Competition between the Heavy Atom Effect and Vibronic Coupling in Donor-Bridge-Acceptor Organometalics: Supporting Information.

Julien Eng, Stuart Thompson, Heather Goodwin, Dan Credgington and Thomas James Penfold

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## S2 Ag-Cz coordinates

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**Table S1:** Cartesian coordinates of the ground state co-planar minimum of Ag-Cz.
Table S2: Cartesian coordinates of the $S_1$ perpendicular minimum of Ag-Cz.
**S3  T$_1$ – Co-planar**

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S4  T₁ – perpendicular
### S3 Cu-Cz coordinates

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**Table S8:** Cartesian coordinates of the $T_1$ co-planar minimum of Cu-Cz.
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**Table S9:** Cartesian coordinates of the $T_1$ perpendicular minimum of Cu-Cz.
#### Table S10: Cartesian coordinates of the T\textsubscript{1} co-planar minimum of Cu-Cz.

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### Table S11: Cartesian coordinates of the T₁ perpendicular minimum of Cu-Cz.

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S4 Spin-vibronic Hamiltonian and Quantum Dynamics

To study the excited state dynamics of the Ag-Cz and Cu-Cz, we adopt a 2-dimensional model spin-vibronic Hamiltonian. The model spin-vibronic Hamiltonian for Au-Cz is described in ref. It include the three lowest triplet states ($T_1$, $T_2$ and $T_3$) as well as either the lowest or the two lowest singlet states ($S_1$ and $S_2$) for Ag-Cz and Au-Cz, respectively. Each of the three $M_s$ components of the triplet states are considered. The Hamiltonian contains therefore 10 or 11 electronic states, for Ag-Cz and Au-Cz, respectively.

The two degrees of freedom are $\varphi$ and $r_{M-N_2}$ discussed in the main text.

The Hamiltonian operator is expressed as:

$$\mathcal{H} = T_N + W$$

where $T_N$ and $W$ are the kinetic and potential energy operators, respectively, and are defined in sections S1 and S2.

S1 The kinetic energy operator

In this work, we adopt a kinetic energy operator (KEO) expressed as a sum of two uncoupled mono-dimensional KEOs,

$$T_N = -\frac{1}{2I} \frac{\partial^2}{\partial \varphi^2} - \frac{1}{2\mu} \frac{\partial^2}{\partial r_{M-N_2}^2}.$$ (2)

The first term is the KEO of the rotation of a solid top, where $I$ is the moment of inertia,

$$I = \sum_i m_i r_i^2$$ (3)

where $i$ denotes all atoms of the rotating carbazole ligand, $m_i$ denotes their mass, and $r_i$ denotes their distance to the rotation axis. The second term is the KEO associated to $r_{M-N_2}$, with $\mu$ being the reduced mass of the system,

$$\mu = \frac{\sum_A m_A (\sum_B m_B)}{\sum_A m_A + \sum_B m_B}$$ (4)

where A and B denote the atoms of the Cz and CAAC (including the metal) moieties, respectively, and $m_A$ and $m_B$ denote their respective mass. The parameters $I$ and $\mu$ are reported in table S12.

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<td>Ag-Cz</td>
<td>5887.63</td>
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Table S12: Moment of inertia $I$ and reduced mass $\mu$ for Cu-Cz and Ag-Cz.

S2 The potential energy

The potential energy component of the Hamiltonian, $W$, is expressed as the sum:

$$W = W^{\text{vib}} + W^{\text{SOC}},$$ (5)

where $W^{\text{vib}}$ contains the diabatic electronic states and the coupling between them, described in sections S1 for Ag-Cz and S2 for Cu-Cz. $W^{\text{SOC}}$ contains the spin-orbit coupling matrix elements (SOCMEs) in
the diabatic picture. They are obtained by transformation of the computed SOCME between the so-called electronic adiabatic states \(V^{\text{SOC}}\). Let \(R\) be the adiabatic to diabatic rotation matrice that transforms the adiabatic electronic states \(V\) into the diabatic electronic states matrix \(W^{\text{vib}}\) through the transformation:

\[
W^{\text{vib}} = R^{-1} V R.
\]

\(W^{\text{soc}}\) is then obtained through the same rotation:

\[
W^{\text{soc}} = R^{-1} V^{\text{soc}} R.
\]

\(W^{\text{soc}}\) and \(V^{\text{soc}}\) are reported, for \textbf{Ag-Cz} and \textbf{Cu-Cz} in tables S15 and S17, respectively, and the rotation matrices for \textbf{Ag-Cz} and \textbf{Cu-Cz} in tables S16 and S18, respectively.

The vibronic coupling occurs between electronic states of same spin multiplicity, \(W^{\text{vib}}\) can therefore be written:

\[
W^{\text{vib}} = \begin{pmatrix}
E_{T_1} & \lambda^{T_1,T_2} & \lambda^{T_1,T_3} & 0 \\
\lambda^{T_1,T_2} & E_{T_2} & \lambda^{T_2,T_3} & 0 \\
\lambda^{T_1,T_3} & \lambda^{T_2,T_3} & E_{T_3} & 0 \\
0 & 0 & 0 & E_{S_1}
\end{pmatrix}
\]

\(E_{T_n}\) and \(E_{S_1}\) being the diabatic potential energy for the triplet and \(S_1\) states, and \(\lambda^{T_n,T_m}\) is the vibronic coupling between the \(T_n\) and \(T_m\) states. \(W^{\text{soc}}\) is written:

\[
W^{\text{soc}} = \begin{pmatrix}
0 & \eta^{T_1,T_2} & \eta^{T_1,T_3} & \eta^{T_1,S_1} \\
\eta^{T_1,T_2} & 0 & \eta^{T_2,T_3} & \eta^{T_2,S_1} \\
\eta^{T_1,T_3} & \eta^{T_2,T_3} & 0 & \eta^{T_3,S_1} \\
\eta^{T_1,S_1} & \eta^{T_2,S_1} & \eta^{T_3,S_1} & 0
\end{pmatrix}
\]

with

\[
\eta^{T_n,T_m} = \begin{pmatrix}
\mathcal{I}(\eta') & -\mathcal{R}(\eta) + \mathcal{I}(\eta) & 0 \\
-\mathcal{R}(\eta) + \mathcal{I}(\eta) & 0 & \mathcal{R}(\eta) + \mathcal{I}(\eta) \\
0 & \mathcal{R}(\eta) + \mathcal{I}(\eta) & \mathcal{I}(\eta')
\end{pmatrix}
\]

and

\[
\eta^{T_n,S_1} = \begin{pmatrix}
\mathcal{R}(\eta) + \mathcal{I}(\eta) \\
\mathcal{I}(\eta') \\
\mathcal{R}(\eta) - \mathcal{I}(\eta)
\end{pmatrix}
\]

\(\mathcal{R}(\eta)\) and \(\mathcal{I}(\eta)\) are the real and imaginary part of the SOCMEs. In the present model we consider them as constant, taking their value at the minimum of \(S_1\) excited state. The \(3\times3\) matrix in Equation 8 represents the the coupling between each of the \(M_\pi\) components of the triplet states. \(W^{\text{vib}}\) is constructed by a fit to the diabatic electronic states along the \(r_{\text{Au-N}_2}\) stretch and torsion, \(\varphi\).

The diabatic electronic states and coupling are computed using the diabatisation scheme \(^6\) implemented within Q-chem. The details of the fit of the diabatic states and coupling for \textbf{Ag-Cz} and \textbf{Cu-Cz} are described in sections S1 and S2.

\section*{S3 Wavepacket Dynamics}

As for ref. \(^5\) The quantum dynamics were performed using the multi-configurational time-dependent Hartree (MCTDH) method as implemented within the Quantics quantum dynamics package. \(^7\) The 2-dimensional model spin-vibronic Hamiltonian was represented on a Fast Fourier Transform (FFT) grid of...
Figure S3: Diabatic potential energy curves (top) and vibronic coupling (bottom) for Cu-Cz (left), Ag-Cz (center), and Au-Cz (right) along $r_{M-N_2}$.

1001 x 801 grid points for the torsion and the stretching modes, respectively. The torsional mode was set with periodic boundary conditions ranging from $-\pi \rightarrow \pi$. The multi-set formalism was adopted, and 10 single particle functions (SPFs) were used for each mode on the $S_1$ and $T_1$ states and 2 SPFs were used for each mode on the $T_2$ and $T_3$ states. The evolution of the A-vector was calculated with the constant mean field integration scheme, and the SPFs were propagated with the Runge-Kutta integrator to eighth order (RK8). One initial wavepacket used in the simulations was obtained from a relaxation of a guessed wavepacket upon the ground state surface along the stretching motion, vertically projected onto the $S_1$ surface. The width and position of the initial wavepacket along the torsion was adopted to better represent the distribution of $\varphi$ associated with the flat nature of the potential along this motion.

S5 Potential Energy Surfaces

S1 The potential Ag-Cz

The diabatic potential energy surface for state i as a function of $\varphi$ and $r$ ($E_i$) can be decomposed as

$$E_i(\varphi, r) = E_i(\varphi) + E_i(r)$$

(12)

where $E_i(\varphi)$ and $E_i(r)$ are the diabatic energies along each coordinate. The analytical expressions fitted to the calculation diabatic energies take the form:

$$E_i(\varphi) = \beta_i \cos(2(\varphi - \tau_i)) + \gamma_i \cos(0.5(\varphi - \psi_i))^{64} + \delta_i \cos(0.5(\varphi - \theta_i))^{64}.$$  

(13)

along the torsion $\varphi$, and is a Morse potential along the stretch coordinate $r$:

$$E_i(r_{Ag-N_2}) = D_i \left( \exp \left( -\alpha_i (r_{Ag-N_2} - r_{0_{Ag-N_2}})^2 \right) - 1 \right)^2.$$  

(14)
where $D_i$ is the dissociation energy, $\alpha$ describes the width of the potential, and $r_{Ag-N_2}^0$ is the bond length at the minimum of energy. The fit parameters are reported in Tab. S13.

The vibronic coupling is decomposed in a similar fashion:

$$\lambda^{i,j}(\varphi, r) = \lambda^{i,j}(\varphi) + \lambda^{i,j}(r)$$

(15)

where the analytical expressions of $\lambda^{i,j}(\varphi)$ and $\lambda^{i,j}(r)$ fitted to the computed coupling take the form:

$$\lambda^{T_n,T_m}(\varphi) = \epsilon_1 \sin(1(\varphi - \nu_1)) + \epsilon_2 \sin(0.5(\varphi - \nu_2)) + \epsilon_3 \sin(0.5(\varphi - \nu_3))$$

(16)

along the torsion $\varphi$, and: Vibronic coupling along the stretch are fitted using a second order polynomial expression:

$$\lambda^{T_n,T_m}(r_{Ag-N_2}) = ar_{Ag-N_2}^2 + br_{Ag-N_2} + \lambda^{T_n,T_m}(\varphi_0).$$

(17)

along the stretch coordinate $r$. All fit parameters for the vibronic coupling are reported in Tab. S13.

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<th>Parameter</th>
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<th>$T_2$</th>
<th>$T_3$</th>
<th>$S_1$</th>
<th>$T_1-T_2$</th>
<th>$T_1-T_3$</th>
<th>$T_2-T_3$</th>
<th>$T_1-T_2$</th>
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Table S13: Fitted parameters of the diabatic states (left) and vibronic coupling (right) along the torsion $\varphi$ (top) and the stretch $r$ (bottom) for the Ag-Cz complex. Do the stretch part
S2 The potential Cu-Cz

Due to the bent C-Cu-N angle, the analytical expressions for both the diabatic energies and the coupling need to be more complex to assess the asymmetry. The diabatic energy along $\varphi$ for the singlet states is

$$S_i(\varphi) = a_1 \cos (2 (\varphi - \tau_1)) + a_2 \cos (0.5 (\varphi - \tau_2))^{64} + a_3 \cos (0.5 (\varphi - \tau_3))^{64}$$
$$+ a_4 \cos (0.5 (\varphi - \tau_4))^{\beta_i} + a_5 \cos (0.5 (\varphi - \tau_5))^{\beta_i} + \varepsilon_i \tag{18}$$

analytical expression and for the triplet states by

$$T_i(\varphi) = a_1 \cos (2 (\varphi - \tau_1)) + a_2 \cos (0.5 (\varphi - \tau_2))^{64} + a_3 \cos (0.5 (\varphi - \tau_3))^{64}$$
$$+ a_4 \cos (4 (\varphi - \tau_4)) + a_5 \cos (0.5 (\varphi - \tau_5))^{64} + \varepsilon_i \tag{19}$$

analytical expression. The energy along the stretch coordinate takes the form of a Morse potential:

$$E_i(r_{Cu-N}) = D_i \left( \exp \left( -\alpha_i (r_{Cu-N} - r^0_{Cu-N}) - 1 \right)^2 \right). \tag{20}$$

The vibronic coupling along $\varphi$ is fitted by:

$$T_1 - T_2(\varphi) = a_1 \sin (x - b_{11}) + a_2 \sin (x - b_{12})^3 + s1$$
$$T_1 - T_3(\varphi) = a_1 \sin (2 (x - b_{1})) + s2$$
$$T_2 - T_3(\varphi) = a_1 \cos (x - b_{1}) + a_2 \cos (0.5 (x - b_{2}))^{36} + a_3 \cos (0.5 (x - b_{3}))^{36}$$
$$S_1 - S_2(\varphi) = a_1 \sin (x - b_{1})^3 + a_2 \sin (x - b_{2})^3 + s4 \tag{21}$$

And along $r_{Cu-N}$ by a linear function:

$$\lambda_{i,j} (r_{Cu-N}) = ar_{Cu-N} + b. \tag{22}$$

All fit parameters are reported in Tab.S14.
Table S14: Fitted parameters of the diabatic states (left) and vibronic coupling (right) along the torsion \( \varphi \) (top) and the stretch \( r \) (bottom) for the Cu-Cz complex.

**S6 The Spin-Orbit Coupling Matrix Elements**

**S1 SOC in Ag-Cz**

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<th>( S_1 )</th>
<th>( S_2 )</th>
<th>( T_3 )</th>
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<td>( b )</td>
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<th>( S_1 )</th>
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<tbody>
<tr>
<td>( D_i ) / eV</td>
<td>6.149</td>
<td>7.060</td>
<td>6.092</td>
<td>7.050</td>
<td>6.316</td>
</tr>
<tr>
<td>( \alpha ) / Å(^{-1})</td>
<td>1.763</td>
<td>1.639</td>
<td>1.769</td>
<td>1.639</td>
<td>1.775</td>
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<tr>
<td>( r_{\text{Cu-N}} ) / Å</td>
<td>-0.002</td>
<td>-0.008</td>
<td>-0.005</td>
<td>-0.008</td>
<td>-0.007</td>
</tr>
<tr>
<td>( \epsilon_i ) / eV</td>
<td>2.793</td>
<td>2.898</td>
<td>3.367</td>
<td>2.908</td>
<td>3.195</td>
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**Diabatic SOC**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>( 3^3\text{CT} )</th>
<th>( 3^3\text{LE}_{\text{CAAC}} )</th>
<th>( 3^3\text{LE}_{\text{Cz}} )</th>
<th>( 1^1\text{CT} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 3^3\text{CT} )</td>
<td>0.00</td>
<td>295.20</td>
<td>26.68</td>
<td>1.92</td>
</tr>
<tr>
<td>( 3^3\text{LE}_{\text{CAAC}} )</td>
<td>295.21</td>
<td>0.00</td>
<td>3.97</td>
<td>142.81</td>
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<tr>
<td>( 3^3\text{LE}_{\text{Cz}} )</td>
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<td>3.97</td>
<td>0.00</td>
<td>13.33</td>
</tr>
<tr>
<td>( 1^1\text{CT} )</td>
<td>1.92</td>
<td>142.81</td>
<td>13.33</td>
<td>0.00</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Parameter</th>
<th>( 3^3\text{CT} )</th>
<th>( 3^3\text{LE}_{\text{CAAC}} )</th>
<th>( 3^3\text{LE}_{\text{Cz}} )</th>
<th>( 1^1\text{CT} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 3^3\text{CT} )</td>
<td>0.00</td>
<td>295.31</td>
<td>27.83</td>
<td>2.58</td>
</tr>
<tr>
<td>( 3^3\text{LE}_{\text{CAAC}} )</td>
<td>295.31</td>
<td>0.00</td>
<td>1.80</td>
<td>142.76</td>
</tr>
<tr>
<td>( 3^3\text{LE}_{\text{Cz}} )</td>
<td>27.83</td>
<td>1.80</td>
<td>0.00</td>
<td>12.84</td>
</tr>
<tr>
<td>( 1^1\text{CT} )</td>
<td>2.58</td>
<td>142.76</td>
<td>12.84</td>
<td>0.00</td>
</tr>
</tbody>
</table>

Table S15: Adiabatic (top) and Diabatic (bottom) SOC (in cm\(^{-1}\)) between the considered states for Ag-Cz
Table S16: Adiabatic to diabatic matrix rotation for Ag-Cz

S2  SOC in Cu-Cz

**Table S17:** Adiabatic (top) and Diabatic (bottom) SOC (in cm$^{-1}$) between the considered states for Cu-Cz

Table S18: Adiabatic to diabatic matrix rotation for Cu-Cz

S7  Supplementary Dynamics

S1  Dynamics Ag-Cz
Figure S4: Evolution of the diabatic population along time for Ag-Cz with the Hamiltonian without $^3$LE(Cz)
Figure S5: Evolution of the diabatic population along time for Ag-Cz with the Hamiltonian without $^3$LE(CAAC)
Figure S6: Evolution of the diabatic population along time for Ag-Cz with the Hamiltonian without $^3$LE(Cz) and $^3$LE(CAAC).
Figure S7: Evolution of the diabatic population along time for Cu-Cz with the Hamiltonian without $^1\text{LE(CAAC)}$. 
Figure S8: Evolution of the diabatic population along time for Cu-Cz with the Hamiltonian without $^3\text{LE(Cz)}$. 
Figure S9: Evolution of the diabatic population along time for Cu-Cz with the Hamiltonian without $^3\text{LE}(\text{Cz})$ and $^1\text{LE}(\text{CAAC})$. 
**Figure S10:** Evolution of the diabatic population along time for Cu-Cz with the Hamiltonian without $^3$LE(CAAC).
Figure S11: Evolution of the diabatic population along time for Cu-Cz with the Hamiltonian without $^3$LE(Cz), $^3$LE(CAAC) and $^1$LE(CAAC).
References


