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

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Supporting Information

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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]PF₆, ATR.



Figure S4. IR absorption spectrum of [2b]PF₆, ATR.



Figure S5. IR absorption spectrum of [2c]PF₆, ATR.



Figure S6. IR absorption spectrum of [3](Cl)₂, ATR.



Figure S7. IR absorption spectrum of [4a](OTf)₄, ATR.



Figure S8. IR absorption spectrum of [4b](PF₆)₂, ATR.



Figure S9. IR absorption spectrum of [5](Cl)₂, ATR.



Figure S10. UV-vis absorption spectra of [1a - b]Cl and $[2a - c]PF_6$ in methanol.



Figure S11. UV-vis absorption spectra of $[3](Cl)_2$, $[4a](OTf)_4$, $[4b](PF_6)_2$, and $[5](Cl)_2$ in methanol.

Electrochemistry



Figure S12. Cyclic voltammogram showing the first reduction of [1a](Cl) at v = 0.1 V/s, 0.5 V/s, and 1 V/s in MeCN with 0.1M NBu₄BF₄



Figure S13. Cyclic voltammogram showing the first reduction of $[3](Cl)_2$ at v = 0.1 V/s, 0.5 V/s, and 1 V/s in MeCN with 0.1M NBu₄BF₄



Figure S14. Cyclic voltammogram showing the first reduction of $[5](Cl)_2$ at v = 0.1 V/s, 0.5 V/s, and 1 V/s in MeCN with 0.1M NBu₄BF₄.



Figure S15. Differential pulse voltammagram showing the 1^{st} reduction (Co^{III}/Co^{II}) of [**3**](Cl)₂ in MeCN with 0.1M NBu₄BF₄ under Taube-Richardson conditions (pulse amplitude = 10 mV).



Figure S16. Differential pulse voltammagram showing the 1^{st} reduction (Co^{III}/Co^{II}) of [**4a**](OTf)₄ in MeCN with 0.1M NBu₄BF₄ under Taube-Richardson conditions (pulse amplitude = 10 mV).



Figure S17. Differential pulse voltammagram showing the 1^{st} reduction (Co^{III}/Co^{II}) of [**4b**](PF₆)₂ in MeCN with 0.1M NBu₄BF₄ under Taube-Richardson conditions (pulse amplitude = 10 mV).



Figure S18. Differential pulse voltammagram showing the 1^{st} reduction (Co^{III}/Co^{II}) of [**5**](Cl)₂ in MeCN with 0.1M NBu₄BF₄ under Taube-Richardson conditions (pulse amplitude = 10 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]PF₆.



Figure S22. ESI-MS of compound [2b]PF₆.



Figure S23. ESI-MS of compound [2c]PF₆.



Figure S24. ESI-MS of compound [3]Cl₂.



Figure S25. ESI-MS of compound [4a](OTf)₂ not solvated.



Figure S26. ESI-MS of compound [4b](Cl)₂ prior to PF₆ counter ion exchange.



Figure S27. ESI-MS of compound [5](Cl)₂.



Figure S28. 1H NMR spectrum (300 MHz, CD₃OD) of [1a]Cl.



Figure S29. 1H NMR spectrum (300 MHz, CDCl₃) of [1b]Cl.



Figure S30. 1H NMR spectrum (300 MHz, CD₃OD) of [2a]PF₆.



Figure S31. 1H NMR spectrum (300 MHz, CD₃OD) of [2b]PF₆.



Figure S32. 1H NMR spectrum (300 MHz, CDCl₃) of [2c]PF₆.

H1 standard parameters, CD30D



Figure S33. 1H NMR spectrum (300 MHz, CD₃OD) of [3]Cl₂.



Figure S34. 1H NMR spectrum (300 MHz, CD₃CN) of [4a](OTf)_{4.}

H1 standard parameters, CD30D



Figure S35. 1H NMR spectrum (300 MHz, CD₃OD) of [4b](PF₆)₂.



Figure S36. 1H NMR spectrum (300 MHz, CD3OD) of [5]Cl₂.

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 K α radiation (λ = 0.71073 Å), 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 α radiation (λ = 1.54184 Å). Data were collected at low temperature (100 or 150 K). Data on the KappaCCD instrument were collected using the Nonius Collect software¹. Data from the R-axis diffractometer were collected using the dtrek option of CrystalClear². All data sets were processed using HKL3000³ and data were corrected for absorption and scaled using Scalepack⁴. The space groups were assigned using XPREP from the Shelxtl suite of programs⁵ and the structures were solved by direct methods with SHELXS⁶ and refined by full matrix least squares against F² with all reflections using the graphical user interface ShelXle⁷ for the refinement program SHELXL⁸. 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 Å for

and aromatic C-H, 1.00, 0.99 and 0.98 Å 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. $U_{iso}(H)$ values were set to a multiple of $U_{eq}(C/B)$ with 1.5 for CH3, and 1.2 for C-H, CH2 and B-H units, respectively. Details of individual structure determinations, including description of disorder, are given in the SI.

In compound $[1a]^+$ 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. U_{ij} components of ADPs of the disordered chlorine and water oxygen atoms were restrained to be similar if closer than 1.7 Å. Subject to these conditions the occupancy rates refined to 0.474(3), 0.419(3) and 0.108(2).

In compound $[2a]^+$ 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 PF₆ moieties were restrained to be similar, and U_{ij} components of ADPs were restrained to be similar. Subject to these conditions the occupancy for the methanol molecule and the major PF₆ moiety refined to 0.756(9).

In compound $[2b]^+$ 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. U_{ij} components of ADPs were restrained to be similar for disordered atoms closer than 1.7 Å. 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 U_{ij} components of ADPs were restrained to be similar for atoms closer than 1.7 Å. 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 U_{ij} components of ADPs were restrained to be similar for atoms closer than 1.7 Å. 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 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. U_{ij} components of ADPs were restrained to be similar for atoms closer than 1.7 Å. 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 S4. 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 $[\mathbf{1a}]^+$, $[\mathbf{2a} - \mathbf{b}]^+$.

	$[\mathbf{1a}]^+$	$[\mathbf{2a}]^+$	$\left[\mathbf{2b}\right]^+$
molecular formula	C ₁₈ H ₃₁ ClCoN ₄ ·1.4724(CH ₄ O)·Cl [•] 0.529(H ₂ O)	C ₁₉ H ₃₁ CoN ₅ F ₆ P [.] 0.756(CH ₄ O)	$2(C_{35}H_{56}CoN_4Si)$ CF ₃ O ₃ S Cl0.880 4(H ₂ O)
fw, g mol ⁻¹	490.06	557.61	1510.32
space group	$P2_{1}/n$	$P2_1/n$	P2/n
<i>a</i> , Å	10.6094(4)	11.9073(10)	8.5624(3)
b, Å	17.5808(6)	17.4468(11)	17.2059(5)
<i>c</i> , Å	12.7464(4)	12.4980(8)	27.3475(10)
α, °	90.00	90.00	90.00
β, °	96.791(2)	102.310(6)	98.582(2)
γ, °	90.00	90.00	90.00
$V, Å^3$	2360.80(14)	2536.7(3)	3983.8(2)
Ζ	4	4	2
$\rho_{\rm calcd}$, g cm ⁻³	1.379	1.460	1.259
<i>Т</i> , К	150	150	150
Radiation type	Μο Κα	Cu <i>K</i> α	Μο <i>Κ</i> α
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	R1 = 0.0392	R1 = 0.0642	R1 = 0.0495
$(I > 2\sigma(I))$	wR2 = 0.0992	wR2 = 0.1586	wR2 = 0.1421
GOF on F^2	1.049	1.041	1.077

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

	$[3]^{2+}$	[4a] ⁴⁺	[5] ²⁺
molecular formula	$2(C_{28}H_{54}Cl_2Co_2N_8)$ '4(Cl)'7(CH ₄ O)	$C_{32}H_{60}Co_2N_{10}$ ·4(CF ₃ O ₃ S)·2.222(C ₂ H ₃ N)	2(C ₁₈ H ₃₀ ClCoN ₄) [•] 2(Cl) [•] 4(CH ₄ O)
fw, g mol ⁻¹	1749.19	1390.26	992.74
space group	$P\overline{1}$	P1	$P2_{1}/c$
a, Å	14.1272(3)	13.1069(5)	19.1438(10)
b, Å	15.6818(4)	14.6343(5)	9.9999(4)
<i>c</i> , Å	19.7114(5)	17.3230(6)	13.7463(5)
α, °	88.280(1)	66.088(3)	90.00
β, °	77.085(1)	81.683(3)	103.304(3)
γ, °	87.828(1)	87.985(3)	90.00
$V, Å^3$	4252.29(18)	3004.6(2)	2560.9
Ζ	2	2	2
$\rho_{\rm calcd}$, g cm ⁻³	1.366	1.537	1.287
Т, К	150	100	200
Radiation type	Μο <i>Κ</i> α	Cu Kα	Μο <i>Κ</i> α
Diffractometer	Nonius Kappa CCD diffractometer	Rigaku Rapid II curved image plate	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	R1 = 0.0543	R1 = 0.0719	R1 = 0.0435
$(I > 2\sigma(I))$	wR2 = 0.1506	wR2 = 0.1907	wR2 = 0.0997
\overrightarrow{OP} on \overrightarrow{F}^2	1.028	1.039	0.986

Computational Details



Figure S38. Contour plots of [1a']⁺, [3']²⁺, and [5']²⁺ and [4b']²⁺.

The LUMO and LUMO +1 in $[\mathbf{4b'}]^{2+}$ are dominated by the antibonding combination of the $d_x^{2} \cdot {}_y^2$ (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 $[\mathbf{3'}]^{2+}$ where the LUMO and LUMO+1 have substantial mixing of the d_z^2 (Co) with the σ^* based orbitals on the *gem*-DEE bridge. The LUMO of $[\mathbf{5'}]^{2+}$ 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 $[\mathbf{1a'}]^+$ are similar to unoccupied orbitals of $[\mathbf{3'}]^{2+}$ and $[\mathbf{4b'}]^{2+}$.

All calculated complexes have similar HOMO, HOMO-1, and HOMO-2 contour plots which represent part of the filled Co t_{2g} set. It is clear from Figure S21 that the HOMO is a combination of the d_{xz} (Co) with the antibonding combination of the π_{\perp} (DEE) (perpendicular, out-of-plane (C=C)) orbitals and vinyl π (C=C), whereas the HOMO-1 is composed of the antibonding combination of the d_{yz} (Co) and the antibonding π_{\parallel} (DEE) (parallel, in-plane (C=C)) orbitals, without contribution from the vinyl π (C=C) unit. The HOMO-2 orbital is solely the antibonding combination of the d_{xz} (Co) and the antibonding combination of the π_{\perp} (DEE). Compounds $[3^{r}]^{2+}$ and $[4b^{r}]^{2+}$ have a HOMO-3 composed of the antibonding combination of the d_{yz} (Co) with the bonding π_{\parallel} (DEE) orbitals and σ^* orbital of the vinyl group, with significantly more contribution from the axial π (C=C) or Cl *p*-orbitals.

Optimized geometries

The geometries of $[3']^+$, $[4a']^{4+}$, and $[4b']^{2+}$ 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 $[3']^{2+}$ using DFT method at the LanL2DZ level. Hydrogen atoms were omitted for clarity.

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

Table S3. Relevant bond lenghts (Å) and angles (deg) computed for $[3']^{2+}$.

Cl1-Co1-C1	179.746
Cl2-Co2-C5	179.745
C1-C2-C3	176.140
C2-C3-C4	117.720



Figure S40. Fully optimized structure of [**4a**']⁴⁺ using DFT method at the LanL2DZ level. Hydrogen atoms were omitted for clarity.

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Table S4 Relevant bond	lengths $(Å)$ and angles	(deg) computed for $[4g']^{4+}$
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Co1-N1	2.016
Co1-N2	2.021
Co1-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 $[4b']^{2+}$ using DFT method at the LanL2DZ level. Hydrogen atoms were omitted for clarity.

Co1-N1	2.020
Co1-N2	2.018
Co1-N3	2.019
Co1-N4	2.019
Co2-N5	2.018
Co2-N6	2.019
Co2-N7	2.019
Co2-N8	2.018
Col-Cl	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

Table S5. Relevant bond lenghts (Å) and angles (deg) computed for $[4b']^{2+}$.

C9-C10	1.247
C11-C12	1.247
C10-Si1	1.869
C12-Si2	1.869
C1-Co1-C9	179.664
C5-Co2-C11	179.594
C1-C2-C3	176.260
C2-C3-C4	117.799

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