A Synthetic Approach to Cross-Conjugated Organometallic Complexes Based on geminal-Diethynylethene and $\mathrm{Co}^{\mathrm{III}}$ (cyclam)

Sean N. Natoli, Tyler J. Azbell, Phillip E. Fanwick, Matthias Zeller and Tong Ren*
Department of Chemistry, Purdue University, West Lafayette, Indiana 47907
Supporting Information

## Table of Contents

1. IR and UV-Vis spectra

S2
2. Electrochemistry

S12
3. ESI-MS

S15
4. NMR Analysis S24
5. Crystal data S33
6. Computational details S38

IR and UV-vis spectra


Figure S1. IR absorption spectrum of [1a]Cl, ATR.


Figure S2. IR absorption spectrum of [1b]Cl, ATR.


Figure S3. IR absorption spectrum of [2a] $\mathrm{PF}_{6}$, ATR.


Figure S4. IR absorption spectrum of [2b] $\mathrm{PF}_{6}$, ATR.


Figure S5. IR absorption spectrum of [2c] $] \mathrm{PF}_{6}$, ATR.


Figure S6. IR absorption spectrum of $[3](\mathrm{Cl})_{2}$, ATR.


Figure S7. IR absorption spectrum of $[\mathbf{4 a}](\mathrm{OTf})_{4}$, ATR.


Figure S8. IR absorption spectrum of $[\mathbf{4 b}]\left(\mathrm{PF}_{6}\right)_{2}$, ATR.


Figure S9. IR absorption spectrum of $[5](\mathrm{Cl})_{2}$, ATR.


Figure S10. UV-vis absorption spectra of $[\mathbf{1 a}-\mathbf{b}] \mathrm{Cl}$ and $[\mathbf{2 a}-\mathbf{c}] \mathrm{PF}_{6}$ in methanol.


Figure S11. UV-vis absorption spectra of $[\mathbf{3}](\mathrm{Cl})_{2},[\mathbf{4 a}](\mathrm{OTf})_{4},[\mathbf{4 b}]\left(\mathrm{PF}_{6}\right)_{2}$, and $[\mathbf{5}](\mathrm{Cl})_{2}$ in methanol.

## Electrochemistry



Figure S12. Cyclic voltammogram showing the first reduction of $[\mathbf{1 a}](\mathrm{Cl})$ at $v=0.1 \mathrm{~V} / \mathrm{s}, 0.5 \mathrm{~V} / \mathrm{s}$, and $1 \mathrm{~V} / \mathrm{s}$ in MeCN with $0.1 \mathrm{M} \mathrm{NBu}{ }_{4} \mathrm{BF}_{4}$


Figure S13. Cyclic voltammogram showing the first reduction of $[3](\mathrm{Cl})_{2}$ at $v=0.1 \mathrm{~V} / \mathrm{s}, 0.5 \mathrm{~V} / \mathrm{s}$, and $1 \mathrm{~V} / \mathrm{s}$ in MeCN with $0.1 \mathrm{M} \mathrm{NBu}{ }_{4} \mathrm{BF}_{4}$


Figure S14. Cyclic voltammogram showing the first reduction of $[\mathbf{5}](\mathrm{Cl})_{2}$ at $v=0.1 \mathrm{~V} / \mathrm{s}, 0.5 \mathrm{~V} / \mathrm{s}$, and $1 \mathrm{~V} / \mathrm{s}$ in MeCN with $0.1 \mathrm{M} \mathrm{NBu}_{4} \mathrm{BF}_{4}$.


Figure S15. Differential pulse voltammagram showing the $1^{\text {st }}$ reduction $\left(\mathrm{Co}^{\mathrm{III}} / \mathrm{Co}^{\mathrm{II}}\right)$ of $[3](\mathrm{Cl})_{2}$ in MeCN with $0.1 \mathrm{M} \mathrm{NBu}{ }_{4} \mathrm{BF}_{4}$ under Taube-Richardson conditions (pulse amplitude $=10 \mathrm{mV}$ ).


Figure S16. Differential pulse voltammagram showing the $1^{\text {st }}$ reduction $\left(\mathrm{Co}^{\mathrm{III}} / \mathrm{Co}^{\mathrm{II}}\right)$ of [4a](OTf) $)_{4}$ in MeCN with $0.1 \mathrm{M} \mathrm{NBu} \mathbf{N F}_{4}$ under Taube-Richardson conditions (pulse amplitude $=10 \mathrm{mV}$ ).


Figure S17. Differential pulse voltammagram showing the $1^{\text {st }}$ reduction $\left(\mathrm{Co}^{\mathrm{III}} / \mathrm{Co}^{\mathrm{II}}\right)$ of $[\mathbf{4 b}]\left(\mathrm{PF}_{6}\right)_{2}$ in MeCN with $0.1 \mathrm{M} \mathrm{NBu}{ }_{4} \mathrm{BF}_{4}$ under Taube-Richardson conditions (pulse amplitude $=$ 10 mV ).


Figure S18. Differential pulse voltammagram showing the $1^{\text {st }}$ reduction $\left(\mathrm{Co}^{\mathrm{III}} / \mathrm{Co}^{\mathrm{II}}\right)$ of $[\mathbf{5}](\mathrm{Cl})_{2}$ in MeCN with $0.1 \mathrm{M} \mathrm{NBu}_{4} \mathrm{BF}_{4}$ under Taube-Richardson conditions (pulse amplitude $=10 \mathrm{mV}$ ).

## ESI-MS



Figure S19. ESI-MS of compound [1a]Cl.


Figure S20. ESI-MS of compound [1b]Cl.


Figure S21. ESI-MS of compound [2a] $\mathrm{PF}_{6}$.


Figure S22. ESI-MS of compound [2b]PF ${ }_{6}$.


Figure S23. ESI-MS of compound [2c]PF ${ }_{6}$.


Figure S24. ESI-MS of compound [3]Cl ${ }_{2}$.


Figure S25. ESI-MS of compound $[\mathbf{4 a}](\mathrm{OTf})_{2}$ not solvated.


Figure S26. ESI-MS of compound $[\mathbf{4 b}](\mathrm{Cl})_{2}$ prior to $\mathrm{PF}_{6}$ counter ion exchange.


Figure S27. ESI-MS of compound $[5](\mathrm{Cl})_{2}$.

H1 standard parameters, CD300
Oata collected on: inova300-1-inovahlfreq
arcmive directory: /mnt/d2/pinmrt/harwood/vimesys/data archive directory: /mnt/d2/pinmrt/harwood/vimrsys/data File: H1

Solvent : Coclu
Relax. detay 2.000 se Pulse 28.6 degrees Widtr 3799 it
36
repetition
SE repetitions Line broadening 0.2 Hz r size 16384
Total time 0 min


Figure S28. 1H NMR spectrum ( $300 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{OD}$ ) of $[\mathbf{1 a}] \mathrm{Cl}$.

H1 standard parameters, COC13
Data collected on: ingoza0-1-inovah1freq
Archive directory: $/ \mathrm{mnt} / \mathrm{d} 2 / \mathrm{p}$ inmrf $/$ harwood/vnmrsys/data Archive directory:
Simple directory:
Pulse Sequence: s2pul Pulse Sequence:
Solvent: CDCli3

```
Relax. delay 2.000 se
Acg
N
LLN
lol
```



Figure S29. 1H NMR spectrum ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) of $[\mathbf{1 b}] \mathrm{Cl}$.


Figure S30. 1H NMR spectrum ( $300 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{OD}$ ) of [2a] $\mathrm{PF}_{6}$.

H1 standard parameters, CD300
Jata Collected on: inova300-1-inovah1freq sample directory: /mnt/d2/Pinnrt/harwood/vnirsys/dat File: H1
ulse Sequence: s2pul
Solvent: COCl3
Relax. delay 2.000 sec Pulse 28.6 degrees
Width 3793.4 Hz
32 repetitions
OBERVE H1 299.9611160 MHz
Line broadening 0.2 Hz
FTine broaden ing
Fotal time 08 min


Figure S31. 1H NMR spectrum $\left(300 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{OD}\right)$ of $[\mathbf{2 b}] \mathrm{PF}_{6}$.

H1 standard paraneters, cocis
Oata collected on: inova300-1-inovahlfreq Archive directory:/mnt/d2/pinmrf/harwood/vnmrsys/dat Sanple ${ }^{\text {file: }} \mathbf{~ H 1}$
Pulse Sequence: s2pul
Pulse Sequence: s 2
Relax. delay 2.000 sec
Pulse 28.6 degres
 Total time 0 min


Figure S32. 1H NMR spectrum ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) of $[\mathbf{2 c}] \mathrm{PF}_{6}$.

H1 standard parameters, C0300
Data Collected on: inova300-1-inovahlfreq
Archive directory: /mat/d2/pinmrf/harwoodfunmesys/data
Sample directory:

## Sample di File: H1

Pulse Sequence: s2pul
Solvent: coclu
Relax. delay 2.000 sec
Pulse 28.6
Acalse 28.6 degrees
Acd time
36 repetitions
OBSERVE HI 299.9611056 MHz
OBSERE PROCESSING
DATA
Line broadening $0.2 ~$
Hz
Line broadening
fizize 16384
Total time 0 min


Figure S33. 1H NMR spectrum ( $300 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{OD}$ ) of $[3] \mathrm{Cl}_{2}$.


Figure S34. 1 H NMR spectrum $\left(300 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{CN}\right)$ of $[4 a](\mathrm{OTf})_{4}$.

H1 standard parameters, CO300
Data collected on: inova300-1-inovah1freq
Archive directory: /mnt/d $2 / \mathrm{pinmrf} /$ harwood/vnmrsys/data
Sile: H 1
Pulse Sequence: s2pul
Solvent: CDCl3



Figure S35. 1H NMR spectrum $\left(300 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{OD}\right)$ of $[\mathbf{4 b}]\left(\mathrm{PF}_{6}\right)_{2}$.

3
Data Collected on: inova300-1-inovah1freq
Archive directory: /mnt/dz/pinnef/harwogd/vnmrsys/data
Sampledirectory: Arcmive directory
Sample directory:
File: Hi
Pulse sequence: s2pul
oivent: CDCl3
Relax. delay 2.000
pulse 28.6 degrees
${ }_{A c q}$ Pulse $\tau$ ime 2.156 sec
Aqg ${ }^{\text {tidet }} 3799.4 \mathrm{~Hz}$
49 repetitions
OBSERVE
H1, $299.9611057 ~ M H z ~$




Figure S36. 1H NMR spectrum (300 MHz, CD3OD) of [5]Cl ${ }_{2}$.

## Crystallographic Details:



Figure S37. ORTEP plot of complex [4b] ${ }^{2+}$ at the $30 \%$ probability level, showing general connectivity. Hydrogen atoms were omitted for clarity.

## Single Crystal X-ray Diffraction

Single crystal data were collected on either a Nonius KappaCCD diffractometer equipped with a graphite crystal and incident beam monochromator and examined with Mo $\mathrm{K} \alpha$ radiation ( $\lambda=$ $0.71073 \AA$ ), or a Rigaku R-axis curved image plate diffractometer equipped with a MicroMax002+ high-intensity copper X-ray source with confocal optics and examined with Cu $K \alpha$ radiation $(\lambda=1.54184 \AA)$. Data were collected at low temperature ( 100 or 150 K ). Data on the KappaCCD instrument were collected using the Nonius Collect software ${ }^{1}$. Data from the Raxis diffractometer were collected using the dtrek option of CrystalClear ${ }^{2}$. All data sets were processed using HKL3000 ${ }^{3}$ and data were corrected for absorption and scaled using Scalepack ${ }^{4}$. The space groups were assigned using XPREP from the Shelxtl suite of programs ${ }^{5}$ and the structures were solved by direct methods with SHELXS ${ }^{6}$ and refined by full matrix least squares against $\mathrm{F}^{2}$ with all reflections using the graphical user interface ShelXle ${ }^{7}$ for the refinement program SHELXL ${ }^{8}$. H atoms attached to carbon and boron atoms were positioned geometrically and constrained to ride on their parent atoms, with carbon hydrogen bond distances of $0.95 \AA$ for
and aromatic C-H, 1.00, 0.99 and $0.98 \AA$ for aliphatic C-H, CH2 and CH3 moieties, respectively. Methyl H atoms were allowed to rotate but not to tip to best fit the experimental electron density. $\mathrm{U}_{\text {iso }}(\mathrm{H})$ values were set to a multiple of $\mathrm{U}_{\mathrm{eq}}(\mathrm{C} / \mathrm{B})$ with 1.5 for CH 3 , and 1.2 for $\mathrm{C}-\mathrm{H}, \mathrm{CH} 2$ and $\mathrm{B}-$ $H$ units, respectively. Details of individual structure determinations, including description of disorder, are given in the SI.

In compound $[\mathbf{1 a}]^{+}$an anion/solvate occupied area exhibits disorder. The major moiety, consisting of a chloride anion and a solvate methanol molecule, was refined as being disordered with two moieties made up of each one chlorine and one water molecule. $\mathrm{U}_{\mathrm{ij}}$ components of ADPs of the disordered chlorine and water oxygen atoms were restrained to be similar if closer than $1.7 \AA$. Subject to these conditions the occupancy rates refined to $0.474(3), 0.419(3)$ and 0.108(2).

In compound $[\mathbf{2 a}]^{+}$a solvate methanol molecule is partially occupied. In its absence the neighboring hexafluoro phosphate anion slightly shifts towards the void created. The geometry of the major and minor $\mathrm{PF}_{6}$ moieties were restrained to be similar, and $\mathrm{U}_{\mathrm{ij}}$ components of ADPs were restrained to be similar. Subject to these conditions the occupancy for the methanol molecule and the major $\mathrm{PF}_{6}$ moiety refined to $0.756(9)$.

In compound $[\mathbf{2 b}]^{+}$a site occupied by mostly chlorine located around an inversion center was refined as disordered between either one chlorine ion, one chlorine ion and one water molecule, or two water molecules. H atoms were omitted for these disordered water molecules. The disorder extended to a nearby water molecule, which was split into two components with the major component having the same occupancy as the single chlorine anion. $\mathrm{U}_{\mathrm{ij}}$ components of ADPs were restrained to be similar for disordered atoms closer than $1.7 \AA$. The sum of chlorine
atoms was constrained to charge neutrality, and the sum of disordered moieties to unity for each disordered site. Subject to these conditions occupancies refined to $0.7081(19), 0.1460(10)$ and $0.1460(10)$.

Two isopropyl moieties were refined as disordered with a common disorder ratio. Major and minor moieties were restrained to have similar geometries, and $\mathrm{U}_{\mathrm{ij}}$ components of ADPs were restrained to be similar for atoms closer than $1.7 \AA$. Subject to these conditions occupancies refined to $0.779(5)$ and $0.221(5)$.

In compound [4a] ${ }^{4+}$ two triflate anions were refined as disordered with each two moieties. The major and minor moieties were restrained to have each similar geometries, and $\mathrm{U}_{\mathrm{ij}}$ components of ADPs were restrained to be similar for atoms closer than $1.7 \AA$. Subject to these conditions the occupancy ratios refined to $0.872(4)$ to $0.128(4)$ for the triflate of S 2 and $0.631(15)$ to $0.368(15)$ for that of S4.

Disordered solvate molecules were refined as multiply disordered acetonitrile. Six independent locations were defined, with another six in the same void created by an inversion operation. The total volume occupied by solvate molecules is ca $14 \%$ of the unit cell volume. All moieties were restrained to have each similar geometries, and the pivot atom's N-C, C-C and N...C distances were restrained to approximate target values. $\mathrm{U}_{\mathrm{ij}}$ components of ADPs were restrained to be similar for atoms closer than $1.7 \AA$. Subject to these conditions the occupancy ratios refined to $0.872(4)$ to $0.128(4)$ for the triflate of S2 and $0.631(15)$ to $0.368(15)$ for that of S 4 . Subject to these conditions the occupancy rates refined to $0.468(15), 0.460(13), 0.238(14), 0.343(13)$, 0.299 (13), and $0.414(13)$ for the molecules of N11 to N16.

A triflate anion is disordered around a twofold axis.

Table S1. Crystal Data For $[\mathbf{1 a}]^{+},[\mathbf{2 a}-\mathbf{b}]^{+}$.

|  | [19] ${ }^{+}$ | [2a] ${ }^{+}$ | [2b] ${ }^{+}$ |
| :---: | :---: | :---: | :---: |
| molecular formula | $\mathrm{C}_{18} \mathrm{H}_{31} \mathrm{ClCoN}_{4} \cdot 1.4724\left(\mathrm{CH}_{4} \mathrm{O}\right) \cdot \mathrm{Cl} \cdot 0.529\left(\mathrm{H}_{2} \mathrm{O}\right)$ | $\mathrm{C}_{19} \mathrm{H}_{31} \mathrm{CoN}_{5} \cdot \mathrm{~F}_{6} \cdot \mathrm{P} \cdot 0.756\left(\mathrm{CH}_{4} \mathrm{O}\right)$ | $2\left(\mathrm{C}_{35} \mathrm{H}_{56} \mathrm{CoN} \mathrm{N}_{4} \mathrm{Si}\right) \cdot \mathrm{CF}_{3} \mathrm{O}_{3} \mathrm{~S} \cdot \mathrm{Cl0.880} \cdot 4\left(\mathrm{H}_{2} \mathrm{O}\right)$ |
| fw, $\mathrm{g} \mathrm{mol}^{-1}$ | 490.06 | 557.61 | 1510.32 |
| space group | $P 2{ }_{1} / n$ | $P 2{ }_{1} / n$ | P2/n |
| $a, \AA$ | 10.6094(4) | 11.9073(10) | 8.5624(3) |
| $b, \AA$ | 17.5808(6) | 17.4468(11) | 17.2059(5) |
| $c, \AA$ | 12.7464(4) | 12.4980(8) | 27.3475 (10) |
| $\alpha,{ }^{\circ}$ | 90.00 | 90.00 | 90.00 |
| $\beta,{ }^{\circ}$ | 96.791(2) | 102.310(6) | 98.582(2) |
| $\gamma,{ }^{\circ}$ | 90.00 | 90.00 | 90.00 |
| $V, \AA^{3}$ | 2360.80(14) | 2536.7(3) | 3983.8(2) |
| $Z$ | 4 | 4 | 2 |
| $\rho_{\text {calcd, }} \mathrm{g} \mathrm{cm}^{-3}$ | 1.379 | 1.460 | 1.259 |
| $T, \mathrm{~K}$ | 150 | 150 | 150 |
| Radiation type | Mo K $\alpha$ | $\mathrm{Cu} K \alpha$ | Mo K ${ }^{\text {a }}$ |
| Diffractometer | Nonius Kappa CCD diffractometer | Rigaku Rapid II curved image plate diffractometer | Nonius Kappa CCD diffractometer |
| Radiation source | fine focus X-ray tube | microfocus X-ray tube | fine focus X-ray tube |
| No. reflections | 6375 | 4511 | 8561 |
| final $R$ indicies | $R 1=0.0392$ | $R 1=0.0642$ | $R 1=0.0495$ |
| $(I>2 \sigma(I))$ | $w R 2=0.0992$ | $w R 2=0.1586$ | $w R 2=0.1421$ |
| GOF on $F^{2}$ | 1.049 | 1.041 | 1.077 |

Table S2. Crystal Data for $[3]^{2+},[4 a]^{4+}$, and $[5]^{2+}$.

|  | [3] ${ }^{2+}$ | $[4 a]^{4+}$ | [5] ${ }^{2+}$ |
| :---: | :---: | :---: | :---: |
| molecular formula | $2\left(\mathrm{C}_{28} \mathrm{H}_{54} \mathrm{Cl}_{2} \mathrm{Co}_{2} \mathrm{~N}_{8}\right)^{\prime} 4(\mathrm{Cl}) \cdot 7\left(\mathrm{CH}_{4} \mathrm{O}\right)$ | $\mathrm{C}_{32} \mathrm{H}_{60} \mathrm{Co}_{2} \mathrm{~N}_{10} \cdot 4\left(\mathrm{CF}_{3} \mathrm{O}_{3} \mathrm{~S}\right) \cdot 2.222\left(\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{~N}\right)$ | $2\left(\mathrm{C}_{18} \mathrm{H}_{30} \mathrm{ClCoN}_{4}\right) \cdot 2(\mathrm{Cl}) \cdot 4\left(\mathrm{CH}_{4} \mathrm{O}\right)$ |
| $\mathrm{fw}, \mathrm{g} \mathrm{mol}^{-1}$ | 1749.19 | 1390.26 | 992.74 |
| space group | $P \overline{1}$ | $P \overline{1}$ | $P 2{ }_{1} / \mathrm{c}$ |
| $a, \AA$ | 14.1272(3) | 13.1069(5) | 19.1438(10) |
| $b, \AA$ | 15.6818(4) | 14.6343(5) | 9.9999(4) |
| $c, \AA$ Å | 19.7114(5) | 17.3230(6) | 13.7463(5) |
| $\alpha{ }^{\circ}$ | 88.280(1) | 66.088(3) | 90.00 |
| $\beta,{ }^{\circ}$ | 77.085(1) | 81.683(3) | 103.304(3) |
| $\gamma,{ }^{\circ}$ | 87.828(1) | 87.985(3) | 90.00 |
| $V, \AA^{3}$ | 4252.29(18) | 3004.6(2) | 2560.9 |
| Z | 2 | 2 | 2 |
| $\rho_{\text {calcd }} \mathrm{g} \mathrm{cm}^{-3}$ | 1.366 | 1.537 | 1.287 |
| $T, \mathrm{~K}$ | 150 | 100 | 200 |
| Radiation type | Mo K ${ }^{\text {d }}$ | $\mathrm{Cu} K \alpha$ | Mo K $\alpha$ |
| Diffractometer | Nonius Kappa CCD diffractometer | Rigaku Rapid II curved image plate diffractometer | Nonius Kappa CCD diffractometer |
| Radiation source | fine focus X-ray tube | microfocus X-ray tube | fine focus X-ray tube |
| No. reflections | 20006 | 11261 | 6222 |
| final $R$ indicies | $R 1=0.0543$ | $R 1=0.0719$ | $R 1=0.0435$ |
| $(I>2 \sigma(I))$ | $w R 2=0.1506$ | $w R 2=0.1907$ | $w R 2=0.0997$ |
| GOF on $F^{2}$ | 1.028 | 1.039 | 0.986 |

## Computational Details



Figure S38. Contour plots of $\left[\mathbf{1 a}^{\prime}\right]^{+},\left[\mathbf{3}^{\prime}\right]^{2+}$, and $\left[\mathbf{5}^{\prime}\right]^{2+}$ and $\left[\mathbf{4 b} \mathbf{b}^{\prime}\right]^{2+}$.

The LUMO and LUMO +1 in $\left[\mathbf{4 b}^{\prime}\right]^{2+}$ are dominated by the antibonding combination of the $\mathrm{d}_{\mathrm{x}-\mathrm{y}}{ }^{2}(\mathrm{Co})$ with the $p$-orbitals of the surrounding cyclam N atoms, with no contribution from either of the axial ligands. This is in contrast with the orbital assembly in complex $\left[\mathbf{3}^{\prime}\right]^{2+}$ where the LUMO and LUMO +1 have substantial mixing of the $\mathrm{d}_{\mathrm{z}}{ }^{2}(\mathrm{Co})$ with the $\sigma^{*}$ based orbitals on the gem-DEE bridge. The LUMO of $\left[5^{\prime}\right]^{2+}$ revealed incomplete mixing of orbitals spanning the gem-DEE bridge, with successive unoccupied orbitals lacking substantial mixing. Contour plots of the LUMO, LUMO+1 obtained for the model cation $\left[\mathbf{1 a}^{\prime}\right]^{+}$are similar to unoccupied orbitals of $\left[\mathbf{3}^{\prime}\right]^{2+}$ and $\left[4 b^{\prime}\right]^{2+}$.

All calculated complexes have similar HOMO, HOMO-1, and HOMO-2 contour plots which represent part of the filled $\operatorname{Co} t_{2 g}$ set. It is clear from Figure S 21 that the HOMO is a combination of the $\mathrm{d}_{\mathrm{xz}}(\mathrm{Co})$ with the antibonding combination of the $\pi_{\perp}$ ( DEE ) (perpendicular, out-of-plane $(\mathrm{C} \equiv \mathrm{C})$ ) orbitals and vinyl $\pi(\mathrm{C}=\mathrm{C})$, whereas the HOMO-1 is composed of the antibonding combination of the $\mathrm{d}_{\mathrm{yz}}(\mathrm{Co})$ and the antibonding $\pi_{\|}(\mathrm{DEE})$ (parallel, in-plane $(\mathrm{C} \equiv \mathrm{C})$ ) orbitals, without contribution from the vinyl $\pi(\mathrm{C}=\mathrm{C})$ unit. The HOMO-2 orbital is solely the antibonding combination of the $\mathrm{d}_{\mathrm{xz}}(\mathrm{Co})$ and the antibonding combination of the $\pi_{\perp}$ (DEE). Compounds $\left[\mathbf{3}^{\prime}\right]^{2+}$ and $\left[\mathbf{4} \mathbf{b}^{\prime}\right]^{2+}$ have a HOMO-3 composed of the antibonding combination of the $\mathrm{d}_{\mathrm{yz}}$ (Co) with the bonding $\pi \|$ (DEE) orbitals and $\sigma^{*}$ orbital of the vinyl group, with significantly more contribution from the axial $\pi(\mathrm{C} \equiv \mathrm{C})$ or $\mathrm{Cl} p-$ orbitals.

## Optimized geometries

The geometries of $\left[\mathbf{3}^{\prime}\right]^{+},\left[\mathbf{4 a}^{\prime}\right]^{4+}$, and $\left[\mathbf{4 b}^{\prime}\right]^{2+}$ in the ground state were fully optimized from the crystal structures reported in this work, using the density functional method B3LYP (Beck's 3 parameter hybrid functional using the Lee-Yang-Parr correlation functional) and employing the LanL2DZ basis sets. Calculation were accomplished using the Gaussian03 program package. ${ }^{9}$


Figure S39. Fully optimized structure of $\left[3^{\prime}\right]^{2+}$ using DFT method at the LanL2DZ level. Hydrogen atoms were omitted for clarity.

Table S3. Relevant bond lenghts ( $\AA$ ) and angles (deg) computed for [ $\left.\mathbf{3}^{\prime}\right]^{2+}$.

| Co1-N1 | 2.017 |
| :--- | :--- |
| Co1-N2 | 2.017 |
| Co1-N3 | 2.009 |
| Co1-N4 | 2.009 |
| Co2-N5 | 2.009 |
| Co2-N6 | 2.017 |
| Co2-N7 | 2.017 |
| Co2-N8 | 2.009 |
| Co1-Cl1 | 2.376 |
| Co2-Cl2 | 2.376 |
| Co1-C1 | 1.924 |
| Co2-C5 | 1.924 |
| C1-C2 | 1.242 |
| C2-C3 | 1.454 |
| C3-C4 | 1.454 |
| C4-C5 | 1.242 |
| C3-C8 | 1.380 |


| C11-Co1-C1 | 179.746 |
| :--- | :--- |
| C12-Co2-C5 | 179.745 |
| C1-C2-C3 | 176.140 |
| C2-C3-C4 | 117.720 |



Figure S40. Fully optimized structure of $\left[\mathbf{4 a}^{\prime}\right]^{4+}$ using DFT method at the LanL2DZ level. Hydrogen atoms were omitted for clarity.

Table S4. Relevant bond lenghts (Á) and angles (deg) computed for $\left[\mathbf{4 a} \mathbf{a}^{\mathbf{4 +}}\right.$.

| Co1-N1 | 2.016 |
| :--- | :--- |
| Co1-N2 | 2.021 |
| Col-N3 | 2.017 |
| Co1-N4 | 2.015 |
| Co2-N5 | 2.017 |
| Co2-N6 | 2.014 |
| Co2-N7 | 2.020 |


| Co2-N8 | 2.015 |
| :--- | :--- |
| Co1-N9 | 2.091 |
| Co2-N10 | 2.088 |
| Co1-C1 | 1.916 |
| Co2-C5 | 1.918 |
| C1-C2 | 1.242 |
| C2-C3 | 1.242 |
| C3-C4 | 1.458 |
| C4-C5 | 1.458 |
| C3-C6 | 1.384 |
| N9-Co1-C1 | 179.426 |
| N10-Co2-C5 | 179.323 |
| C1-C2-C3 | 173.865 |
| C2-C3-C4 | 174.417 |



Figure S41. Fully optimized structure of $\left[\mathbf{4 b}^{\prime}\right]^{2+}$ using DFT method at the LanL2DZ level. Hydrogen atoms were omitted for clarity.

Table S5. Relevant bond lenghts ( $\AA$ ) and angles (deg) computed for $\left[\mathbf{4 b} \mathbf{b}^{2+}\right.$.

| Col-N1 | 2.020 |
| :---: | :---: |
| Col-N2 | 2.018 |
| Co1-N3 | 2.019 |
| Col-N4 | 2.019 |
| Co2-N5 | 2.018 |
| Co2-N6 | 2.019 |
| Co2-N7 | 2.019 |
| Co2-N8 | 2.018 |
| Col-C1 | 1.979 |
| Co2-C5 | 1.979 |
| Co1-C9 | 1.944 |
| Co2-C11 | 1.944 |
| C1-C2 | 1.246 |
| C2-C3 | 1.454 |
| C3-C4 | 1.454 |
| C4-C5 | 1.246 |
| C3-C6 | 1.380 |


| C9-C10 | 1.247 |
| :---: | :---: |
| $\mathrm{C} 11-\mathrm{C} 12$ | 1.247 |
| $\mathrm{C} 10-\mathrm{Si1}$ | 1.869 |
| $\mathrm{C} 12-\mathrm{Si} 2$ | 1.869 |
| $\mathrm{C} 1-\mathrm{Co} 1-\mathrm{C} 9$ | 179.664 |
| $\mathrm{C} 5-\mathrm{Co} 2-\mathrm{C} 11$ | 179.594 |
| $\mathrm{C} 1-\mathrm{C} 2-\mathrm{C} 3$ | 176.260 |
| $\mathrm{C} 2-\mathrm{C} 3-\mathrm{C} 4$ | 117.799 |

[1] Nonius. Delft, The Netherlands 1998.
[2] Rigaku Corp. Rigaku Corporation: The Woodlands, TX 2014.
[3] Otwinowski, Z.; Minor, W. In Methods in Enzymology; 1997, 276, 307-326.
[4] Otwinowski, Z.; Minor, W. In Methods in Enzymology; 1997, 276, 307-326.
[5] Bruker Advanced X-ray Solutions. Bruker AXS Inc.: Madison, WI 2003.
[6] Sheldrick, G. M. Acta Crystallogr., Sect. A 2008, 64, 112-122.
[7] Hübschle, C. B.; Sheldrick, G. M.; Dittrich, B. J. Appl. Crystallogr. 2011, 44, 12811284.
[8] Sheldrick, G. M. Acta Crystallogr., Sect. C 2015, 71, 3-8.
[9] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian, Inc., Wallingford, CT, 2003.

