# General Design Rules for Bimetallic Platinum(II) Complexes

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#### Abstract

A series of platinum(II) bimetallic complexes were studied to investigate the effects of ligands on both the geometric and electronic structure. Modulating the Pt-Pt distance through the bridging ligand architecture was found to dictate the nature of the lowest energy electronic transitions, localized in one half of the molecule, or delocalized across the entire molecule. By reducing the separation between the platinum atoms, the lowest energy electronic transitions will be dominated by the metal-metalto-ligand charge transfer transition. Conversely, by increasing the distance between the platinum atoms, the lowest electronic transition will be largely localized metal-toligand charge transfer or ligand centered in nature. Additionally, the cyclometalating ligands were observed to have a noticeable stabilizing effect on the triplet excited states as the conjugation increased, arising from geometric reorientation and increased electron delocalization of the ligands. Such stabilization of the triplet state energy has been shown to alter the excited state potential energy landscape as well as the excited state trajectory.

### 1 Introduction

Square-planar transition metal complexes are often studied because of their attractive photophysical and photochemical properties making them excellent candidates for advancing molecular materials.<sup>1–3</sup> Platinum(II) complexes of this design are of particular interest because of their rich excited-state properties extending from long lifetimes and versatile photoluminescence to easily accessible redox profiles.<sup>4–8</sup> Notable applications capitalizing on these properties include organic light emitting diodes,<sup>9–13</sup> bio-sensors,<sup>14</sup> and catalysis.<sup>15</sup>

Binuclear platinum(II) complexes, in particular, have gained traction because of their increased tunability accessed through modifying both the conjugation and bulkiness of the attached ligands. The choice of ligand strongly influences whether the complex behaves as a mononuclear system or takes advantage of the binuclear nature of the complex. A large array of platinum(II) complexes have been synthesized with attachments ranging from simple monodentate ligands<sup>1</sup> to large chelating cyclometalating ligands<sup>2,6,11,16</sup> to fine-tune and manipulate the electronic structure and geometric configuration for the aforementioned applications.<sup>17–19</sup>

The primary use of these platinum dimer complexes has been to induce charge transfer from the metal centers to adjacent electron-accepting ligands. Experimentally, transient absorption spectroscopy is used to observe large structural rearrangements<sup>2</sup> and intersystem crossing (ISC) to long-lived triplet states;<sup>20–22</sup> future studies will explore the possibility of further transferring the charge-separated electron coherently to additional ligands to drive additional chemical processes. To that end, a series of platinum dimers were synthesized according to a butterfly motif.<sup>9,23</sup> Bridging ligands connecting the platinum atoms rigidly enforce a given metal-metal separation in both the ground and excited states, with direct implications for the nature and ordering of the electronic states. Shorter Pt-Pt separations destabilize the occupied  $5d_{z^2}$ - $5d_{z^2} \sigma^*$  orbital, lowering the energy of metal-metal-to-ligand charge-transfer (MMLCT) states relative to more local ligand-centered (LC) or monometallic metal-to-ligand-charge-transfer (MLCT) states. The former deplete an antibonding orbital between the metal centers, increasing the bond order and inducing large structural changes.<sup>2,6,11,13,24–26</sup> Cyclometalating ligands then function either as the location of local  $\pi$ - $\pi^*$  excitations or as electron-accepting ligands in the case of (M)MLCT, with  $\pi$ -stacking interactions further influencing the shape of the complex. The butterfly design allows for both a fixed metal-metal separation and flexible motion as the complex relaxes in the excited state.

To gauge the effects of various input factors, the suite of molecules studied in this paper systematically varies the constituent ligands. Smaller, pyridyl derivative, bridging ligands enforce a narrower Pt-Pt separation and architecturally encourage MMLCT transitions, while bulkier fused rings hold the Pt atoms farther apart and lead to more low-lying local LC and MLCT states. Cyclometalating ligands considered in this study are planar aromatic hydrocarbons that form suitable electron acceptors. Compared to the 2-phenylpyridine cyclometalting ligand, 7,8-benzoquinoline ligands have a smaller  $\pi$ - $\pi$ \* splitting and therefore lower the energy of the lowest-unoccupied molecular orbital. These tunable elements vary the HOMO-LUMO energy gap, the degree of flexibility in the molecule, and perhaps most importantly the relative energetic ordering of the low-lying excited states. As fast ISC is desired, it is important to have triplet states with local (LC) character<sup>27</sup> of lower energy than the bright <sup>1</sup>MMLCT state, as ISC is fastest between states of different orbital character.<sup>28</sup>

Recent theoretical work by the authors have shown that square planar bimetallic platinum(II) complexes are capable of supporting long-lived electronic coherence if the interplatinum distance is reasonably small.<sup>7</sup> Coherent electronic behavior is of great fundamental interest because of its influence over excited-state processes prevalent in nature such as efficient light harvesting.<sup>29</sup> It is, however, recognized that the anticipated coherence in molecules of this design quickly dissipates once molecular vibrational motions are considered as coupling to these modes begins to dominate and encourage decoherence.<sup>30</sup> To compliment experimental results suggesting ultrafast photochemical processes, a theoretical study was conducted to support rapid intersystem crossing, which is expected to take place within tens of femtoseconds.<sup>8</sup> Those results demonstrated that in the presence of strong spin-orbit coupling, ultrafast intersystem crossing can be anticipated.<sup>27</sup> These findings prompted further investigation on the complex's architectural influence over the electronic structure and excited-state behavior.

Herein, we investigate a collection of platinum dimers to devise a set of molecular design guidelines to fine-tune the electronic structure and charge transfer character of binuclear platinum(II) complexes. This study focuses on the effects of the steric bulkiness and conjugation of the bridging and cyclometalating ligands, respectively. Through these modifications greater control over the excited-states can be realized and the long-lived electronic or vibrational coherences can be exploited to drive valuable excited-state processes.

### 2 Methods

To study the geometric features of these platinum dimers, optimized geometries are calculated in GAUSSIAN16 using spin-restricted density functional theory (DFT).<sup>31</sup> Linear response time-dependent (TD) DFT is utilized for all excited-state calculations. The charge transfer (CT) character for each complex is determined quantitatively via linear-response TDDFT in order to assign CT character to select excited states that have the potential to participate in the relaxation process. Charge transfer numbers are calculated using a locally modified developmental version of GAUSSIAN16 following the methods outlined in previous work.<sup>32–34</sup> Unless otherwise stated, all calculations are completed using the  $\omega$ B97X-D<sup>35</sup> functional with the LanL2DZ effective core potential<sup>36</sup> and associated double- $\zeta$  basis set on the platinum atoms and the 6-31g(d) basis set on all other atoms. Finally, all calculations are completed in the gas phase as environmental effects (e.g. solvent) are expected to have a uniform effect on the systems studied given their structural similarities.



### 3 Results & Discussion

Figure 1. Structures of bimetallic platinum(II) dimers

A series of bimetallic platinum(II) complexes were synthesized by Castellano and coworkers with varying cyclometalating (CML) and bridging ligands (BL) to modulate the geometric and excited-state properties.<sup>2</sup> In this report, we discuss the effects of varying ligand compositions and devise design rules that can be derived from these observations. The CMLs for all dimers in this study are either 2-phenylpyridine (ppy) or 7,8-benzoquinoline (bpy). The bridging ligands, on the other hand, vary by both core architecture and substituent composition. Structures **1-9** feature a pyridine derivative as the bridging ligand with either an oxygen or sulfur heteroatom atom attached alpha to the nitrogen (see **Fig. 1**). Additionally, dimers **3** and **6-9** have either a methyl or phenyl substituent in the other alpha position (6-substitution) to increase the bulkiness of the ligand and ideally to modulate the platinum-platinum distance. The influence of this coordinate is further explored in structures **4-5** and **10-11** by exchanging the pyridine group for a quinoline ligand that has a sulfur attached in the second position or an oxygen attached in the eighth position. It should be noted that the nitrogens of the CMLs in the sulfur series (**1-5**) have a *cis* configuration while the nitrogens of the oxygen series (**6-11**) have been arranged in a *trans* orientation; this is likely a consequence of "trans effects" often observed in square-planar complexes.<sup>37,38</sup>



Figure 2. General numbering scheme for all dimers in this study. Note that N1 of the sulfur series will be on the opposite ring of the corresponding CML.

To identify the optimum basis set/functional combination, benchmarking is completed on complexes 6-9. Pairings include B3LYP with 6-31g(d)/LanL2DZ, CAM-B3LYP with 6-31g(d)/LanL2DZ,  $\omega$ B97X-D with 6-31g(d)/LanL2DZ, and  $\omega$ B97X-D with def2-TZVP/SDD. Qualitatively, a substantial difference is observed in the orientation of the CM ligands when



Figure 3. Optimized geometries of complex 7 using a.) B3LYP and 6-31g(d)/LanL2DZ, b.) CAM-B3LYP and 6-31g(d)/LanL2DZ, c.)  $\omega$ B97X-D and 6-31g(d)/LanL2DZ, and d.)  $\omega$ B97X-D and def2-TZVP/SDD, where the first basis set listed is applied to all light atoms and the second basis set is used exclusively on the Pt atoms.

moving from B3LYP and CAM-B3LYP to  $\omega$ B97X-D, as seen in **Figure 3**. While B3LYP and CAM-B3LYP find an A-frame orientation of the molecule, the dispersion corrections in  $\omega$ B97X-D induce an increased  $\pi$ - $\pi$  interaction between the CML ligands, leading a more Hframe configuration that closely matches the experimental crystal structure.<sup>2</sup> Complex **7** is further analyzed in **Table 1** to quantitatively demonstrate the increased agreement between the calculated structure and the experimentally reported geometry. In addition to using long-range and dispersion correction, the data presented support the use of a smaller basis set as the larger basis set shows minute improvement, if any, when comparing the equilibrium geometries calculated at the same level of theory.

Additionally, the static electronic spectra are calculated at the same level of theory used to find the corresponding equilibrium geometries. The resulting spectra show the line

shape remains relatively consistent across all basis sets and functionals for the lowest energy transition. Large differences begin to show up in the local character of the second, higher energy peak of the spectra simulated via CAM-B3LYP. Notable differences between these simulated spectra and the experimentally observed spectra are found, specifically, in the line shapes of complexes 7 and 9, which display multiple peaks in the region just under 350 nm. Interestingly, better agreement between simulated and experimental spectra is seen when using B3LYP, which finds the correct lower energy peak ordering across the complexes considered. The relative ordering between 7 and 8 appears to have changed once long-range correction is included, which is demonstrated by both CAM-B3LYP and  $\omega$ B97X-D. However, given the increased agreement between the calculated ground state geometry using the latter functional and the experimentally observed crystal structure, this study employs  $\omega B97X$ -D for the remaining calculations. Although not demonstrated here, the authors found, in a previous study, that including range correction is significant as it finds the correct ordering of the triplet states, further supporting the use of  $\omega$ B97X-D.<sup>27</sup> Finally, a larger basis set is used with  $\omega B97X$ -D to simulate the static electronic spectra (see Figure S1). The only notable difference seen when increasing the basis set is a slight red-shift in the transition energies, justifying the use of a smaller basis.

#### Ground State Structural Characterization

The effects of the various ligands on the geometric characteristics at the ground-state equilibrium geometry are presented in **Tab. 2**. At the ground-state geometry, complexes **1-9** appear to have very similar Pt-Pt distances at around  $\sim 2.9$  Å. Unsurprisingly, moving the

Table 1. Selected bond lengths, angles, and dihedrals of 7 at the ground-state geometry in units of angstroms and degrees (see Figure 2 for atom reference).

Basis set	6-31g(d)/LanL2DZ	6-31g(d)/LanL2DZ	6-31g(d)/LanL2DZ	def2-TZVP/SDD	-
Functional	B3LYP	CAM-B3LYP	$\omega$ B97X-D	$\omega$ B97X-D	$Exp.^2$
Pt1-Pt2	3.071	3.023	2.911	2.913	2.816
Pt1-N1	2.057	2.045	2.048	2.042	2.017
Pt1-N3	2.081	2.066	2.068	2.065	2.041
Pt1-Pt2-N2	98.69	97.57	90.49	90.81	91.25
N1-Pt1-Pt2-N2	63.13	62.32	64.21	64.69	61.37

interacting atoms of the BL from the second to the eighth position substantially increases the distance between the platinum atoms. This is demonstrated in complexes 10 and 11 where the distance between the two transition metals was calculated to be roughly 0.3 Å greater than the previous nine complexes. This is an immediate reflection of the increased role played by the BL in mediating the position of the transition metals.

As expected, the choice of chalcogen greatly influences the distance between the Pt atom and the BL. By simply increasing the atomic size, the bridging ligand is forced further away from the heart of the structure. The distance between these two BLs, calculated via the center of mass point of pyridyl ring, seems to be unaffected by the chalcogen and instead appears to be largely dependent on the CML architecture. Generally speaking, as the CML becomes more rigid, and the flexibility of the molecule becomes hindered, the BLs are forced further from one another. This effect can be countered by incorporating a bulky, free-rotating, substituent on the BL. As demonstrated by the sulfur series through the BL-Pt1-BL coordinate, the methyl group introduced in **3** shows some influence over the BL-BL positions by slightly decreasing the angle, compared to **2**, and forcing the BLs closer than they would be otherwise.

The impact of the free-rotating substituent becomes more pronounced in the oxygen series when comparing 7 to 9. The bulkiness of the phenyl group has a much greater influence over the BL-BL distance than the comparatively smaller methyl group. The effects of the

Table 2. Selected bond lengths, angles, and dihedrals of 1-11 at the ground-state geometry in units of angstroms and degrees (see Figure 2 for atom reference). Calculations including BLs and CMLs were completed by identifying the center of mass points on the respective ligands. For uniformity purposes, only the pyridyl ring of the BL was considered when finding the center of mass point.

	1	2	3	4	5	6	7	8	9	10	11
Pt1-Pt2	2.945	2.946	2.950	2.938	2.934	2.911	2.911	2.940	2.912	3.257	3.258
Pt2-N4	2.222	2.217	2.237	2.239	2.231	2.073	2.064	2.071	2.075	2.091	2.087
Pt1-O1/S1	2.345	2.339	2.371	2.343	2.336	2.185	2.177	2.203	2.183	2.175	2.165
BL-BL	4.379	4.494	4.504	4.615	4.840	4.668	4.845	5.147	4.342	3.641	3.624
CML-CML	3.582	3.579	3.646	3.641	3.609	3.751	3.723	3.717	3.748	4.416	4.425
BL-Pt1-BL	64.632	66.668	65.861	67.354	71.168	72.253	75.391	79.973	67.161	66.374	67.362
Pt-Pt-C1	89.180	88.182	91.543	93.582	92.220	103.932	103.245	105.799	101.035	115.660	114.951

larger hanging substituent are further explored by comparing 8 to 9 where the CML is the only differing feature between the complexes. Based on the previous observations, one might expect 8 to have slightly closer BLs since the complex has not assumed a locked configuration induced by the rigid CML; this is, however, not the case. In fact, the BL-Pt1-BL angle and the distance between the BLs is substantially greater in 8 than 9. This is a consequence of the phenyl group substituents of the BL, which have the freedom to orient in space in various ways and subsequently influence the overall geometry. The influence of the CML can, however, be preserved as the BL increases in size if the BL maintains reduced mobility. This is supported by comparing 4 with 5 and 10 with 11, which both have BLs composed of fused rings.

#### Static Electronic Spectra

The calculated absorption spectra for all complexes in this study are presented in **Figure 4** and **Figure 5**. The lower energy peaks of the absorption spectra, for complexes 1-9, are assigned as having metal-metal-to-ligand charge-transfer (MMLCT) character, which is consistent with findings reported in the literature.<sup>2,39,40</sup>

This MMLCT character is not observed in structures 10-11 of the oxygen series. Instead 10-11 yield lowest excited states that are generally centered on the bridging ligand. The absence of MMLCT character in these structures is anticipated considering the MMLCT state arises when the  $d_{z^2}$  orbitals of the two Pt atoms are sufficiently close; thus forming a noticeable gap between both the  $d\sigma$  and  $d\sigma^*$  orbitals and promoting the latter to the HOMO. The excitation out of the  $d\sigma^*$  orbital into the  $\pi^*$  orbital is what characterizes the MMLCT transition and in turn increases the bond order between the Pt atoms upon excitation. Recalling the Pt-Pt distance in complexes 10 and 11, it is recognized that their natural positioning prevents them from interacting.

#### Stabilization of the MMLCT State

The internal heavy metal effect can be considered for these complexes as they hold two platinum atoms at the heart of their structure. The heavy metal effect is simply the increase in spin-orbit coupling between the singlets and triplets thus increasing the probability of intersystem crossing (ISC).<sup>41,42</sup> Considering this and experimental evidence of ISC, additional electronic transitions to the triplet excited states, at the ground-state equilibrium geometry, are analyzed via charge transfer numbers and natural transition orbitals (NTOs).<sup>2</sup>

To emphasize the influence of the functional on the characterization of the electronic structure and the energetic landscape, the charge transfer (CT) numbers were calculated using different functionals. Figure 6 demonstrates the change in the energetic landscape as the functional, and subsequently the geometry, changes for 6; the chosen representative complex for this analysis. Although the electronic character of the first singlet excited state of complex 6 is consistently assigned to  ${}^{1}MM(CM)LCT$  character, with an average charge-transfer ratio of 0.849, the energy of this state is observed to be quite sensitive to the functional. This CT state undergoes considerable destabilization ( $\sim 1 \text{ eV}$ ) when moving from B3LYP to CAM-B3LYP. This energy sensitivity carries over to the triplets as well and is most notable in states exhibiting strong charge transfer character. The change in CT state ordering can be attributed to the inclusion of range-correction, which has been shown to better predict charge-transfer excitation energies.<sup>43</sup> This correction has a greater impact on CT states as contributions from both the exchange functional and Hartree-Fock exchange integral are modified as a function of distance, thus giving rise to a better description of the long-range orbital-orbital interactions.<sup>44</sup> Provided this, states with local transitions are expected to be less affected by this correction, which is generally what is observed in **Figure** 6 considering the yellow states vary by only about 0.2 eV. The CT numbers were also calculated for complexes 7-9 and can be found in the SI showing similar trends to those observed here.

The effects of both the geometry and functional can be observed by comparing panels **II-IV** of **Figure 6**. Like CAM-B3LYP,  $\omega$ B97X-D is a range-corrected functional, but it also directly includes dispersion corrections. To tease apart the two effects, **III** gives the excited-state spectrum calculated using  $\omega$ B97X-D at the same molecular geometry as in **II**:

the state orderings and characters are nearly identical between the two functionals, with a slight energetic shift. However, in allowing the molecule to relax to the  $\omega$ B97X-D optimized geometry in **IV**, additional changes are observed. The CT states are observed to stabilize once the CM ligands are brought in close proximity via dispersion-corrections. Additionally, this change in geometry allows states that were previously strongly CT in character to mix with states that had predominately local character; giving rise to "mixed" states that have large contributions from both (CM)LC and MM(CM)LCT electronic character. This is more quantitatively represented in **Table 3** where the elements of  $\Omega$  are as follows:

$$\Omega = \begin{pmatrix} MC & MM(CM)LCT\\ (CM)MCT & (CM)LC \end{pmatrix}$$
(1)

the MC notation indicates metal-centered, MM(CM)LCT is metal-metal-to-ligand CT, (CM)MCT is ligand-to-metal CT, and (CM)LC is ligand centered. All of the elements within this matrix correspond to either the platinum atoms, the CM ligand, or both.

The energetic landscape strongly impacts the dynamic processes that can be observed theoretically, which makes selecting the appropriate functional of utmost importance. Given prior studies have demonstrated that these systems undergo fast ISC, there should be low-lying triplet states with different character from the first singlet state; per El-Sayed's rules.<sup>2,21,27,28</sup> This leaves CAM-B3LYP and  $\omega$ B97X-D as the remaining viable options, from this analysis, for properly predicting the electronic structure. Recalling the increased agreement between the equilibrium geometry found via  $\omega$ B97X-D, calculations going forward will utilize this functional.

Table 4 outlines the charge transfer numbers for the first singlet excited state of select complexes extending from sulfur derivatives to the larger oxygen derivatives. These calculations show the  $S_1$  state having <sup>1</sup>MMLCT character for complexes with a Pt-Pt distance < 3 Å and <sup>1</sup>BLC character for systems with a Pt-Pt distance > 3 Å. This assignment is determined considering the contribution of charge transfer from the metal to the *cis*-CML

and the metal to the *trans*-CML. If a noticeable contribution is observed to come from the M(trans-CM)LCT, in addition to the M(cis-CM)LCT, then the metal atoms are considered close enough to facilitate MMLCT. This assumption implies the leaving orbital,  $d\sigma$ \*, is shared among the platinum atoms, which is visualized in **Figure 7** 

The dramatic difference in CT character of both **10** and **11** compared to all other complexes in this study has largely to do with the bridging ligand composition, which inhibits many of the sought-after features in binuclear transition metal systems. This ligand not only forces the platinum atoms to maintain a great distance from one another, it increases the conjugation of the overall complex allowing greater dispersion of electron density about the BL. The increased delocalization in turn lowers the energy of the accepting orbitals making transitions more energetically competitive.

Selected NTOs are displayed in **Figure 7** to both support the CT assignment and visually demonstrate the electronic character of various excited states. As mentioned previously, complexes **1-9** support <sup>1</sup>MMLCT where electrons are promoted out of the  $d\sigma^*$  orbital onto the ligand  $\pi^*$  orbital (**Figure 7a**). Conversely, **10-11** experience bridging-ligand-centered (BLC) electronic character as a consequence of their inherent architecture. Similar character is seen in the low-lying triplet of **4**, which is shown in **Figure 7b**. Surprisingly, the <sup>3</sup>BLC appears in **5** at higher energy triplets as opposed to the low-lying triplet. The low-lying triplet of this complex is consistent with complexes **1-9**, which all have cyclometalating ligand centered (CMLC) character. Perhaps this is a result of the differing conjugation between the BL and CMLs.

Bringing attention to **Figure 8**, it seems the increased conjugation of the CML plays a significant role in stabilizing the triplet states while increasing the bulkiness of the BL has a minor stabilizing effect on the singlet state, in most cases. This can be qualitatively analyzed by considering the differences between the singlet and triplet states in the Jablonski diagram.

The most direct comparison of complexes across the oxygen and sulfur series is between

**3** and **7**, which differ only by the choice of chalcogen. When comparing these two complexes it becomes obvious that introducing a larger atom in the second position of the BL causes increased electronic destabilization, which is reflected in the higher energy of the <sup>1</sup>MMLCT state of **3**. This destabilization is further emphasized in both **4-5** and **10-11** by incorporating sizable fused rings in close proximity. Though the BL composition clearly plays a role in the <sup>1</sup>MMLCT state, the positioning of the CMLs does show some influence over the <sup>1</sup>MMLCT energy. Considering only complexes with a Pt-Pt bond length < 3.0 Å, there appears to be a linear relationship between the <sup>1</sup>MMLCT energy and the distance between the center of mass point of the CMLs. An increase in distance of ~0.025 Å can stabilize the <sup>1</sup>MMLCT state by nearly 0.1 eV. The Pearson correlation coefficient was found to be -0.92 indicating a strong negative correlation between this particular geometric feature and energy (**Figure S16**). This suggests that through controlling the position of the CML the energy of the <sup>1</sup>MMLCT can be fine-tuned to create a more accessible state. Other explored geometric features do not show a significant correlation with the energy. Complexes **10-11** are neglected in this calculation because of the significant architectural difference in the BL.

Additionally, it is recognized that the energy of the <sup>3</sup>CMLC state is minimally changed when comparing **3** and **7**, indicating the BL has little to no influence over the triplet states. Similarly, looking explicitly at the oxygen series, the relative positioning of the <sup>3</sup>CMLC state for **6** and **8** are reasonably consistent with one another while **7** shows noticeably different behavior. Complex **7** shows decent stabilization of the <sup>3</sup>CMLC states compared to **6** as a result of well separated conjugated CMLs. As noted, the triplet states of **8** show no such stabilization with the addition of the phenyl group on the bridging ligand compared to **6**. Complex **8** does, however, show a slight stabilization of the <sup>1</sup>MMLCT state as a result of the modified bridging ligand. Considering these observations, it comes as no surprise that both <sup>1</sup>MMLCT and <sup>3</sup>CMLC states are stabilized by the bulkier BL and conjugated CMLs of **9** (see **Figure S18**). The stabilization of the triplet states, as the CML increases in conjugation, is observed for all complex pairs in this study as a consequence of increased electron delocalization.<sup>45</sup>

#### **Charge Transfer Modulation**

The extent to which the Pt-Pt distance influences the charge transfer character is investigated by manually modulating the positions of the transition metals in complexes 10 and 11. A series of geometries are interpolated between the ground-state equilibrium and an optimized geometry that has a fixed Pt-Pt distance of ~2.6 Å. Single-point energy calculations are then completed to evaluate the energy of the first singlet excited state at each geometry to build potential energy surfaces (PESs) for further analysis (**Figure 9**).

In decreasing the distance between the platinum atoms, there is a noticeable rise and subsequent fall in  $S_1$  energy as the complex proceeds toward a shorter bond length. This rise in the energy can be attributed to the geometric rearrangement forcing the complex into a less than optimal configuration. In directing the complex toward a geometry with a decreased distance between the Pt atoms, metal-metal interactions can be accessed allowing the system to experience <sup>1</sup>MMLCT, which is expected considering the results presented earlier. Through this experiment, the exact distance required to facilitate <sup>1</sup>MMLCT can be identified via NTO analysis.

To determine the minimum distance needed to encourage a shift in electronic character, geometries about the maximum point of the  $S_1$  surface are sampled and their NTOs are collected. A noticeable change in the CT character is observed in increments of just 0.008 Å, as seen in **Figure 10**. The LC character about the bridging ligand is maintained until the Pt-Pt distance reached 2.996 Å, at which point the CT transitions to mixed character. Among the mixed character observed at this geometry, some contribution is found to come from <sup>1</sup>MMLCT; though this does not become the dominate contributing character until a further 0.008 Å decrease is experienced. This same trend is seen in complex **10**, however, the mixed character is observed at a slightly longer Pt-Pt distance (3.102 Å). Similarly, by decreasing the distance only 0.008 Å, the dominating charge transfer character is observed to be <sup>1</sup>MMLCT for the first singlet excited state. Alternatively, the Pt-Pt bond length of complex 7 is increased to study the necessary bond length required to stabilize the <sup>1</sup>MMLCT state and destabilize the LC state in systems with a significantly smaller bridging ligand. Comparing the relevant surfaces, there is a substantially steeper increase in energy as the system is forced out of the equilibrium geometry and finds a metal separation of > 3 Å (see **Figure S19**). Though this increase is expected, it is noticeably more dramatic than the change in energy observed for complexes **10** and **11**. This is likely due to the increased strain forced on the smaller bridging ligand in order to obtain such separation. As before, NTOs for geometries about the "hill-like" region are sampled to identify the transition between <sup>1</sup>MMLCT and the new electronic character. Complex **7** is observed to host <sup>1</sup>LC character about the CML, which is unsurprising given the CML architecture is well suited for greater electronic delocalization compared to the smaller BL.

#### **Excited State Geometries**

The first singlet excited-state equilibrium geometries are calculated to build a better understanding of the structural characteristics post-photoexcitation and beyond the Franck-Condon point. The most notable and consistent geometric changes, across all isomers in this study, are those seen in both the distance between the Pt atoms and the shifting of the CMLs relative to one another. **Figure 11** compares the geometries of both **3** and **7** to analyze the impact of modifying the chalcogen of the BL. Interestingly, this did not appear to have a substantial influence over the Pt-Pt contraction from the  $S_0$  to the  $S_1$  geometry. In fact, complexes **1-9** all experience a Pt-Pt contraction of just over 0.2 Å. Systems **10** and **11**, on the other hand, undergo a slight increase in distance; though this is perhaps unsurprising considering the bridging ligand composition.

The change in bridging ligand position between the  $S_0$  and  $S_1$  geometries is, however, inconsistent across the complexes. As before, the position of the BLs were evaluated by determining the center of mass of the pydridyl rings then calculating the distance between the two points. It is observed that the BLs in the complexes belonging to the sulfur series undergo a noticeable shift towards one another from  $S_0$  to  $S_1$ . Complexes **10-11**, of the oxygen series, also experience a shift in BLs toward one another with a comparable magnitude of  $\sim 0.4$ -0.5 Å as seen in **4-5**. This rearrangement is allowed as a result of the CMLs distancing themselves from each other through a twisting, divergent-type motion. Conversely, complexes **6-9** generally see a slight repulsion between the bridging ligands when going from the ground-state geometry to the first singlet excited-state geometry. As a consequence, systems **6-9** experience the opposite distortion in their CMLs and instead see them shifting toward one another.

Perhaps the most interesting geometric change seen in these structures is that of the angle formed by atoms Pt1-Pt2-C1. The difference in this angle for the sulfur series was far more dramatic than that observed for the oxygen series. All sulfur complexes undergo a change of  $\sim 10$  degrees while the oxygen complexes have a modest change of  $\sim 4.5$  degrees. This large difference may be attributed to the difference in size between the oxygen and sulfur atoms forcing a greater shift in the CMLs of the sulfur complexes to accommodate the structural limitations.

### 4 Conclusions

Although DFT does an exceptional job at simulating experimental results, it should be emphasized that (TD)DFT is a non-relativistic, single reference method. Although relativistic effects, namely spin-orbit coupling, are expected to be strong in these bimetallic systems, they are largely neglected in this study. Instead, scalar relativistic effects are indirectly considered via effective core potentials. Remaining within the non-relativistic scheme allows a more direct analysis of the electronic structure by representing states as spin-pure; thus excluding state splitting and additional state mixing. A more rigorous treatment of relativistic effects is not expected to have a significant impact on the calculated equilibrium geometry or simulated spectra presented in this study. Though the density of states will increase, given additional transitions would become allowed under the relativistic regime, explicit inclusion

of relativistic effects is not expected to substantially improve the intense spectral signals.<sup>46</sup> Additionally, since exchange-correlation kernels are fundamentally frequency-independent, the calculations presented in this study are confined to the adiabatic approximation. Finally, some evidence of double excitations, in the form of satellite peaks, can be seen in the experimental spectra, the agreement between the observed and simulated spectra suggests single excitations are dominant in these systems. Despite the limitations noted, DFT is able to adequately describe these systems and provide results with excellent agreement to experimental findings.

In conclusion, quantum mechanical calculations on the ground and excited-state structures have been carried out for a series of square-planar platinum(II) dimers with a diverse selection of bridging and cyclometalating ligands. These calculations aim at giving insight to the effects of bridging ligand bulkiness and cyclometalating ligand conjugation. Through this study, it was further confirmed the bridging ligand architecture and composition is largely responsible for modulating the platinum-platinum distance. Additionally, it was observed that the position of the bridging ligands relative to one an other were somewhat influenced by the rigidity of the CML.

As anticipated, the geometric changes were accompanied by electronic structure differences. The  $\pi$ -conjugation within the CML was found to have a noticeable stabilizing effect on the triplet states of the bimetallic complexes while the bridging ligand composition appeared to have a greater, albeit less dramatic, influence over the energy of the singlet state. Though the composition of the CMLs also seemed to slightly stabilize the singlet states, the lowering of energy in the singlet states became more pronounced when the CML positions changed. This stabilization can be attributed to both the increase of delocalization, as a result of increased conjugated structures, and the system reorienting in space to accommodate structural features. These results reveal individual effects of ligand replacements as well as their mutual influence in both electronic and nuclear structures in both the ground and excited states, which serves as guidance in future molecular design and chemical tuning of transition metal complexes for various applications.

### Supporting Information

Additional simulated spectra, natural transition orbitals, charge transfer numbers, geometries, and plots can be found in the supporting information.

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## Graphical TOC Entry





Figure 4. Collected absorption spectra for complexes 6 (black), 7 (red), 8 (blue), and 9 (green). The spectra presented were found experimentally<sup>2</sup> (top left) and computationally using the following functional and light/heavy atom basis sets: CAM-B3LYP with 6-31g(d)/LanL2DZ (top right), B3LYP with 6-31g(d)/LanL2DZ (lower left), and  $\omega$ B97X-D with 6-31g(d)/LanL2DZ (lower right).



Figure 5. Calculated absorption spectra for complexes 1-5 and 10-11. The far left panel holds 1 (black), 2 (red), and 3 (blue). The center panel shows both 4 (magenta) and 5 (orange) and the far right panel displays both 10 (gold) and 11 (grey).



Figure 6. Jablonski diagram of complex 6 using I) B3LYP with 6-31g(d)/LanL2DZ, II) CAM-B3LYP with 6-31g(d)/LanL2DZ, III)  $\omega$ 97X-D with 6-31g(d)/LanL2DZ at the CAM-B3LYP optimized geometry, and IV.) $\omega$ 97X-D with 6-31g(d)/LanL2DZ at the  $\omega$ 97X-D optimized geometry. The states considered in this analysis are: <sup>1</sup>MM(CM)LCT (blue), <sup>3</sup>MM(CM)LCT (red), <sup>3</sup>(CM)LC (yellow), <sup>3</sup>Mixed (orange), and <sup>3</sup>(BD)LC (green).

Table 3. CT numbers of 6 corresponding to Figure 6 where group I) uses B3LYP with 6-31g(d)/LanL2DZ, II) uses CAM-B3LYP with 6-31g(d)/LanL2DZ, III) uses  $\omega$ 97X-D with 6-31g(d)/LanL2DZ at the CAM-B3LYP optimized geometry, and IV.) uses  $\omega$ 97X-D with 6-31g(d)/LanL2DZ at the  $\omega$ 97X-D optimized geometry. \* Mixed state with <sup>3</sup>MC and <sup>3</sup>MM(CM)LCT contributions

	State	Energy $(eV)$	Ω	Charge-Transfer Ratio	Designation
	1	2.402	$\left(\begin{array}{cc} 0.05 & 0.68 \\ 0.01 & 0.14 \end{array}\right)$	0.804	<sup>3</sup> MM(CM)LCT
I.	2	2.519	$\left(\begin{array}{cc} 0.03 & 0.62 \\ 0.01 & 0.26 \end{array}\right)$	0.713	$^{3}MM(CM)LCT$
	3	2.543	$\left(\begin{array}{cc} 0.04 & 0.78 \\ 0.01 & 0.06 \end{array}\right)$	0.906	$^{1}MM(CM)LCT$
	5	2.669	$\left(\begin{array}{cc} 0.03 & 0.34 \\ 0.03 & 0.53 \end{array}\right)$	0.438	<sup>3</sup> Mixed
	6	2.677	$\left(\begin{array}{cc} 0.03 & 0.43 \\ 0.02 & 0.43 \end{array}\right)$	0.540	<sup>3</sup> Mixed
	1	2.745	$\left(\begin{array}{cc} 0.02 & 0.12\\ 0.03 & 0.82 \end{array}\right)$	0.162	$^{3}(CM)LC$
II.	2	2.759	$\left(\begin{array}{ccc} 0.01 & 0.10 \\ 0.03 & 0.85 \end{array}\right)$	0.138	$^{3}(CM)LC$
	3	3.137	$\left(\begin{array}{ccc} 0.11 & 0.61 \\ 0.01 & 0.17 \end{array}\right)$	0.719	$^{3}MM(CM)LCT$
	4	3.285	$\left(\begin{array}{cc} 0.06 & 0.70 \\ 0.01 & 0.12 \end{array}\right)$	0.816	$^{1}MM(CM)LCT$
	5	3.314	$\left(\begin{array}{cc} 0.01 & 0.01 \\ 0.00 & 0.00 \end{array}\right)$	0.067	$^{3}(B)LC$
	1	2.852	$\left(\begin{array}{cc} 0.02 & 0.16\\ 0.03 & 0.77 \end{array}\right)$	0.210	$^{3}(CM)LC$
III.	2	2.869	$\left(\begin{array}{cc} 0.01 & 0.13 \\ 0.03 & 0.81 \end{array}\right)$	0.173	$^{3}(CM)LC$
	3	3.196	$\left(\begin{array}{cc} 0.10 & 0.61 \\ 0.01 & 0.18 \end{array}\right)$	0.718	$^{3}MM(CM)LCT$
	4	3.312	$\left(\begin{array}{cc} 0.06 & 0.71 \\ 0.01 & 0.12 \end{array}\right)$	0.814	$^{1}MM(CM)LCT$
	5	3.375	$\left(\begin{array}{cc} 0.25 & 0.17 \\ 0.01 & 0.01 \end{array}\right)$	0.400	$^{3}$ Mixed*
	1	2.788	$\left(\begin{array}{cc} 0.05 & 0.38\\ 0.02 & 0.48 \end{array}\right)$	0.469	<sup>3</sup> Mixed
IV.	2	2.869	$\left(\begin{array}{cc} 0.02 & 0.14 \\ 0.03 & 0.79 \end{array}\right)$	0.192	$^{3}(CM)LC$
	3	2.963	$\left(\begin{array}{cc} 0.06 & 0.41 \\ 0.02 & 0.46 \end{array}\right)$	0.485	<sup>3</sup> Mixed
	4	3.03	$\left(\begin{array}{cc} 0.06 & 0.75\\ 0.01 & 0.07 \end{array}\right)$	0.861	$^{1}MM(CM)LCT$
	5	3.228	$\left(\begin{array}{cc} 0.04 & 0.74 \\ 0.01 & 0.14 \end{array}\right)$	0.818	<sup>3</sup> MM(CM)LCT

**Table 4.** CT numbers for select complexes at the ground-state geometry for the first singlet excited state where MMLCT is the metal-metal-to-ligand CT to the specified ligand in parentheses and LC is ligand centered about the ligand denoted in parentheses.

Complex	MM(CM)LCT	MM(B)LCT	(CM)LC	(B)LC	Misc.
3	0.7155	0.0205	0.0956	0.0063	0.1623
4	0.6517	0.0274	0.0875	0.0263	0.2072
6	0.7499	0.0085	0.1075	0.0019	0.1322
7	0.7719	0.0056	0.1167	0.0012	0.1046
8	0.7467	0.0083	0.0974	0.0020	0.1455
10	0.0038	0.0874	0.0018	0.8539	0.0531



Figure 7. Representative NTOs of excited states are shown here where a.) is <sup>1</sup>MMLCT of 3, b.) is <sup>3</sup>BLC of 4, and c.) is <sup>3</sup>CMLC of 5 at the ground-state geometry. The hole orbital is found in the top row and the particle orbital can be found on the bottom row.



Figure 8. Jablonski diagram for complexes 3-4, 6-8, and 10.



Figure 9. Potential energy surfaces of complexes 10 and 11 where the groundstates are blue and red, respectively. The first two singlet excited-states for 10 are represented by the purple  $(S_1)$  and green  $(S_2)$  surfaces while the grey  $(S_1)$ and orange  $(S_2)$  are 11 surfaces. It should be noted the ground-state surfaces have been shifted up by 1.25 eV for plotting purposes.



Figure 10. NTOs of complex 11 with a Pt-Pt bond length (from right to left) of 2.987, 2.996, and 3.004 Å and electronic character MMLCT, mixed, and LC, respectively. The hole orbital is in the top row and the particle orbital is in the bottom row.



**Figure 11.** Optimized geometries for the  $S_0$  and  $S_1$  states of both **3** (a and b, respectively) and **7** (c and d, respectively). The platinum, sulfur/oxygen, nitrogen, carbon, and hydrogen atoms are represented by the cyan, yellow/red, blue, grey, and white spheres.