unless otherwise indicated. <sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P NMR spectra were recorded on a Bruker AVANCE-500 spectrometer. <sup>1</sup>H and <sup>13</sup>C chemical shifts were referenced to residual solvent peaks. <sup>31</sup>P chemical shifts were referenced to external 85% phosphoric acid ( $\delta$  = 0 ppm). Electrospray ionization mass spectrometry (ESI-MS) spectra were recorded on a ThermoQuest Finnigan LCQ Duo mass spectrometer. Elemental analyses (C and H) were carried out with a Vario EL CHNOS elemental analyzer from Elementar Analytical, and quantitative analyses of phosphorus for **L<sub>Me</sub>**, **L<sub>Et</sub>**, and **L<sub>iPr</sub>** were performed at the Advanced Technology Support Division of RIKEN Advanced Science Institute. For emission studies, dissolved oxygen was removed by repeated freeze–pump–thaw cycles. Steady-state absorption and emission spectra were recorded at room

temperature and 77 K using a Hitachi U-3010 spectrophotometer and a Hitachi F-7000 spectrofluorometer, respectively. The light-intensity distribution of a xenon lamp incorporated in the spectrofluorometer was corrected using Rhodamine B in ethylene glycol. The output of the photomultiplier was calibrated in the wavelength range of 300–850 nm using a secondary standard lamp. Absorption spectra were measured at 77 K using a specially constructed low-temperature quartz Dewar with four optical windows. The absorption coefficient of the complexes in 2-MeTHF at 77 K was calculated on the assumption that the density of 2-MeTHF was 1.06 g/mL. Laser photolysis studies were carried out using a Nd:YAG laser (Sure Light 400, Hoya Continuum Ltd.) equipped with second-, third-, and fourth-harmonic generators. The excitation light used for emission lifetime measurements was the third harmonic (355 nm). The duration and energy of the laser pulse were 5 ns and 30 mJ/pulse, respectively. The system used to monitor the decay of emission has been reported elsewhere.<sup>8</sup> Emission quantum yields in solution at room temperature and 77 K were determined with an absolute photoluminescence (PL) quantum yield measurement system (C-9920-02G, Hamamatsu).<sup>9</sup> Electrochemical measurements were obtained with an electrochemical analyzer (ALS/CHI, model 600A) equipped with a single-compartment cell under an argon atmosphere. A glassy carbon electrode and coiled platinum wire were used as the working and counter electrodes, respectively. The reference electrode was Ag/AgNO<sub>3</sub> in CH<sub>3</sub>CN, and the scan rate was 100 mV/s. Sample solutions were prepared by dissolving a sample (1 mM) in an electrolyte solution of [(Bu)<sub>4</sub>N][PF<sub>6</sub>] in CH<sub>3</sub>CN (0.1 M, 8 mL). The reference electrode was calibrated before measurements using an external ferrocene standard.

**Crystal Structure Determination.** The crystallographic data and the results of structure refinements are summarized in Table S1 in the Supporting Information (SI). In the reduction of data, Lorentz and polarization corrections and empirical absorption corrections were made. The structures were solved by direct methods (SIR2004).<sup>10</sup> All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were fixed at calculated positions. The X-ray crystallographic data of **1** have been reported previously.<sup>3a</sup> CCDC reference numbers are 756865 for **1**, 865271 for **2**, and 865272 for **3**.

**Computational Details.** Optimization of the geometries of the singlet ground (*S*<sub>0</sub>) and lowest triplet excited (*T*<sub>1</sub>) states in tetrahydrofuran (THF; dielectric constant  $\epsilon$  = 7.4257) was computed using density functional theory (DFT)<sup>11</sup> with Becke three-parameter exchange with the Perdew–Wang 1991 correlation (B3PW91).<sup>12</sup> Calculations of excitation energies and oscillator strengths in THF for the above optimized structures were performed by time-dependent (TD)-DFT with B3PW91. The LANL2DZ effective core potentials and valence basis set<sup>13</sup> were used to describe the valence electrons of silver. Phosphorus, carbon, and hydrogen were described with 6-31+G\*, 6-31G\*, and 6-31G basis sets, respectively. Solvent effects were described by exploiting the integral equation formalism<sup>14</sup> version of the polarizable continuum model,<sup>15</sup> as implemented in Gaussian03<sup>16</sup> and Gaussian09.<sup>17</sup>

A compact orbital representation for the electronic transition density matrix<sup>18</sup> was calculated to interpret the qualitative nature of the *T*<sub>1</sub> state. The transition density matrix is given by  $T_{ia} = \langle \phi_i | \hat{T} | \phi_a \rangle$ , where  $\phi_i$  and  $\phi_a$  are occupied and virtual canonical MOs, respectively. The “natural transition orbitals” (NTOs) were obtained by orbital transformation followed by a singular value decomposition of the transition density matrix. In the NTO representation, the electronic transitions can be expressed by one single “electron–hole” pair with an associated eigenvalue of essentially 1, even transitions that are highly mixed in the canonical MO basis set. This procedure gives us a simple orbital interpretation of “what got excited to where”.<sup>19</sup> All quantum-chemical calculations were carried out on a PC cluster system (Fujitsu). NTO calculations were performed using a laboratory-made code.

**Synthesis of Compounds.** 1,2-Bis[bis(2-methylphenyl)phosphino]benzene (**L<sub>Me</sub>**). A THF solution of (2-methylphenyl)magnesium bromide (1 M, 25 mL, 25 mmol) was added dropwise to a solution of 1,2-bis(dichlorophosphino)benzene (1.0 g, 3.57 mol) in THF (20 mL) at 0 °C. The reaction mixture was stirred for 4 h at

room temperature, and then a solution of saturated aqueous  $\text{NH}_4\text{Cl}$  (100 mL) was added to the reaction mixture. The product was extracted with  $\text{CH}_2\text{Cl}_2$  ( $3 \times 60$  mL). The combined organic extracts were washed with saturated aqueous  $\text{NaCl}$  (150 mL) and dried over  $\text{MgSO}_4$ . The drying agent was removed by filtration, and then the solvent was removed in vacuo to give a pale-yellow oil. The residue was purified by column chromatography on silica gel (*n*-hexane/ $\text{CH}_2\text{Cl}_2$ , 2:1) to afford  $\text{L}_{\text{Me}}$  (1.35 g, 75%) as a colorless solid.  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_2\text{Cl}_2$ , 300 K):  $\delta$  2.19 (s, 12H), 6.76 (m, 4H), 6.92 (m, 2H), 7.02 (t, 4H,  $J = 7.3$  Hz), 7.23–7.15 (m, 8H), 7.26 (m, 2H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CD}_2\text{Cl}_2$ , 300 K):  $\delta$  20.92 (t,  $J(^{13}\text{C}-^{31}\text{P}) = 11.0$  Hz), 125.91, 128.52, 130.00, 133.61, 133.94, 135.44, 142.64 (t,  $J(^{13}\text{C}-^{31}\text{P}) = 13.1$  Hz), 142.84 (t,  $J(^{13}\text{C}-^{31}\text{P}) = 11.7$  Hz).  $^{31}\text{P}\{^1\text{H}\}$  NMR (202 MHz,  $\text{CD}_2\text{Cl}_2$ , 300 K):  $\delta$  -27.10. Anal. Calcd for  $\text{C}_{34}\text{H}_{32}\text{P}_2$ : C, 81.26; H, 6.42; P, 12.33. Found: C, 80.99; H, 6.30; P, 12.18.

**1,2-Bis[bis(2-ethylphenyl)phosphino]benzene ( $\text{L}_{\text{Et}}$ ).** A solution of (2-ethylphenyl)magnesium bromide in THF (25 mL) was prepared from magnesium (2.2 g, 90 mmol) and (2-bromoethyl)benzene (15.9 g, 86 mmol) and then cooled to 0 °C. A solution of 1,2-bis(dichlorophosphino)benzene (3.0 g, 10.1 mmol) in THF (20 mL) was added dropwise to the THF solution of (2-ethylphenyl)magnesium bromide. The reaction mixture was heated under reflux for 4 h. The mixture was cooled to room temperature. A solution of saturated aqueous  $\text{NH}_4\text{Cl}$  (150 mL) was added to the reaction mixture, and then the product was extracted with  $\text{CH}_2\text{Cl}_2$  ( $3 \times 60$  mL). The combined organic extracts were washed with saturated aqueous  $\text{NaCl}$  (150 mL) and dried over  $\text{MgSO}_4$ . The drying agent was removed by filtration, and the solvent was removed in vacuo to give a pale-yellow oil. The residue was purified by column chromatography on silica gel (*n*-hexane/ $\text{CH}_2\text{Cl}_2$ , 2:1) to afford  $\text{L}_{\text{Et}}$  (2.15 g, 36%) as a colorless solid.  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_2\text{Cl}_2$ , 300 K):  $\delta$  0.99 (t, 12H,  $J = 7.5$  Hz), 2.60 (m, 8H), 6.79 (m, 4H), 6.91 (m, 2H), 7.02 (t, 4H,  $J = 7.3$  Hz), 7.20–7.26 (m, 10H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CD}_2\text{Cl}_2$ , 300 K):  $\delta$  14.91, 27.51 (t,  $J(^{13}\text{C}-^{31}\text{P}) = 11.3$  Hz), 125.81, 128.19 (t,  $J(^{13}\text{C}-^{31}\text{P}) = 2.6$  Hz), 128.73, 129.08, 134.16, 134.43 (t,  $J(^{13}\text{C}-^{31}\text{P}) = 3.1$  Hz), 135.56 (t,  $J(^{13}\text{C}-^{31}\text{P}) = 3.3$  Hz), 143.74 (t,  $J(^{13}\text{C}-^{31}\text{P}) = 12.0$  Hz), 148.69 (t,  $J(^{13}\text{C}-^{31}\text{P}) = 12.8$  Hz).  $^{31}\text{P}\{^1\text{H}\}$  NMR (202 MHz,  $\text{CD}_2\text{Cl}_2$ , 300 K):  $\delta$  -29.81. Anal. Calcd for  $\text{C}_{38}\text{H}_{40}\text{P}_2$ : C, 81.69; H, 7.22; P, 11.09. Found: C, 81.38; H, 6.89; P, 10.91.

**1,2-Bis[bis(2-isopropylphenyl)phosphino]benzene ( $\text{L}_{\text{IPr}}$ ).** This compound was prepared using the same procedure as that of  $\text{L}_{\text{Et}}$ , except that (2-bromoisopropyl)benzene (17.1 g, 86 mmol) was used instead of (2-bromoethyl)benzene. Column chromatography on silica gel (*n*-hexane/ $\text{CH}_2\text{Cl}_2$ , 2:1) gave analytically pure  $\text{L}_{\text{IPr}}$  (805 mg, 12%) as a colorless solid.  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_2\text{Cl}_2$ , 300 K):  $\delta$  0.90 (d, 12H,  $J = 6.7$  Hz), 1.03 (br s, 12H), 3.34 (br s, 4H), 6.80 (m, 4H), 6.92 (m, 2H), 7.03 (t, 4H,  $J = 7.3$  Hz), 7.23 (m, 2H), 7.30 (m, 8H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CD}_2\text{Cl}_2$ , 300 K):  $\delta$  23.19 (br), 23.85, 31.28 (t,  $J(^{13}\text{C}-^{31}\text{P}) = 13.0$  Hz), 125.27 (t,  $J(^{13}\text{C}-^{31}\text{P}) = 2.3$  Hz), 125.72, 128.86, 129.06, 134.21, 134.44 (t,  $J(^{13}\text{C}-^{31}\text{P}) = 2.7$  Hz), 134.99, 144.46 (t,  $J(^{13}\text{C}-^{31}\text{P}) = 12.3$  Hz), 153.35 (t,  $J(^{13}\text{C}-^{31}\text{P}) = 12.3$  Hz).  $^{31}\text{P}\{^1\text{H}\}$  NMR (202 MHz,  $\text{CD}_2\text{Cl}_2$ , 300 K):  $\delta$  -31.47. Anal. Calcd for  $\text{C}_{42}\text{H}_{48}\text{P}_2$ : C, 82.05; H, 7.87; P, 10.08. Found: C, 82.24; H, 7.69; P, 10.31.

**$[\text{Ag}(\text{L})_2]\text{PF}_6$  (1).** This compound was synthesized according to the literature.<sup>3a</sup>  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_2\text{Cl}_2$ , 300 K):  $\delta$  7.53 (m, 8H), 7.33 (m, 8H), 7.11–7.10 (m, 32H).  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_2\text{Cl}_2$ , 220 K):  $\delta$  7.05 (br m, 32H), 7.28 (br m, 8H), 7.52 (m, 4H), 7.55 (m, 4H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CD}_2\text{Cl}_2$ , 220 K):  $\delta$  128.19, 129.64, 129.90 (m), 130.54, 132.66 (m), 133.32, 139.05 (m).  $^{31}\text{P}\{^1\text{H}\}$  NMR (202 MHz,  $\text{CD}_2\text{Cl}_2$ , 300 K):  $\delta$  0.81 (d,  $^1J(^{31}\text{P}-^{109}\text{Ag}) = 264$  Hz,  $^2J(^{31}\text{P}-^{109}\text{Ag}) = 229$  Hz). ESI-MS. Calcd for  $\text{C}_{60}\text{H}_{48}\text{AgP}_4$ :  $m/z$  999.18. Found:  $m/z$  999.2 ( $[\text{M} - \text{PF}_6]^-$ ). Anal. Calcd for  $\text{C}_{60}\text{H}_{48}\text{AgF}_6\text{P}_5$ : C, 62.90; H, 4.22. Found: C, 62.76; H, 4.39.

**$[\text{Ag}(\text{L})(\text{L}_{\text{Me}})]\text{BF}_4$  (2).** Silver(I) tetrafluoroborate (39 mg, 0.20 mmol) was added to a solution of  $\text{L}_{\text{Me}}$  (100 mg, 0.20 mmol) in THF (15 mL). The mixture was stirred and heated under reflux. After 2 h,  $\text{L}$  (89 mg, 0.20 mmol) was added, and again the mixture was stirred and heated under reflux for 2 h. Upon cooling, an insoluble solid was removed from the reaction mixture by filtration, and then the solvent was

removed in vacuo. The residue was purified by recrystallization from THF to give colorless crystals  $[\text{Ag}(\text{L})(\text{L}_{\text{Me}})]\text{BF}_4 \cdot 2\text{THF}$  (2·2THF). Yield: 199 mg, 82%.  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_2\text{Cl}_2$ , 300 K):  $\delta$  1.88 (s, 12H), 6.71 (m, 8H), 6.77 (m, 6H), 6.88 (m, 2H), 7.11 (m, 4H), 7.16–7.26 (m, 8H), 7.28–7.44 (m, 8H), 7.49 (m, 2H), 7.54 (m, 4H), 7.60 (m, 2H).  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_2\text{Cl}_2$ , 220 K):  $\delta$  1.60 (s, 6H), 1.76 (s, 6H), 6.60 (m, 8H), 6.66 (m, 4H), 6.79 (m, 2H), 6.81 (m, 2H), 7.03 (m, 4H), 7.18 (m, 6H), 7.21 (m, 2H), 7.24 (m, 2H), 7.30 (t, 2H,  $J = 7.5$  Hz), 7.34 (m, 2H), 7.40 (t, 2H,  $J = 7.5$  Hz), 7.44 (m, 2H), 7.50 (m, 2H), 7.54 (t, 2H,  $J = 7.5$  Hz), 7.58 (m, 2H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CD}_2\text{Cl}_2$ , 220 K):  $\delta$  21.17 (t,  $J(^{13}\text{C}-^{31}\text{P}) = 8.4$  Hz), 21.36 (m), 125.91, 126.21, 127.73 (t,  $J(^{13}\text{C}-^{31}\text{P}) = 4.3$  Hz), 128.30 (t,  $J(^{13}\text{C}-^{31}\text{P}) = 13.0$  Hz), 128.43, 129.12, 129.37 (t,  $J(^{13}\text{C}-^{31}\text{P}) = 11.6$  Hz), 129.54, 129.57 (t,  $J(^{13}\text{C}-^{31}\text{P}) = 12.4$  Hz), 129.79, 129.94, 130.57, 130.65, 130.87, 131.24, 131.43, 131.49, 131.55, 131.97 (t,  $J(^{13}\text{C}-^{31}\text{P}) = 13.9$  Hz), 133.24 (t,  $J(^{13}\text{C}-^{31}\text{P}) = 8.8$  Hz), 134.89, 137.12, 137.13 (t,  $J(^{13}\text{C}-^{31}\text{P}) = 28.1$  Hz), 137.59 (t,  $J(^{13}\text{C}-^{31}\text{P}) = 30.6$  Hz), 140.05 (t,  $J(^{13}\text{C}-^{31}\text{P}) = 9.6$  Hz), 141.24 (t,  $J(^{13}\text{C}-^{31}\text{P}) = 9.1$  Hz).  $^{31}\text{P}\{^1\text{H}\}$  NMR (202 MHz,  $\text{CD}_2\text{Cl}_2$ , 300 K):  $\delta$  -12.76 (2dt,  $^1J(^{31}\text{P}-^{107}\text{Ag}) = 231$  Hz,  $^1J(^{31}\text{P}-^{109}\text{Ag}) = 268$  Hz,  $^2J(^{31}\text{P}-^{31}\text{P}) = 23$  Hz), -2.86 (2dt,  $^1J(^{31}\text{P}-^{107}\text{Ag}) = 227$  Hz,  $^1J(^{31}\text{P}-^{109}\text{Ag}) = 262$  Hz,  $^2J(^{31}\text{P}-^{31}\text{P}) = 31$  Hz). ESI-MS. Calcd for  $\text{C}_{64}\text{H}_{56}\text{AgP}_4$ :  $m/z$  1055.24. Found:  $m/z$  1055.2 ( $[\text{M} - \text{BF}_4]^-$ ). Anal. Calcd for  $\text{C}_{72}\text{H}_{72}\text{AgBF}_4\text{O}_2\text{P}_4$  (2·2THF): C, 67.15; H, 5.63. Found: C, 67.34; H, 5.58.

**$[\text{Ag}(\text{L})(\text{L}_{\text{Et}})]\text{BF}_4$  (3).** Silver(I) tetrafluoroborate (39 mg, 0.20 mmol) was added to a solution of  $\text{L}_{\text{Et}}$  (110 mg, 0.20 mmol) in THF (15 mL). The mixture was stirred and heated under reflux. After 2 h,  $\text{L}$  (89 mg, 0.20 mmol) was added, and then the mixture was again stirred and heated under reflux for 2 h. Upon cooling, an insoluble solid was removed from the reaction mixture by filtration, and then the solvent was removed in vacuo. The residue was purified by recrystallization from acetone to give colorless crystals  $[\text{Ag}(\text{L})(\text{L}_{\text{Et}})]\text{BF}_4 \cdot (\text{CH}_3)_2\text{CO}$  (3·(CH<sub>3</sub>)<sub>2</sub>CO). Yield: 221 mg, 88%.  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_2\text{Cl}_2$ , 300 K):  $\delta$  0.17 (t, 6H,  $J = 7.3$  Hz), 0.38 (t, 6H,  $J = 7.3$  Hz), 2.12 (dq, 2H,  $J = 15.8$  and 7.8 Hz), 2.31 (m, 4H), 2.57 (dq, 2H,  $J = 15.8$  and 7.8 Hz), 6.62 (m, 4H), 6.75 (m, 4H), 6.79 (m, 6H), 7.01 (m, 2H), 7.13–7.18 (m, 8H), 7.23 (t, 2H,  $J = 7.5$  Hz), 7.24–7.29 (m, 4H), 7.38 (t, 2H,  $J = 7.5$  Hz), 7.43 (m, 4H), 7.45 (m, 2H), 7.54 (m, 2H), 7.60 (m, 2H), 7.65 (t, 2H,  $J = 7.5$  Hz).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CD}_2\text{Cl}_2$ , 300 K):  $\delta$  10.99, 11.84, 27.52 (t,  $J(^{13}\text{C}-^{31}\text{P}) = 9.6$  Hz), 27.75 (m), 126.49, 127.02, 128.19, 128.28, 128.84 (t,  $J(^{13}\text{C}-^{31}\text{P}) = 4.4$  Hz), 129.25 (t,  $J(^{13}\text{C}-^{31}\text{P}) = 4.7$  Hz), 130.17, 130.23 (t,  $J(^{13}\text{C}-^{31}\text{P}) = 10.5$  Hz), 130.48, 130.62, 130.76 (t,  $J(^{13}\text{C}-^{31}\text{P}) = 17.3$  Hz), 130.90, 131.32, 131.43 (t,  $J(^{13}\text{C}-^{31}\text{P}) = 13.2$  Hz), 134.88, 131.96, 132.43, 132.82 (t,  $J(^{13}\text{C}-^{31}\text{P}) = 8.1$  Hz), 132.88 (t,  $J(^{13}\text{C}-^{31}\text{P}) = 8.7$  Hz), 133.76 (t,  $J(^{13}\text{C}-^{31}\text{P}) = 8.7$  Hz), 135.80, 138.29, 138.92 (t,  $J(^{13}\text{C}-^{31}\text{P}) = 26.4$  Hz), 139.17 (t,  $J(^{13}\text{C}-^{31}\text{P}) = 25.1$  Hz), 146.02 (t,  $J(^{13}\text{C}-^{31}\text{P}) = 9.1$  Hz), 146.90 (t,  $J(^{13}\text{C}-^{31}\text{P}) = 8.7$  Hz).  $^{31}\text{P}\{^1\text{H}\}$  NMR (202 MHz,  $\text{CD}_2\text{Cl}_2$ , 300 K):  $\delta$  -15.16 (2dt,  $^1J(^{31}\text{P}-^{109}\text{Ag}) = 267$  Hz,  $^1J(^{31}\text{P}-^{107}\text{Ag}) = 233$  Hz,  $^2J(^{31}\text{P}-^{31}\text{P}) = 31$  Hz), -4.25 (2dt,  $^1J(^{31}\text{P}-^{109}\text{Ag}) = 263$  Hz,  $^1J(^{31}\text{P}-^{107}\text{Ag}) = 228$  Hz,  $^2J(^{31}\text{P}-^{31}\text{P}) = 31$  Hz). ESI-MS. Calcd for  $\text{C}_{68}\text{H}_{64}\text{AgP}_4$ :  $m/z$  1111.30. Found:  $m/z$  1111.3 ( $[\text{M} - \text{BF}_4]^-$ ). Anal. Calcd for  $\text{C}_{68}\text{H}_{64}\text{AgBF}_4\text{O}_2\text{P}_4$ : C, 68.07; H, 5.38. Found: C, 67.82; H, 5.21.

## RESULTS AND DISCUSSION

**Synthesis and Characterization of dppb Derivatives and Heteroleptic Silver(I) Complexes.** Bidentate bisphosphine ligands were synthesized from bis(dichlorophosphino)benzene and the appropriate Grignard reagents: (2-methylphenyl)magnesium bromide for  $\text{L}_{\text{Me}}$ , (2-ethylphenyl)magnesium bromide for  $\text{L}_{\text{Et}}$ , and (2-isopropylphenyl)magnesium bromide for  $\text{L}_{\text{IPr}}$ .<sup>20</sup> Large alkyl substituents at the ortho position of the peripheral phenyl groups of dppb considerably decreased the yield of the derivative because of their steric encumbrances; the yields were 75% for  $\text{L}_{\text{Me}}$ , 36% for  $\text{L}_{\text{Et}}$  and 12% for  $\text{L}_{\text{IPr}}$ . Heteroleptic complex 2 was prepared by heating 1 equiv of  $\text{L}_{\text{Me}}$  and 1 equiv of  $\text{AgPF}_6$  under reflux in THF under a

dinitrogen atmosphere with stirring. After reaction for 2 h, the solid silver salt completely dissolved and the solution became clear, presumably because of the formation of  $\text{Ag}(\text{L}_{\text{Me}})(\text{THF})_n$  ( $n = 1$  or  $2$ ). A total of 1 equiv of **L** was then added, and the solution was heated under reflux for a further 2 h. The reaction mixture was filtered, and then the solvent was removed in vacuo to give the crude heteroleptic complex. Recrystallization from THF was sufficient to purify **2** by removing a small amount of the homoleptic byproduct  $[\text{Ag}(\text{L})_2]\text{BF}_4$ . Complex **3** was prepared in a manner similar to **2**, except that **3** was recrystallized from acetone. High yields of 82% and 88% were obtained for **2** and **3**, respectively.

We were unable to synthesize  $[\text{Ag}(\text{L}_{\text{iPr}})(\text{L})]\text{BF}_4$  using  $\text{L}_{\text{iPr}}$  under the reaction conditions described above. The isolated product was solely a stoichiometric amount of homoleptic  $[\text{Ag}(\text{L})_2]\text{BF}_4$ , suggesting that heteroleptic  $[\text{Ag}(\text{L}_{\text{iPr}})(\text{L})]\text{BF}_4$ , if produced, readily undergoes disproportionation to yield the homoleptic complex. It is concluded that the bulkiness of the alkyl group at the ortho position of the phenyl groups in the dppb derivatives governs the stability of the resulting heteroleptic complexes; the more bulky the alkyl group, the less stable the heteroleptic complex. Furthermore, attempts to prepare homoleptic complexes  $[\text{Ag}(\text{L}_{\text{R}})_2]\text{BF}_4$  ( $\text{R} = \text{Me}, \text{Et}$ , and  $\text{iPr}$ ) only generate mono-diphosphine silver(I) complexes.

The crystal structures of complexes **1–3** are shown in Figure 1a–c. Selected bond lengths and angles are summarized in Table 1. The *o*-methyl and *o*-ethyl groups are oriented in the direction of the central metal, resulting in interligand steric interactions between the four peripheral phenyl groups of the other ligand (**L**) in solution. The coordination geometries of **1–3** are distorted from a  $D_{2d}$  pseudotetrahedral geometry that

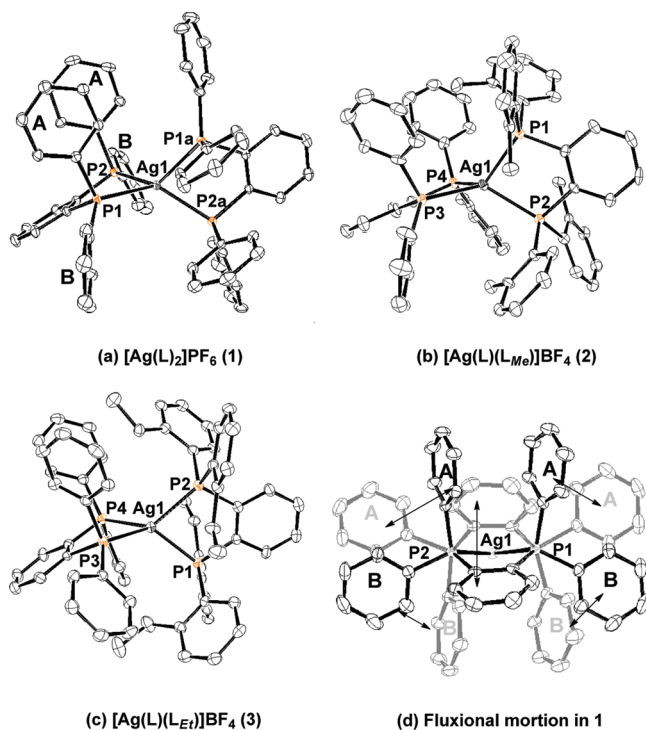
**Table 1.** Selected Bond Distances (Å) and Angles (deg) for **1–3**

|                             | <b>1</b> <sup>c</sup> |           | <b>2</b>   | <b>3</b>   |
|-----------------------------|-----------------------|-----------|------------|------------|
| Ag–P1 <sup>a</sup>          | 2.4592(6)             | 2.5435(6) | 2.553(2)   | 2.5147(10) |
| Ag–P2 <sup>a</sup>          | 2.5027(6)             | 2.4611(6) | 2.4958(19) | 2.5063(10) |
| Ag–P3                       |                       |           | 2.501(2)   | 2.5030(10) |
| Ag–P4                       |                       |           | 2.519(2)   | 2.5216(10) |
| average (Ag–P)              | 2.492                 |           | 2.517      | 2.511      |
| dihedral angle <sup>b</sup> | 82.56(3)              | 85.25(3)  | 84.91(10)  | 81.38(4)   |

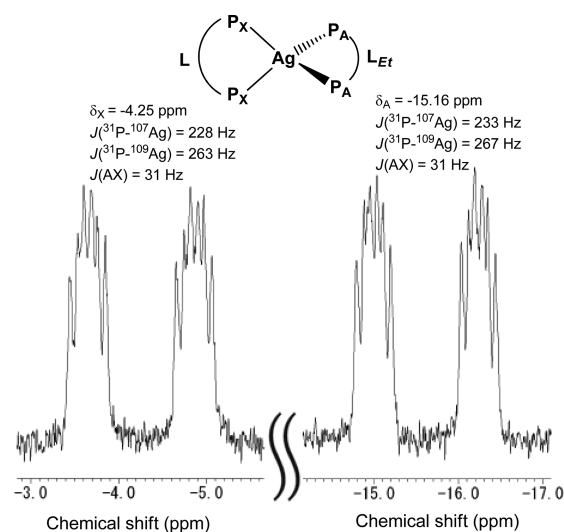
<sup>a</sup>P1 and P2 belong to **L** for **1**,  $\text{L}_{\text{Me}}$  for **2**, and  $\text{L}_{\text{Et}}$  for **3**. <sup>b</sup>The dihedral angle between two planes, P1–Ag–P2 and P3(1a)–Ag–P4(2a). <sup>c</sup>Two molecules in the unit cell.

might be expected for a  $\text{d}^{10}$  ion. The dihedral angles between the two planes defined by P1–Ag<sup>I</sup>–P2 and P3(1a)–Ag<sup>I</sup>–P4(2a) are 81.38(4)–85.25(3)°. The average bond lengths (Ag–P) in **2** and **3** are almost equal to those in **1**, suggesting that the chelating abilities of  $\text{L}_{\text{Me}}$  and  $\text{L}_{\text{Et}}$  are similar to that of **L**.

The strong chelating abilities of the dppb derivatives were confirmed by  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopic measurements in  $\text{CD}_2\text{Cl}_2$ . It is known that Ag–P coupling in the room temperature spectra of silver phosphine complexes is unresolved because of the rapid exchange equilibria.<sup>21</sup> Complexes **1–3**, however, show typical Ag–P couplings even at ambient temperature. Complex **1** shows two doublet of doublets with  $J(^{31}\text{P}–^{107}\text{Ag}) = 229$  Hz and  $J(^{31}\text{P}–^{109}\text{Ag}) = 264$  Hz, and **2** and **3** exhibit two doublet of triplets ( $A_2X_2$  systems). As an example, the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **3** is shown in Figure 2. Two well-resolved pairs of doublet of triplets are



**Figure 1.** ORTEP drawings of the structures of cations in **1** (a), **2** (b), and **3** (c). Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms and counteranions  $\text{PF}_6$  and  $\text{BF}_4$  are omitted for clarity. The two types of phenyl groups (A and B) and fluxional motion in **1** are shown in parts a and d, respectively.



**Figure 2.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **3** (in  $\text{CD}_2\text{Cl}_2$  at 300 K).

observed at  $-15.16$  and  $-4.25$  ppm with  $^2J(\text{AX}) = 31/{}^1J(^{31}\text{P}–^{107}\text{Ag}) = 233/{}^1J(^{31}\text{P}–^{109}\text{Ag}) = 267$  Hz and  $^2J(\text{AX}) = 31/{}^1J(^{31}\text{P}–^{107}\text{Ag}) = 228/{}^1J(^{31}\text{P}–^{109}\text{Ag}) = 263$  Hz, respectively. Because no signals from disproportionation products were observed, the heteroleptic structures of **2** and **3** are concluded to be very stable even in solution. Furthermore,  $^1\text{H}$  NMR experiments revealed that **3** has the most rigid structure in solution. The ring protons of the two types of phenyl groups (labeled as A and B in Figure 1a)

bonded to the phosphorus atom in **1–3** are nonequivalent because of the weak  $\pi$ – $\pi$  interaction between two type A phenyl groups. However, the  $^1\text{H}$  NMR spectra of **1** in  $\text{CD}_2\text{Cl}_2$  at 300 and 220 K show ring protons of A and B as a single broad peak (see Figure S8 in the SI). This can be attributed to rapid interconversion based on a dynamic fluxional process in **1** (Figure 1d). In the case of **2** at 220 K, the protons attached to phenyl and tolyl groups are observed as four kinds of well-resolved signals consistent with aryl groups, and the methyl protons of  $\text{L}_{\text{Me}}$  appear as two sharp singlets (see Figure S9 in the SI). These two singlets become one broad singlet at 300 K in  $\text{CD}_2\text{Cl}_2$  (see Figure S10 in the SI). However, the four multiplets observed for the two kinds of tolyl and phenyl groups are still observed at 300 K (see Figure S8 in the SI), suggesting there is no fluxional motion of **2** at either 220 or 300 K. A possible explanation for this is that a small waving motion of the two diphosphine ligands in **2** makes the methyl protons of  $\text{L}_{\text{Me}}$  chemically equivalent at 300 K. In contrast, the  $^1\text{H}$  NMR spectrum of **3** exhibits two sharp triplets [ $\text{CH}_3(\text{A})$ , 0.17 ppm;  $\text{CH}_3(\text{B})$ , 0.38 ppm] corresponding to the terminal methyl protons of  $\text{L}_{\text{Et}}$  (Figure 3). Moreover, the methylene protons of

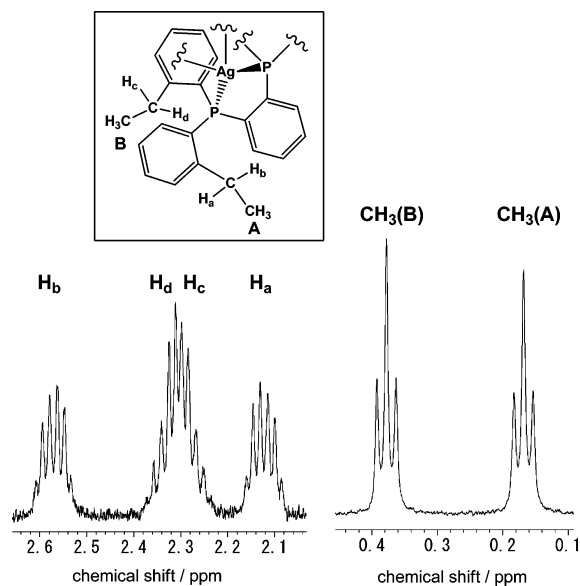


Figure 3.  $^1\text{H}$  NMR spectrum of **3** (in  $\text{CD}_2\text{Cl}_2$  at 300 K).

the ethyl substituents are split into two doublet of quartets and one multiplet consisting of two doublet of quartets ( $\text{H}_a$ – $\text{d}$ ) with  $J = 7.8$  and  $15.8$  Hz in  $\text{CD}_2\text{Cl}_2$  at 300 K. Resonance signals ( $\text{H}_a$ , 2.12 ppm;  $\text{H}_b$ , 2.57 ppm;  $\text{H}_c$ , 2.29 ppm;  $\text{H}_d$ , 2.32 ppm) were assigned using COSY  $^1\text{H}$  NMR spectra. These results demonstrate that complex **3** does not exhibit fluxional motion or rotation about the  $\text{C}_{\text{aryl}}\text{--C}_{\text{ethylene}}$  bonds. Similarly, the motion of the  $\text{P}\text{--C}_{\text{aryl}}$  bonds in **3** is obstructed in solution at ambient temperature on the NMR time scale. The NMR studies of **1–3** lead to the conclusion that interligand steric interactions fix the geometry of **3** in solution.

**Photophysical Properties of dppb Derivatives.** dppb derivatives have two types of aromatic groups attached to phosphorus atoms; a bridging *o*-phenylene group and four peripheral phenyl groups (phenyl for **L**, methylphenyl for  $\text{L}_{\text{Me}}$ , ethylphenyl for  $\text{L}_{\text{Et}}$  and isopropyl for  $\text{L}_{\text{iPr}}$ ). The absorption and phosphorescence spectra of the diphosphine ligands in 2-MeTHF at 77 K are shown in Figure 4, and their photophysical

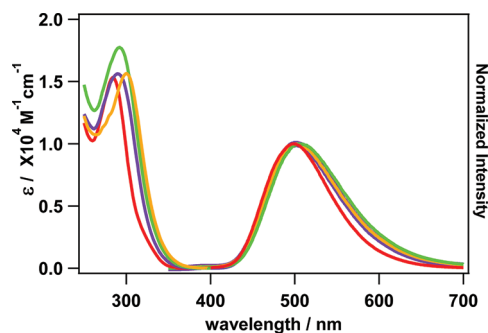


Figure 4. Absorption and corrected emission spectra of **L** (red),  $\text{L}_{\text{Me}}$  (purple),  $\text{L}_{\text{Et}}$  (green), and  $\text{L}_{\text{iPr}}$  (orange) in 2-MeTHF at 77 K;  $\lambda_{\text{exc}} = 300$  nm.

properties are summarized in Table 2. These diphosphine ligands exhibit quite similar behavior; the absorption spectra

Table 2. Photophysical Data for Diphosphine Ligands in 2-MeTHF

| ligand                  | absorption $\lambda_{\text{max}}/\text{nm}$ ( $\epsilon/\text{M}^{-1}\text{cm}^{-1}$ ) <sup>a</sup> | emission $\lambda_{\text{max}}/\text{nm}$ <sup>a</sup> | $\Phi_{\text{PL}}$ <sup>b</sup> | $E_{\text{pa}}$ (V) vs Fc/ $\text{Fc}^+$ <sup>c</sup> |
|-------------------------|-----------------------------------------------------------------------------------------------------|--------------------------------------------------------|---------------------------------|-------------------------------------------------------|
| <b>L</b>                | 284 ( $1.51 \times 10^4$ )                                                                          | 499                                                    | 0.68                            | +0.36                                                 |
| $\text{L}_{\text{Me}}$  | 290 ( $1.53 \times 10^4$ )                                                                          | 500                                                    | 0.75                            | +0.40                                                 |
| $\text{L}_{\text{Et}}$  | 292 ( $1.73 \times 10^4$ )                                                                          | 505                                                    | 0.70                            | +0.44                                                 |
| $\text{L}_{\text{iPr}}$ | 300 ( $1.58 \times 10^4$ )                                                                          | 500                                                    | 0.69                            | +0.38                                                 |

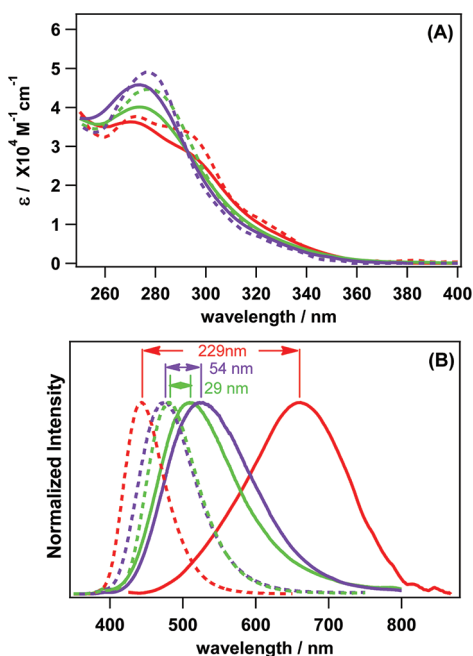
<sup>a</sup>Absorption and PL peak wavelength in 2-MeTHF at 77 K;  $\lambda_{\text{exc}} = 300$  nm. <sup>b</sup>Absolute PL quantum yield in 2-MeTHF at 77 K;  $\lambda_{\text{exc}} = 300$  nm.

<sup>c</sup>Anodic peak potential in argon-saturated  $\text{CH}_3\text{CN}$  at 293 K. These waves are irreversible.

display broad, intense bands at 284–300 nm [extinction coefficient ( $\epsilon$ ) =  $\sim 16000 \text{ M}^{-1} \text{ cm}^{-1}$ ], which are characteristic of arylphosphine compounds, as shown in Figure 4.<sup>22</sup> These bands are assigned to a mixed transition of  $1\text{--}\pi^*$  and  $\pi\text{--}\pi^*$ ; the former is the transition of an electron from the lone-pair orbital on phosphorus to an empty antibonding  $\pi$  orbital on an *o*-phenylene or phenyl-type ring, while the latter are transitions localized on a phenyl-type or phenylene ring and those from a phenyl-type ring to a phenylene ring. These assignments are consistent with recent MO calculations on dppb.<sup>23</sup> Solutions of all of these diphosphine ligands are not emissive at room temperature, but strong blue-green emission ( $\lambda_{\text{max}} = 499\text{--}505$  nm;  $\Phi_{\text{p}} = 0.68\text{--}0.75$ ) is observed in frozen 2-MeTHF at 77 K (Figure 4). Our calculations revealed that the emitting state of dppb is mainly the charge-transfer state from the lone pair on the phosphorus atoms to the *o*-phenylene groups.<sup>9</sup> The dppb derivatives exhibit absorption and phosphorescence spectra quite similar to those of dppb, suggesting that alkyl substituents (methyl, ethyl, and isopropyl) at ortho positions in peripheral aryl rings have a small effect on the electronic states of these ligands.

The electrochemical properties of the diphosphine ligands were investigated by cyclic voltammetry (CV). The oxidation potentials of diphosphine ligands (**L**,  $\text{L}_{\text{Me}}$ ,  $\text{L}_{\text{Et}}$  and  $\text{L}_{\text{iPr}}$ ) are very similar to each other, as shown in Table 2.

**Photophysical Properties of Silver(I) Complexes 1–3 in 2-MeTHF Glasses at 77 K and a Comparison with MO Calculations.** Figure 5 shows the absorption and emission spectra of silver(I) complexes **1–3** at 77 K in 2-MeTHF. Absorption and emission peaks, lifetimes ( $\tau_{\text{T}}$ ),  $\Phi_{\text{p}}$  at 77 K, and DFT calculation data (dihedral angles and  $T_1$  energy levels) are



**Figure 5.** (A) Absorption and (B) corrected emission spectra for **1** (red), **2** (purple), and **3** (green) in 2-MeTHF at 77 (dashed lines) and 293 K (solid lines);  $\lambda_{\text{exc}} = 300$  nm.

summarized in Table 3. The optimized  $S_0$  structures in THF were used for these calculations. Complexes **1–3** show

**Table 3. Photophysical Data for Complexes 1–3 in 2-MeTHF at 77 K**

| complex  | absorption $\lambda_{\text{max}}/\text{nm}$<br>( $\epsilon/\text{M}^{-1}\text{cm}^{-1}$ ) <sup>a</sup> | $\lambda_{\text{max}}/\text{nm}$<br>( $\tau/\text{ms}$ ) <sup>a</sup> | $\Phi_{\text{PL}}$ <sup>b</sup> | dihedral<br>angle/deg <sup>c</sup> | $T_1/\text{nm}^c$ |
|----------|--------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------|---------------------------------|------------------------------------|-------------------|
| <b>1</b> | 272 ( $3.77 \times 10^4$ )                                                                             | 441 (2.3)                                                             | 0.88                            | 81                                 | 360               |
| <b>2</b> | 276 ( $4.01 \times 10^4$ )                                                                             | 473 (2.5)                                                             | 0.75                            | 78                                 | 365               |
| <b>3</b> | 278 ( $4.46 \times 10^4$ )                                                                             | 480 (2.8)                                                             | 0.70                            | 77                                 | 365               |

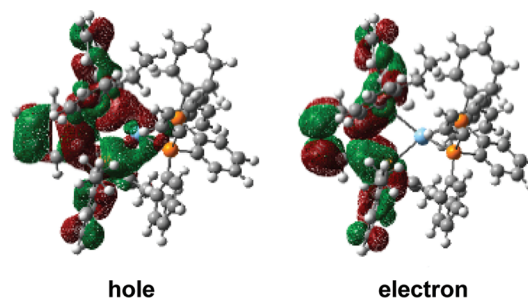
<sup>a</sup>Absorption and PL peak wavelength in 2-MeTHF at 77 K;  $\lambda_{\text{exc}} = 300$  nm. <sup>b</sup>Absolute PL quantum yield in 2-MeTHF at 77 K;  $\lambda_{\text{exc}} = 300$  nm. <sup>c</sup>Dihedral angle between two planes, P1–Ag–P2 and P3(1a)–Ag–P4(2a), and the  $T_1 \leftarrow S_0$  energy were calculated for the optimized  $S_0$  structures of **1–3**.

absorption spectra typical of diphosphine ligands; broad bands with maxima at 272–278 nm are assigned to a mixed transition of  $\sigma \rightarrow \pi^*$  and  $\pi-\pi^*$ . Complexes **1–3** show efficient luminescence performance at 77 K, as listed in Table 3. Strong blue phosphorescence from **1–3** was observed in frozen 2-MeTHF ( $\lambda_{\text{max}} = 441\text{--}480$  nm;  $\Phi_{\text{p}} = 0.70\text{--}0.88$ ). Because a change of the structure of the excited state is highly restricted in 2-MeTHF glass at 77 K because of the rigidity of the medium, blue phosphorescence is concluded to arise from an excited state with a tetrahedral structure.

The MO calculations determined the dihedral angles between the two planes P1–Ag–P2 and P3(1a)–Ag–P4(2a) for **1–3** in a THF solution to be 81, 78, and 77°, respectively, which are smaller than those found in X-ray crystal structures. This can be attributed to the presence of a  $\text{BF}_4^-$  counteranion, trapped solvent in the crystal lattice, and weak noncovalent interactions ( $\pi-\pi$ , hydrogen-bonding, and  $\text{CH}-\pi$  interactions) in single crystals.

NTO analyses were performed to clarify the origin of phosphorescence in the complexes. Maps of the hole

[approximately the highest occupied molecular orbitals (HOMO)] and electron [approximately the lowest unoccupied molecular orbital (LUMO)] in  $T_1$  in the optimized  $S_0$  structure of **3** are shown in Figure 6. The hole distribution in **3** is mainly



**Figure 6.** NTO pairs for the lowest triplet excited state of **3** in the optimized  $S_0$  geometry. The generation probability is 56%.

confined to the orbitals of the  $\sigma$  bonds between the silver(I) and two phosphorus ( $\text{L}_{\text{Et}}$ ) atoms and slightly extended over the  $\pi$  system of  $\text{L}_{\text{Et}}$ ; the contributions from the silver, phosphorus, and other ( $\pi$ ) systems are 4, 22, and 74%, respectively (see Table S2 in the SI). The electron distribution is essentially delocalized over  $\text{L}_{\text{Et}}$ . These results indicate that strong blue phosphorescence mainly results from  $\pi-\pi^*$  transitions (the contribution is about 81%), which include transitions localized on a phenyl group and a phenylene ring as well as those with charge-transfer character from a phenyl-type ring to a phenylene ring. The long lifetimes (2.3–2.8 ms) of **1–3** at 77 K support the assignment of the origin of phosphorescence as  $\pi-\pi^*$ . Meanwhile, the contribution from the  $\sigma-\pi^*$  transition to phosphorescence is 19%. The  $\sigma-\pi^*$  transition contains contributions from MLCT (4%) and intraligand charge-transfer (ILCT, 15%) transitions because the  $\sigma$  orbital is primarily composed of d orbitals (silver atom;  $d_{xy}$ ,  $d_{yz}$ ,  $d_{zx}$ ) and p orbitals (phosphorus atoms) including lone-pair electrons. Complexes **1** and **2** show similar NTO maps (see Figures S17 and S18 in the SI) and origin of phosphorescence to **3** (see Tables S3 and S4 in the SI); the contribution from  $\pi-\pi^*$  is 78% for **1** and 82% for **2**.

Molecular motion in 2-MeTHF at 77 K is strongly prohibited in both the ground and excited states because of the high viscosity of the medium. Thus, the structures of complexes **1–3** resemble the optimized  $S_0$  with pseudotetrahedral geometry even in the  $T_1$  state.  $\lambda_{\text{max}}$  is located at 441 nm for **1**, 473 nm for **2**, and 480 nm for **3**. From Table 3, it is obvious that  $\lambda_{\text{max}}$  shifts to longer wavelength as the dihedral angle of the optimized  $S_0$  structure of the complex decreases.

**Photophysical Properties of Silver Complexes 1–3 at Room Temperature.** Figure 5 shows the absorption and emission spectra of silver complexes **1–3** at 293 K in 2-MeTHF. Photophysical and calculated data are summarized in Table 4. The optimized  $T_1$  structures in THF were used for these calculations. Complex **1** exhibits bright blue emission in 2-MeTHF glasses, whereas it shows weak orange luminescence ( $\lambda_{\text{max}} = 670$  nm;  $\Phi_{\text{p}} = 0.05$ ) in degassed 2-MeTHF at room temperature (red dashed and solid lines in Figure 5B). Although the MLCT character responsible for the Jahn–Teller effect is not strong (4% for **1**), the large red shift of the emission peak of 230 nm and the low  $\Phi_{\text{p}}$  in 2-MeTHF at room temperature indicate that a large change in the geometry of **1** occurs in the excited state from pseudotetrahedral to a more

Table 4. Photophysical Data for Complexes 1–3 in 2-MeTHF at 293 K

| complex | absorption $\lambda_{\text{max}}/\text{nm}$ ( $\epsilon/\text{M}^{-1} \text{cm}^{-1}$ ) <sup>a</sup> | $\lambda_{\text{max}}/\text{nm}$ ( $\tau/\mu\text{s}$ ) <sup>a</sup> | $\Phi_{\text{PL}}$ <sup>b</sup> | dihedral angle/deg ( $\Delta\theta^d/\text{deg}$ ) <sup>c</sup> | $T_1/\text{nm}^c$ | $E_{1/2}/\text{V}^e$ ( $\Delta E_{\text{p}}/\text{mV}$ ) <sup>f</sup> |
|---------|------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------|---------------------------------|-----------------------------------------------------------------|-------------------|-----------------------------------------------------------------------|
| 1       | 270 ( $3.63 \times 10^4$ )                                                                           | 670 (22)                                                             | 0.05                            | 30 (51)                                                         | 612               | +0.48 (80)                                                            |
| 2       | 274 ( $4.58 \times 10^4$ )                                                                           | 527 (10)                                                             | 0.33                            | 65 (13)                                                         | 596               | +0.70 (80)                                                            |
| 3       | 274 ( $4.01 \times 10^4$ )                                                                           | 509 (15)                                                             | 0.26                            | 70 (7)                                                          | 526               | +0.72 (130)                                                           |

<sup>a</sup>Absorption and PL peak wavelength in 2-MeTHF at 77 K;  $\lambda_{\text{exc}} = 300 \text{ nm}$ . <sup>b</sup>Absolute PL quantum yield in 2-MeTHF at 77 K;  $\lambda_{\text{exc}} = 300 \text{ nm}$ .

<sup>c</sup>Dihedral angle between two planes, P1–Ag–P2 and P3(1a)–Ag–P4(2a), and  $T_1 \leftarrow S_0$  energy were calculated for the optimized  $T_1$  structures of 1–3. <sup>d</sup>Difference in dihedral angles between optimized  $S_0$  and  $T_1$  structures. <sup>e</sup>Half-wave potential (vs Fc/Fc<sup>+</sup>) recorded in argon-saturated CH<sub>3</sub>CN.

<sup>f</sup>Peak-to-peak separation.

flattened structure, which is accompanied by energetic relaxation. The calculated dihedral angle (30°) and  $T_1$  energy (612 nm) of **1** in the optimized  $T_1$  structure also suggest that the structure of the excited state is flatter; the angular difference from the optimized  $S_0$  structure is as large as 51° (Table 4).

Complexes **2** and **3** exhibit intense green phosphorescence ( $\Phi_{\text{p}} = 0.33$  and 0.26) in a 2-MeTHF solution at 293 K (purple lines for **2** and green for **3** in Figure S8). The phosphorescence peaks are located at longer wavelengths than those at 77 K. However, the shifts are smaller: 54 nm for **2** and 29 nm for **3**. Therefore, the excited states of **2** and **3** undergo some changes in geometry at room temperature, resulting in a small energetic relaxation of the phosphorescent state.

The emitting state in solution at 293 K is considered to have the optimized  $T_1$  structure. The MO calculations revealed that the calculated dihedral angles between two planes, P1–Ag–P2 and P3(1a)–Ag–P4(2a), in the optimized  $T_1$  structures are 65° for **2** and 70° for **3**. These angles are at most 13° smaller than those in the optimized  $S_0$  structures. The interligand steric interactions caused by alkyl substituents at the ortho positions in  $L_{\text{Me}}$  and  $L_{\text{Et}}$  probably prevent adoption of a flattened geometry.

A single reversible wave was observed for silver complexes **1**–**3** by CV at  $E_{1/2} = +0.48$ , +0.70, and +0.72V vs Fc/Fc<sup>+</sup> in CH<sub>3</sub>CN, respectively (Table 4). Silver(I) in **1** is oxidized more readily than that in **2** and **3**. This result is consistent with the fact that interligand steric interactions stabilize the tetrahedral silver(I) versus flattened silver(II) complexes in **2** and **3** in solution at 293 K. A similar correlation between the degree of steric effects and the one-electron-oxidation potential was reported for tetrahedral copper(I) diimine complexes.<sup>24</sup>

NTO analysis based on the optimized  $T_1$  structure in THF showed that transitions can be described as single-electron pairs, which reproduce over 90% of the transition density. The maps from NTO analysis based on the optimized  $T_1$  structure of **3** in THF are shown in Figure 7 as an example. It is clear that the hole distribution of **3** mainly lies on  $\sigma$  orbitals composed of

silver and four phosphorus atoms, and the distribution on the  $\pi$  system appreciably decreases compared to that of **3** in the optimized  $S_0$  structure, as seen in Figure 6. The electron distribution is largely confined to the *o*-phenylene group. Thus, the contribution of  $\pi-\pi^*$  in phosphorescence decreases from 81% to 47%, and that of  $\sigma-\pi^*$  increases to 53%; attributable fractions of MLCT and ILCT are 10% and 43%, respectively (see Table S5 in the SI). It is noteworthy that a small distortion (difference of the dihedral angle is 7°) between the optimized  $S_0$  and  $T_1$  structures in the excited state of **3** considerably alters the origin of phosphorescence. The distortion increases the hole energy levels by reducing the symmetry (from  $D_{2d}$ ), which removes the degeneracy of the HOMO energy levels. If the hole energy levels increase, the contribution of  $\pi$  orbitals in diphosphine ligands to the hole decreases, so the  $\pi-\pi^*$  character of phosphorescence is reduced.

When the contribution of the d orbitals in the silver atom and p orbitals in phosphorus atoms to the hole increases, the  $\sigma-\pi^*$  character of phosphorescence increases. Complex **2** possesses NTO maps similar to those of **3** (see Figure S19 in the SI), while details of the origin of phosphorescence are shown in Table S6 in the SI. The contributions of  $\sigma-\pi^*$  and  $\pi-\pi^*$  transitions are 52% and 48%, respectively, for **2**.

## CONCLUSIONS

The synthesis and photophysics of heteroleptic tetrahedral silver(I) complexes **2** and **3** containing diphosphine ligands have been reported. <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR experiments confirmed that the stability of heteroleptic silver(I) complexes **2** and **3** in solution and the alkyl substituents at the ortho positions of phenyl groups bonded to phosphorus atoms in diphosphine ligands induce a rigid environment around the silver center in **2** and **3**. Interligand steric interactions between the alkyl groups inhibit geometric relaxation of the excited state, leading to intense green phosphorescence from **2** and **3** in solution even at ambient temperature. The quantum yields of phosphorescence for **2** and **3** at 293 K are 0.33 and 0.26, which are ca. 6 times as large as that of the homoleptic complex **1**. On the basis of theoretical studies, the origin of green phosphorescence from the complexes **1**–**3** is ascribed to a mixture of  $\sigma-\pi^*$  and  $\pi-\pi^*$  transitions.

We believe that the introduction of *o*-alkyl substituents onto the phenyl groups of dppb ligands is an effective way to induce interligand steric interactions in metal complexes. Interligand steric interactions are expected to improve the luminescence of metal complexes in both solid crystals and solution.

## ASSOCIATED CONTENT

### Supporting Information

X-ray crystallographic data for complexes **2** and **3** in CIF format, X-ray crystallographic data of complexes **1**–**3**, NMR spectra and cyclic voltammograms of ligands and complexes **1**–

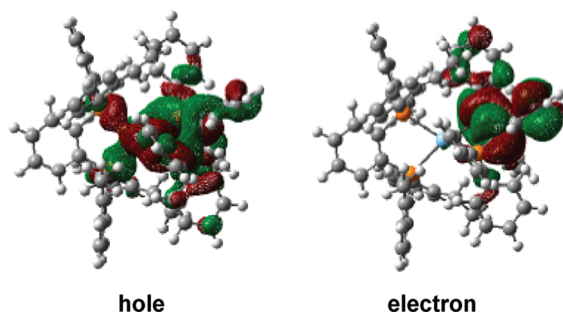


Figure 7. NTO pairs for the lowest triplet excited state of **3** in the optimized  $T_1$  geometry. The generation probability is 90%.

3, NTO pairs for the  $T_1$  state, compositions of the hole and electron in the  $T_1$  state, and geometry data for the optimized structures of 1–3. 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.

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