# Theoretical Insights into the Effect of Ligand on Platinum(II) Complexes with Bidentate Bis(o-carborane) Ligands structure

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Table S1. The optimized ground-state geometries of complex 1 obtained by different functionals with the available experimental structure parameters.

| | B3LYP | PBE0 | BMK | M062X | M052X | CAM-B3LYP | BP86-D3 | Exp.a |
|---|---|---|---|---|---|---|---|---|
| Band length 1 | 2.065 | 2.043 | 2.068 | 2.029 | 2.037 | 2.059 | 2.044 | 2.036 |
| Band length 2 | 2.089 | 2.075 | 2.076 | 2.041 | 2.047 | 2.081 | 2.068 | 2.073 |
| Band length 5 | 1.690 | 1.675 | 1.728 | 1.663 | 1.656 | 1.669 | 1.709 | 1.704 |
| Band length 6 | 1.529 | 1.522 | 1.530 | 1.526 | 1.519 | 1.526 | 1.527 | 1.517 |
| Band length 7 | 1.726 | 1.721 | 1.584 | 1.720 | 1.725 | 1.716 | 1.736 | 1.725 |
| Band length 3 | 2.309 | 2.255 | 2.259 | 2.349 | 2.309 | 2.277 | 2.257 | 2.175 |
| Band length 4 | 2.146 | 2.107 | 2.169 | 2.173 | 2.137 | 2.127 | 2.110 | 2.053 |
| Band angle 1-Pt-2 | 86.22 | 86.26 | 85.26 | 86.69 | 86.80 | 86.15 | 86.56 | 87.02 |
| Band angle 1-C-5 | 116.29 | 116.68 | 113.52 | 116.83 | 116.35 | 116.34 | 116.59 | 115.78 |
| Band angle 5-C-6 | 110.70 | 110.68 | 109.88 | 110.20 | 110.66 | 110.97 | 109.91 | 110.73 |
| Band angle 6-C-7 | 114.29 | 113.99 | 115.47 | 113.69 | 113.61 | 114.10 | 113.95 | 114.11 |
| Band angle 7-C-2 | 112.33 | 112.22 | 115.70 | 112.43 | 111.86 | 112.26 | 112.66 | 112.04 |
| Band angle 1-Pt-4 | 173.82 | 174.78 | 171.71 | 173.45 | 174.09 | 174.55 | 174.93 | 176.55 |
| Band angle 2-Pt-3 | 171.54 | 171.72 | 175.82 | 171.85 | 170.28 | 171.66 | 170.55 | 168.82 |
| Dihedral angle 5-6-7 | 4.14 | 4.44 | -2.20 | 4.41 | 9.18 | 4.49 | 6.18 | 6.10 |
| Dihedral angle 8-9-10 | 10.49 | 8.28 | -4.30 | 10.02 | 13.68 | 9.50 | 6.83 | 4.43 |
| | 11.11% | 7.55% | 6.20% | 10.60% | 16.37% | 9.33% | 4.07% | |

[a] The experimental value obtains from Reference 2.

Table S2. Main optimized geometry structural parameters of the investigated complexes in the ground state $S_0$ and the lowest-lying triplet state $T_1$ along the RMSD at the DFT/BP86-D3 level.

| | **1** | | **1a** | | **1a-N** | | **1a-O** | | **1a-PO** | |
|---|---|---|---|---|---|---|---|---|---|---|
| | $S_0$ | $T_1$ | $S_0$ | $T_1$ | $S_0$ | $T_1$ | $S_0$ | $T_1$ | $S_0$ | $T_1$ |
| Band length 1 | 2.044 | 2.059 | 2.038 | 2.083 | 2.037 | 2.059 | 2.037 | 2.075 | 2.042 | 2.086 |
| Band length 2 | 2.068 | 2.082 | 2.055 | 2.130 | 2.057 | 2.077 | 2.057 | 2.165 | 2.053 | 2.116 |
| Band length 3 | 2.257 | 2.242 | 2.272 | 2.212 | 2.282 | 2.238 | 2.277 | 2.286 | 2.287 | 2.216 |
| Band length 4 | 2.110 | 2.062 | 2.110 | 2.133 | 2.110 | 2.102 | 2.107 | 2.142 | 2.105 | 2.123 |
| Band angle 1-Pt-2 | 86.56 | 86.49 | 87.74 | 90.03 | 87.38 | 87.39 | 87.41 | 91.23 | 87.91 | 89.30 |
| Band angle 3-Pt-4 | 82.97 | 83.07 | 82.96 | 83.07 | 81.69 | 81.20 | 81.35 | 78.90 | 86.045 | 87.30 |
| Band angle 1-Pt-4 | 174.93 | 175.95 | 178.75 | 177.18 | 178.59 | 177.80 | 178.05 | 174.00 | 173.35 | 178.43 |
| Band angle 2-Pt-3 | 170.55 | 172.40 | 168.06 | 132.09 | 166.86 | 161.12 | 167.79 | 110.69 | 170.30 | 139.77 |
| Dihedral angle 5-6-7 | 6.18 | 8.40 | 4.14 | -11.49 | 4.60 | 3.54 | 4.42 | -12.43 | -0.20 | -9.69 |
| Dihedral angle 8-9-10 | 6.83 | -5.82 | 2.06 | -15.65 | 5.36 | 18.01 | 5.32 | 23.34 | 12.84 | -13.70 |
| RMSD | 0.329 | | 0.705 | | 0.915 | | 2.153 | | 1.011 | |
| | **1** | | **1b** | | **1b-N** | | **1b-O** | | **1b-PO** | |
| | $S_0$ | $T_1$ | $S_0$ | $T_1$ | $S_0$ | $T_1$ | $S_0$ | $T_1$ | $S_0$ | $T_1$ |
| Band length 1 | 2.044 | 2.059 | 2.043 | 2.061 | 2.024 | 2.041 | 2.021 | 2.038 | 2.034 | 2.049 |
| Band length 2 | 2.068 | 2.082 | 2.070 | 2.084 | 2.044 | 2.061 | 2.041 | 2.061 | 2.061 | 2.078 |
| Band length 3 | 2.257 | 2.242 | 2.245 | 2.267 | 2.411 | 2.399 | 2.463 | 2.418 | 2.304 | 2.269 |
| Band length 4 | 2.110 | 2.062 | 2.107 | 2.047 | 2.144 | 2.079 | 2.146 | 2.087 | 2.122 | 2.103 |
| Band angle 1-Pt-2 | 86.56 | 86.49 | 86.53 | 86.44 | 88.14 | 88.14 | 88.34 | 88.37 | 87.15 | 87.28 |
| Band angle 3-Pt-4 | 82.97 | 83.07 | 75.12 | 75.63 | 80.17 | 81.44 | 80.54 | 82.35 | 77.20 | 79.11 |
| Band angle 1-Pt-4 | 174.93 | 175.95 | 174.85 | 174.09 | 173.82 | 170.64 | 173.47 | 170.05 | 174.62 | 174.99 |
| Band angle 2-Pt-3 | 170.55 | 172.40 | 171.19 | 172.52 | 176.02 | 177.85 | 176.21 | 178.12 | 173.70 | 173.23 |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Dihedral angle 5-6-7 | 6.18 | 8.40 | 5.34 | 6.76 | 3.27 | 2.38 | 3.22 | 1.19 | 3.55 | 1.86 |
| Dihedral angle 8-9-10 | 6.83 | -5.82 | 1.35 | 0.43 | 0.41 | -0.08 | 0.48 | -0.39 | 0.55 | 0.01 |
| RMSD | 0.329 | | 0.103 | | 0.075 | | 0.077 | | 0.056 | |

Table S3. Simulated emissive spectra of the complex 1 obtained by different functions with the available experimental spectra.

| nm | BP86-D3 | PBE0 | CAM-B3LYP | wB97X | M05X | M062X | Exp.a |
|---|---|---|---|---|---|---|---|
| λem | 790 | 618 | 619 | 580 | 531 | 498 | 497 |

[a] The experimental value obtains from Reference 2.

Table S4. The analysis of the molecular orbital compositions in the lowest-lying triplet state for all complexes at the TD-DFT/M062X level.

| | MO compositions | | | | | |
|---|---|---|---|---|---|---|
| | Orbitals | Energy(eV) | Et-bc | Pt | dtp-bpy | Composition contribution>10% |
| **1** | L | -2.42 | 1 | 3 | 96 | dtp-bpy |
| | H-1 | -8.04 | 18 | 57 | 26 | Et-bc+ Pt+ dtp-bpy |
| | H-5 | -8.57 | 44 | 8 | 48 | Et-bc+ dtp-bpy |
| **1a** | H | -6.24 | 40 | 43 | 17 | Et-bc+ Pt+ dtp-bpy |
| | L | -1.39 | 10 | 10 | 80 | Et-bc+ Pt+ dtp-bpy |
| | L+3 | -0.3 | 16 | 14 | 71 | Et-bc+ Pt+ dtp-bpy |
| | L+4 | 0.12 | 15 | 34 | 51 | Et-bc+ Pt+ dtp-bpy |
| **1a-N** | L | -1.39 | 10 | 10 | 80 | Et-bc+ Pt+ dtp-bpy |
| | H | -6.24 | 40 | 43 | 17 | Et-bc+ Pt+ dtp-bpy |
| | H-1 | -7.98 | 21 | 74 | 5 | Et-bc+ Pt |
| **1a-O** | H | -6.49 | 26 | 50 | 25 | Et-bc+ Pt+ dtp-bpy |
| | L | -1.58 | 28 | 18 | 54 | Et-bc+ Pt+ dtp-bpy |
| | L+2 | -0.58 | 17 | 25 | 58 | Et-bc+ Pt+ dtp-bpy |
| **1a-PO** | H | -6.76 | 42 | 41 | 16 | Et-bc+ Pt+ dtp-bpy |
| | L | -1.8 | 6 | 6 | 88 | dtp-bpy |
| | L+4 | -0.1 | 22 | 55 | 23 | Et-bc+ Pt+ dtp-bpy |
| **1b** | L | -2.25 | 1 | 2 | 96 | dtp-bpy |
| | H-1 | -7.83 | 11 | 41 | 48 | Et-bc+ Pt+ dtp-bpy |
| **1b-N** | L | -2.12 | 1 | 3 | 96 | dtp-bpy |
| | H | -7.54 | 30 | 66 | 3 | Et-bc+ Pt |
| | H-1 | -7.81 | 17 | 54 | 29 | Et-bc+ Pt+ dtp-bpy |
| **1b-O** | L | -2.36 | 1 | 3 | 96 | dtp-bpy |
| | H | -7.66 | 32 | 65 | 3 | Et-bc+ Pt |
| | H-1 | -7.99 | 21 | 60 | 19 | Et-bc+ Pt+ dtp-bpy |

| | | | | | | |
|---|---|---|---|---|---|---|
| | H-5 | -8.75 | 20 | 7 | 73 | Et-bc+ dtp-bpy |
| | L | -2.79 | 1 | 2 | 97 | dtp-bpy |
| **1b-PO** | H-1 | -8.27 | 23 | 59 | 18 | Et-bc+ dtp-bpy |
| | H-5 | -8.86 | 27 | 11 | 62 | Et-bc+ dtp-bpy |
| | H-6 | -8.89 | 48 | 26 | 26 | Et-bc+ dtp-bpy |

Table S5. Transition dipole moments $\mu_j$ (Debye) for $S_0$–$S_n$ transitions, singlet–triplet splitting energies $\Delta E(S_n–T_1)$ (eV) and the SOC matrix elements $<T_1|H_{SOC}|S_n>$ ($cm^{-1}$) of complexes.

| | $S_n$ | $\mu_j$ | $\Delta E(S_n–T_1)$ | $<T_1\|H_{SOC}\|S_n>$ | | $S_n$ | $\mu_j$ | $\Delta E(S_n–T_1)$ | $<T_1\|H_{SOC}\|S_n>$ |
|---|---|---|---|---|---|---|---|---|---|
| **1** | $S_1$ | 0.11 | 0.064 | 29.918 | | | | | |
| | $S_2$ | 0.18 | 0.423 | 1628.919 | | | | | |
| | $S_3$ | 1.52 | 0.797 | 1443.740 | | | | | |
| | $S_4$ | 0.89 | 1.171 | 312.805 | | | | | |
| | $S_5$ | 0.55 | 1.207 | 146.871 | | | | | |
| | $S_6$ | 0.16 | 1.282 | 115.923 | | | | | |
| | $S_7$ | 0.07 | 1.298 | 144.080 | | | | | |
| | $S_8$ | 0.24 | 1.337 | 78.091 | | | | | |
| | $S_9$ | 0.11 | 1.419 | 50.353 | | | | | |
| | $S_{10}$ | 0.19 | 1.459 | 47.585 | | | | | |
| **1a** | $S_1$ | 0.73 | 0.214 | 47.074 | **1b** | $S_1$ | 0.09 | 0.053 | 7.645 |
| | $S_2$ | 0.27 | 0.548 | 79.900 | | $S_2$ | 0.12 | 0.343 | 70.858 |
| | $S_3$ | 0.49 | 0.887 | 91.130 | | $S_3$ | 0.38 | 0.444 | 1617.387 |
| | $S_4$ | 0.57 | 1.116 | 93.561 | | $S_4$ | 0.18 | 0.691 | 158.115 |
| | $S_5$ | 0.47 | 1.627 | 1392.679 | | $S_5$ | 1.42 | 0.753 | 1305.894 |
| | $_{S6}$ | 0.59 | 1.732 | 422.079 | | $S_6$ | 1.59 | 1.049 | 516.842 |
| | $S_7$ | 0.17 | 1.830 | 1139.549 | | $S_7$ | 1.74 | 1.130 | 454.413 |
| | $S_8$ | 0.80 | 2.021 | 252.019 | | $S_8$ | 0.15 | 1.265 | 55.623 |
| | $S_9$ | 0.37 | 2.216 | 200.323 | | $S_9$ | 0.40 | 1.281 | 273.223 |
| | $S_{10}$ | 0.61 | 2.309 | 222.704 | | $S_{10}$ | 0.15 | 1.322 | 40.896 |
| **1a-N** | $S_1$ | 0.21 | 0.073 | 183.615 | **1b-N** | $S_1$ | 0.24 | 0.083 | 216.247 |
| | $S_2$ | 0.29 | 0.345 | 1448.872 | | $S_2$ | 0.47 | 0.441 | 1621.410 |
| | $S_3$ | 0.35 | 0.610 | 1172.835 | | $S_3$ | 2.14 | 0.807 | 1417.158 |
| | $S_4$ | 0.78 | 0.670 | 746.907 | | $S_4$ | 0.37 | 1.067 | 111.384 |
| | $S_5$ | 0.24 | 0.911 | 500.061 | | $S_5$ | 0.29 | 1.138 | 168.396 |
| | $S_6$ | 0.80 | 0.937 | 384.013 | | $S_6$ | 0.07 | 1.330 | 161.727 |
| | $S_7$ | 0.64 | 1.130 | 50.199 | | $S_7$ | 0.07 | 1.403 | 101.442 |
| | $S_8$ | 0.82 | 1.179 | 148.284 | | $S_8$ | 0.18 | 1.469 | 28.322 |
| | $S_9$ | 0.86 | 1.374 | 41.059 | | $S_9$ | 1.79 | 1.537 | 377.533 |
| | $S_{10}$ | 0.15 | 1.396 | 84.860 | | $S_{10}$ | 0.76 | 1.600 | 140.305 |
| **1a-O** | $S_1$ | 0.61 | 0.169 | 31.127 | **1b-O** | $S_1$ | 0.29 | 0.082 | 252.036 |
| | $S_2$ | 0.76 | 0.900 | 179.100 | | $S_2$ | 0.49 | 0.437 | 1606.019 |
| | $S_3$ | 0.54 | 1.156 | 234.710 | | $S_3$ | 2.07 | 0.783 | 1416.350 |
| | $S_4$ | 0.32 | 1.397 | 1372.351 | | $S_4$ | 0.31 | 1.120 | 218.355 |
| | $S_5$ | 1.20 | 1.618 | 718.850 | | $S_5$ | 0.41 | 1.176 | 95.051 |
| | $S_6$ | 1.17 | 1.717 | 1136.311 | | $S_6$ | 0.16 | 1.290 | 206.929 |
| | $S_7$ | 0.68 | 2.058 | 217.452 | | $S_7$ | 0.24 | 1.368 | 171.842 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | $S_8$ | 1.05 | 2.098 | 165.283 | | $S_8$ | 0.08 | 1.429 | 48.091 |
| | $S_9$ | 0.46 | 2.120 | 171.222 | | $S_9$ | 1.59 | 1.583 | 51.860 |
| | $S_{10}$ | 0.45 | 2.219 | 241.21 | | $S_{10}$ | 0.14 | 1.623 | 264.417 |
| **1a-PO** | $S_1$ | 0.70 | 0.212 | 45.312 | **1b-PO** | $S_1$ | 0.12 | 0.042 | 61.303 |
| | $S_2$ | 0.58 | 0.571 | 61.447 | | $S_2$ | 0.11 | 0.397 | 1632.214 |
| | $S_3$ | 0.47 | 0.889 | 88.369 | | $S_3$ | 1.23 | 0.726 | 1399.484 |
| | $S_4$ | 0.35 | 1.035 | 110.091 | | $S_4$ | 0.57 | 0.768 | 429.292 |
| | $S_5$ | 0.50 | 1.367 | 1360.640 | | $S_5$ | 0.30 | 1.111 | 145.111 |
| | $S_6$ | 0.25 | 1.612 | 1088.240 | | $S_6$ | 0.56 | 1.120 | 82.949 |
| | $S_7$ | 0.48 | 1.769 | 127.664 | | $S_7$ | 0.03 | 1.232 | 154.310 |
| | $S_8$ | 0.47 | 1.959 | 204.027 | | $S_8$ | 0.04 | 1.306 | 92.081 |
| | $S_9$ | 0.48 | 2.018 | 365.148 | | $S_9$ | 0.06 | 1.328 | 124.059 |
| | $S_{10}$ | 0.58 | 2.071 | 298.735 | | $S_{10}$ | 0.21 | 1.406 | 52.755 |

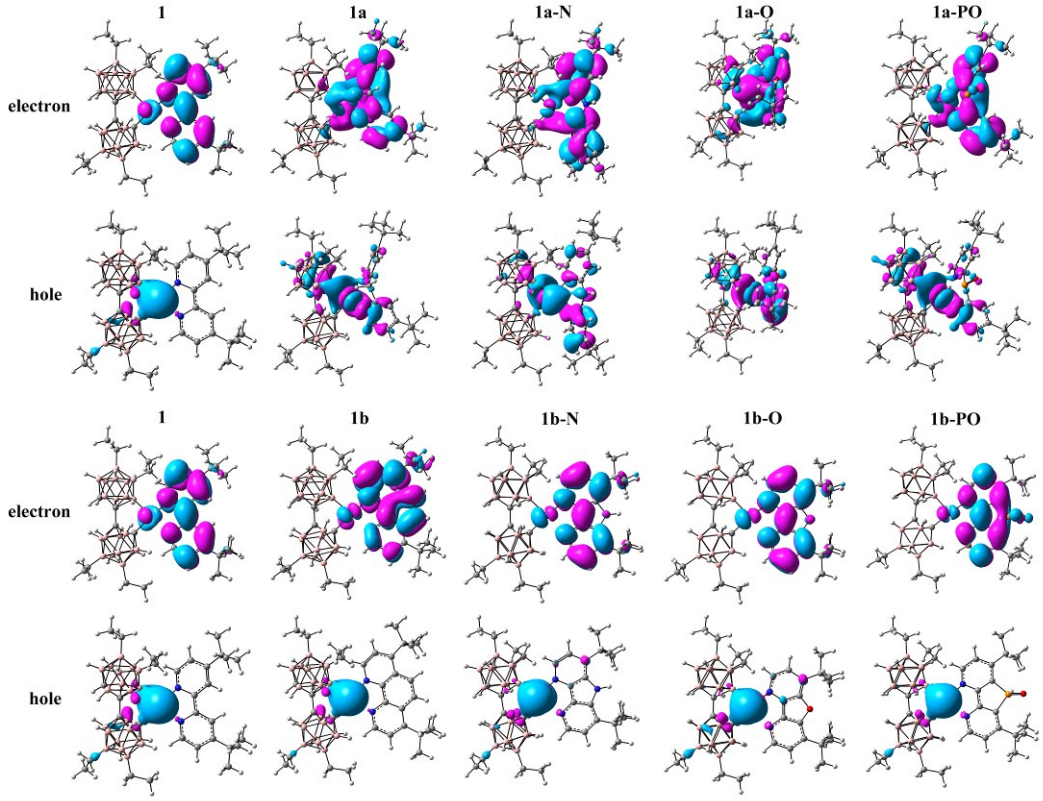
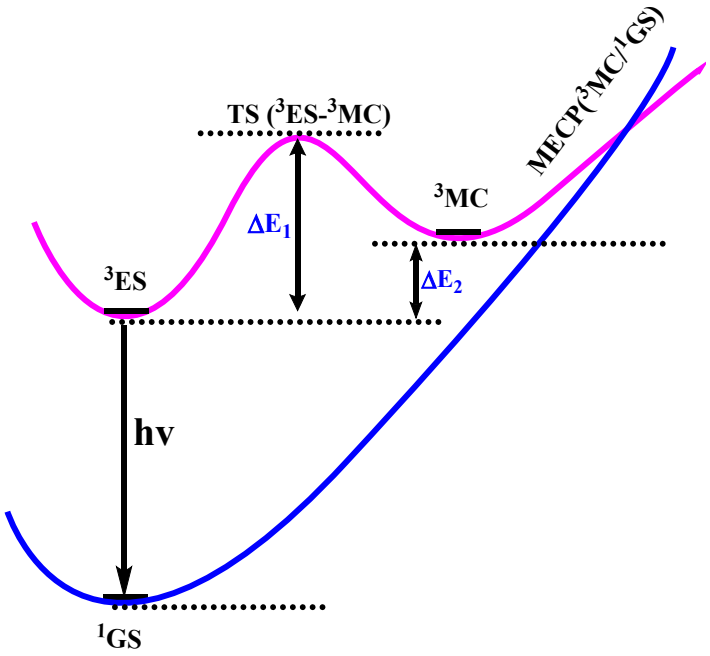



Figure 2 NTO pairs calculated at the excited $T_1$ state for the two class complexes




Scheme 2 The potential energy curves of thermal decay channels