Supporting Information

Stepwise Synthesis of Bis-Alkynyl Co^{III}(cyclam) Complexes under Ambient Conditions

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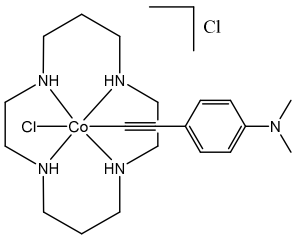
Contents

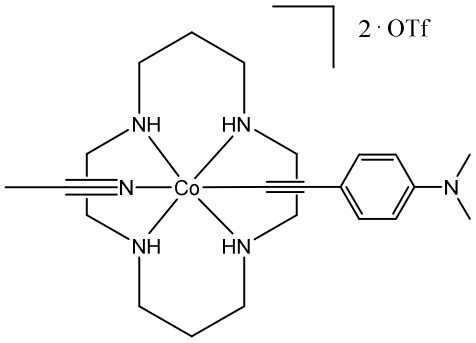
Experimental Details

General Experimental. All reagents were used as received. (Pentafluorophenyl)acetylene was synthesized using literature procedures.[1] UV-vis spectra were obtained with a Jasco V-670 spectrophotometer. FT-IR spectra were measured on a Jasco FT/IR-6300 as neat samples. ^{1}H-NMR spectra were obtained using a Varian Mercury 300 NMR, with chemical shifts (δ) referenced to the residual solvent signal (CH_3CN at 1.93 ppm). Voltammograms were recorded on a CHI620A voltammetric analyzer with a glassy carbon working electrode (diameter = 2 mm), a Pt-wire auxiliary electrode and a $Ag/AgNO_3$ reference electrode filled with 10 mM $AgNO_3$ and 0.1 M Bu_4NPF_6 in dry MeCN or DCM. The concentration of analyte was always 1.0 mM in 4 mL dry MeCN or DCM (thoroughly degassed by Ar purging). Potentials were corrected using an internal ferrocene standard at the end of runs.



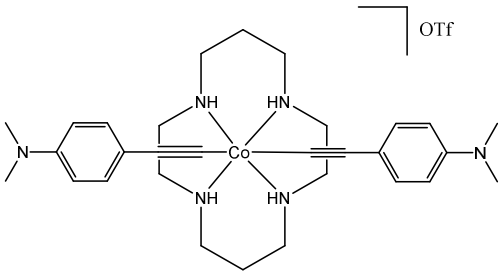
Preparation of [Co(cyclam)($C_2C_6H_4NMe_2$)Cl]Cl (1): In a round bottom flask 350 mg (0.96 mmol) of [Co(cyclam)Cl_2]Cl[2] was dissolved in 70 ml of MeOH. To the solution was added 1 ml (7 mmol) of Et_3N and 153 mg (1.05 mmol) of $HC_2C_6H_4NMe_2$. The solution was refluxed for 24h, and a gradual shift in color from green to red was observed. Solvent was removed and purification was performed on a silica gel pad, rinsing first with EtOAc, and then eluting **1** with an EtOAc/MeOH (5:1) mixture. Complex **1** was then recrystallized by the addition of Et_2O to a concentrated solution in MeOH yielding a red crystalline material. Crystals suitable for single crystal X-ray diffraction were obtained from the slow diffusion of Et_2O into a concentrated

solution in MeOH. Yield: 335 mg (0.71 mmol) (74% based on [Co(cyclam)Cl_2]Cl) Data for **1**: ESI-MS (MeOH): 438-[Co(cyclam)($C_2C_6H_4NMe_2$)Cl]$^+$. Elem. Anal. Found (calcd) for $C_{20}H_{34}N_5CoCl_2$ (**1** · H_2O): C, 48.31 (48.79); H, 7.67 (7.31); N, 13.07 (14.22). IR(cm^{-1}): Co-C≡C- 2113 (s). Electrochemistry ($E_{1/2}$ or $E_{p,a}$ or $E_{p,c}$, V; ΔE_p, V; $i_{backward}/i_{forward}$): A, 0.64, 0.0, 0.0; B, 0.26, 0.072, 0.56; C, -1.62, 0.0, 0.0; D, -2.021, 0.0, 0.0. ^{1}H NMR (CD_3CN, δ): 7.29 (d, *J* = 9.0 Hz, 2H, Ar-*H*), 6.66 (d, *J* = 9.3 Hz, 2H, Ar-*H*), 4.56 (br s, 2H, N-*H*), 4.48 (br s, 2H, N-*H*), 2.92 (s, 6H, N-C*H*$_3$), 2.90-2.39 (m, 16H, C*H*$_2$), 1.90 (t, 2H, CH_2), 1.49 (q, 2H, CH_2). Absorption spectrum (MeCN): λ_{max} (ε_{max}, $Lmol^{-1}cm^{-1}$): 510 (403), 395 (892).



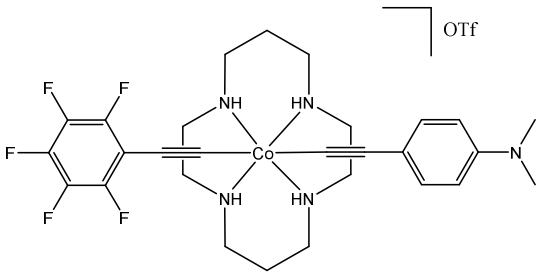
Preparation of [Co(cyclam)($C_2C_6H_4NMe_2$)NCMe](OTf)$_2$ (2): In a round bottom flask 300 mg (0.63 mmol) of **1** was dissolved in 50 ml of MeCN. To the solution was added 490 mg (1.91 mmol) of AgOTf. The solution was refluxed for 48h. Solvent was removed and purification was performed on a silica gel pad by first rinsing with EtOAc, and then eluting **2** with MeCN. Complex **2** was then recrystallized by the addition of Et_2O/EtOAc (1:1 v/v) to a concentrated solution in MeCN yielding a red-orange crystalline material. Crystals suitable for single crystal X-ray diffraction were obtained from the slow diffusion of Et_2O into a concentrated solution of MeCN. Yield: 310 mg (0.42 mmol) (66% based on Co of **1**) Data for **2**: ESI-MS (MeCN): 552-[Co(cyclam)(OTf)($C_2C_6H_4NMe_2$)]$^+$. Elem. Anal. Found (calcd) for $C_{24}H_{39}N_6O_7CoF_6S_2$ (**2**· H_2O): C, 37.72 (37.90); H, 4.88 (5.17); N, 10.84 (11.09). IR(cm^{-1}): (Co-C≡C-) 2128. Electrochemistry

($E_{1/2}$ or $E_{p,a}$ or $E_{p,c}$, V; ΔE_p, V; $i_{backward}/i_{forward}$): A, 1.22, 0.0, 0.0; B, 0.31, 0.074, 0.87; C, -1.39, 0.0, 0.0; D, -2.0, 0.0, 0.0. ^{1}H NMR (CD_3CN, δ): 7.05 (d, *J* = 8.4 Hz, 2H, Ar-*H*), 6.42 (d, *J* = 7.8 Hz, 2H, Ar-*H*), 4.48 (br s, 2H, N-*H*), 4.36 (br s, 2H, N-*H*), 2.66 (s, 6H, N-C*H*$_3$), 2.58-2.12 (m, 16H, C*H*$_2$), 1.71 (t, 2H, CH_2), 1.35 (q, 2H, CH_2). Absorption spectrum (MeCN): λ_{max} (ε_{max}, $Lmol^{-1}cm^{-1}$) 489 (252), 379 (338).



Preparation of [Co(cyclam)($C_2C_6H_4NMe_2$)$_2$]OTf (3): In a round bottom flask 100 mg (0.13 mmol) of **2** was dissolved in 50 ml of MeCN. To the solution was added 1 ml (7 mmol) of Et_3N and 85 mg (0.58 mmol) of $HC_2C_6H_4NMe_2$. The solution was refluxed for 24h, and a gradual shift in color from red to yellow was observed. Solvent was removed and purification was performed on a silica gel pad by first rinsing with EtOAc, and then eluting **3** with an EtOAc/MeOH (9:1) mixture. Complex **3** was then recrystallized by the addition of pentane to a concentrated solution in methylene chloride yielding a yellow crystalline material. Crystals suitable for single crystal X-ray diffraction were obtained from the slow diffusion of Et_2O into a concentrated solution of CD_3CN. Yield: 41 mg (0.06 mmol) (44% based on **2**) Data for **3**: ESI-MS (MeCN): 547-[Co(cyclam)($C_2C_6H_4NMe_2$)$_2$]$^+$. Elem. Anal. Found (calcd) for $C_{31}H_{44}N_6CoF_3O_3S$ (**3** · H_2O): C, 52.61 (52.09); H, 6.49 (6.49); N, 11.99 (11.76). IR(cm^{-1}): (Co-C≡C-) 2100. Electrochemistry ($E_{1/2}$ or $E_{p,a}$ or $E_{p,c}$, V; ΔE_p, V; $i_{backward}/i_{forward}$): A, 0.92, 0.0, 0.0; B, 0.23, 0.186, 0.90; C, -2.08, 0.0, 0.0. ^{1}H NMR (CD_3CN, δ): 7.06 (d, *J* = 8.7 Hz, 4H, Ar-*H*), 6.43 (d, *J* = 9.0 Hz, 4H, Ar-*H*),

3.87 (br s, 4H, N-*H*), 2.67 (s, 12H, N-CH_3), 2.62-2.12 (m, 16H, CH_2), 1.66 (t, 2H, CH_2), 1.05 (q, 2H, CH_2). Absorption spectrum (MeCN): λ_{max} (ε_{max}, $Lmol^{-1}cm^{-1}$) 470 (180), 328 (10155).



Preparation of [Co(cyclam)($C_2C_6H_4NMe_2$)($C_2C_6F_5$)]OTf (4): In a round bottom flask 100 mg (0.13 mmol) of **2** was dissolved in 50 ml of MeCN. To the solution was added 1 mL (7 mmol) of Et_3N and 110 mg (0.58 mmol) of $HC_2C_6F_5$. The solution was refluxed for 24h, and a gradual shift in color from red to yellow was observed. Solvent was removed and purification was performed on a silica gel pad by first rinsing with EtOAc, and then eluting **4** with an EtOAc/MeOH (7:1) mixture. Complex **4** was then recrystallized by the addition of pentane to a concentrated solution in methylene chloride yielding a yellow crystalline material. Crystals suitable for single crystal X-ray diffraction were obtained from the slow diffusion of hexane into a concentrated solution of methylene chloride. Yield: 47 mg (0.06 mmol) (47% based on **2**) Data for **4**: ESI-MS (MeOH): 594-[Co(cyclam)($C_2C_6F_5$)($C_2C_6H_4NMe_2$)]$^+$. Elem. Anal. Found (calcd) for $C_{29}H_{34}N_5CoF_8O_3S$ (**4**$\cdot 2H_2O$): C, 44.50 (44.68); H, 4.48 (4.91); N, 8.78 (8.98). IR(cm^{-1}): (Co-*C*≡*C*-C_6F_5) 2115, (Co-*C*≡*C*- $C_6H_4N(CH_3)_2$) 2094. Electrochemistry ($E_{1/2}$ or $E_{p,a}$ or $E_{p,c}$, V; ΔE_p, V; $i_{backward}/i_{forward}$): A, 1.05, 0.0, 0.0; B, 0.23, 0.126, 0.93; C, -1.86, 0.134, 0.59. ^{1}H NMR (CD_3CN, δ): 7.11 (d, *J* = 8.7 Hz, 2H, Ar-*H*), 6.47 (d, *J* = 8.7 2H, Ar-*H*), 4.02 (br s, 2H, N-*H*), 3.83 (br s, 2H, N-*H*), 2.69 (s, 6H, N-CH_3), 2.63-2.13 (m, 16H, CH_2), 1.65 (t, 2H, CH_2), 1.12 (q, 2H, CH_2). Absorption spectrum (MeCN): λ_{max} (ε_{max}, $Lmol^{-1}cm^{-1}$) 460 (183), 369 (703).

IR and UV-vis spectra

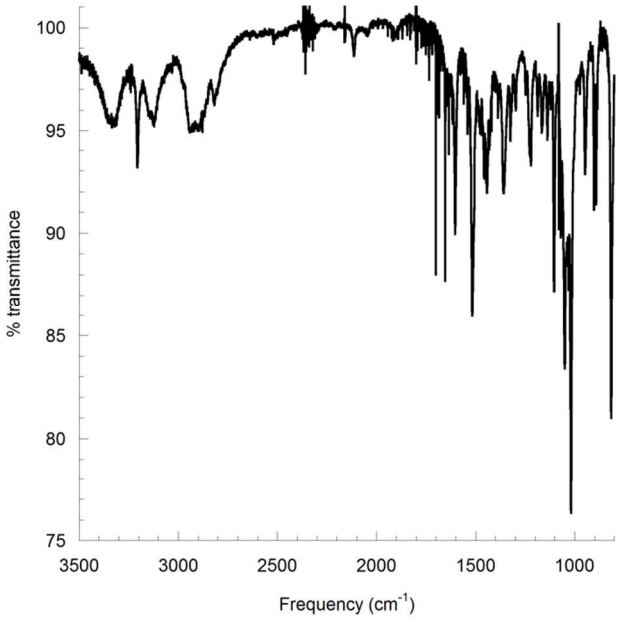


Figure S1. IR absorption spectrum of **1**.

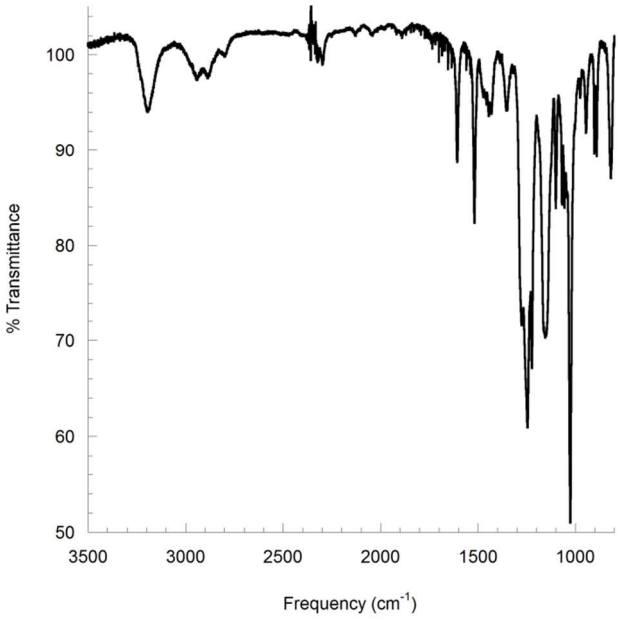


Figure S2. IR absorption spectrum of **2**.

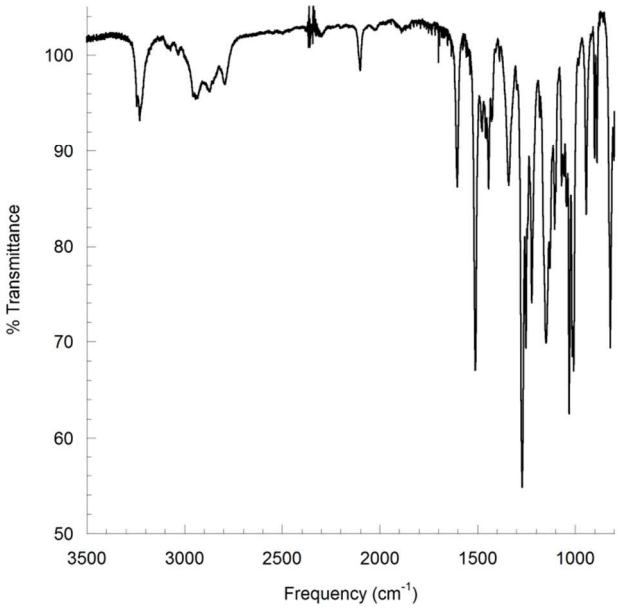


Figure S3. IR absorption spectrum of **3**.

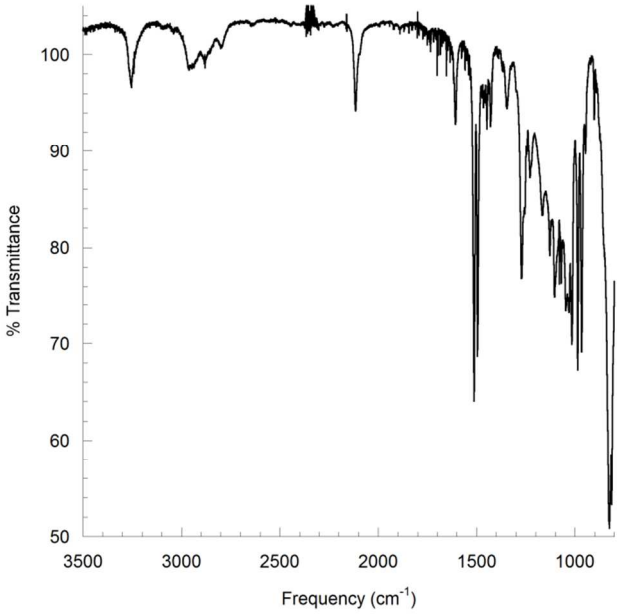


Figure S4. IR absorption spectrum of **4**.

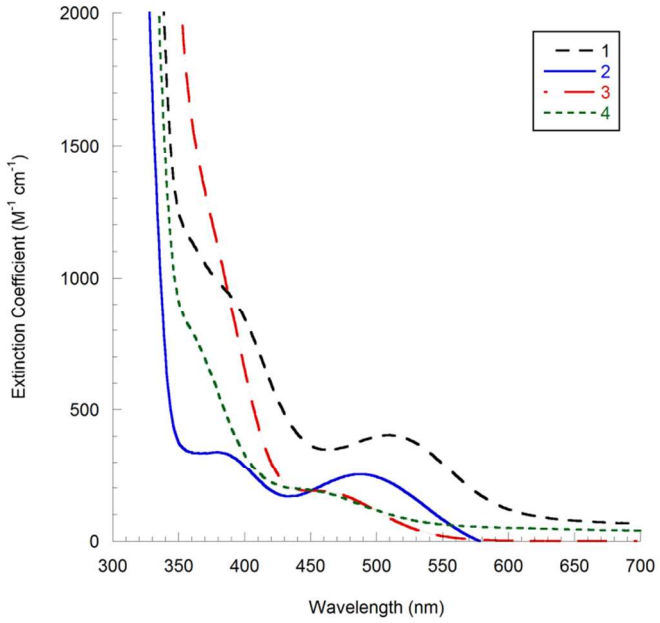


Figure S5. UV-vis absorption spectra of **1**-**4** in acetonitrile.

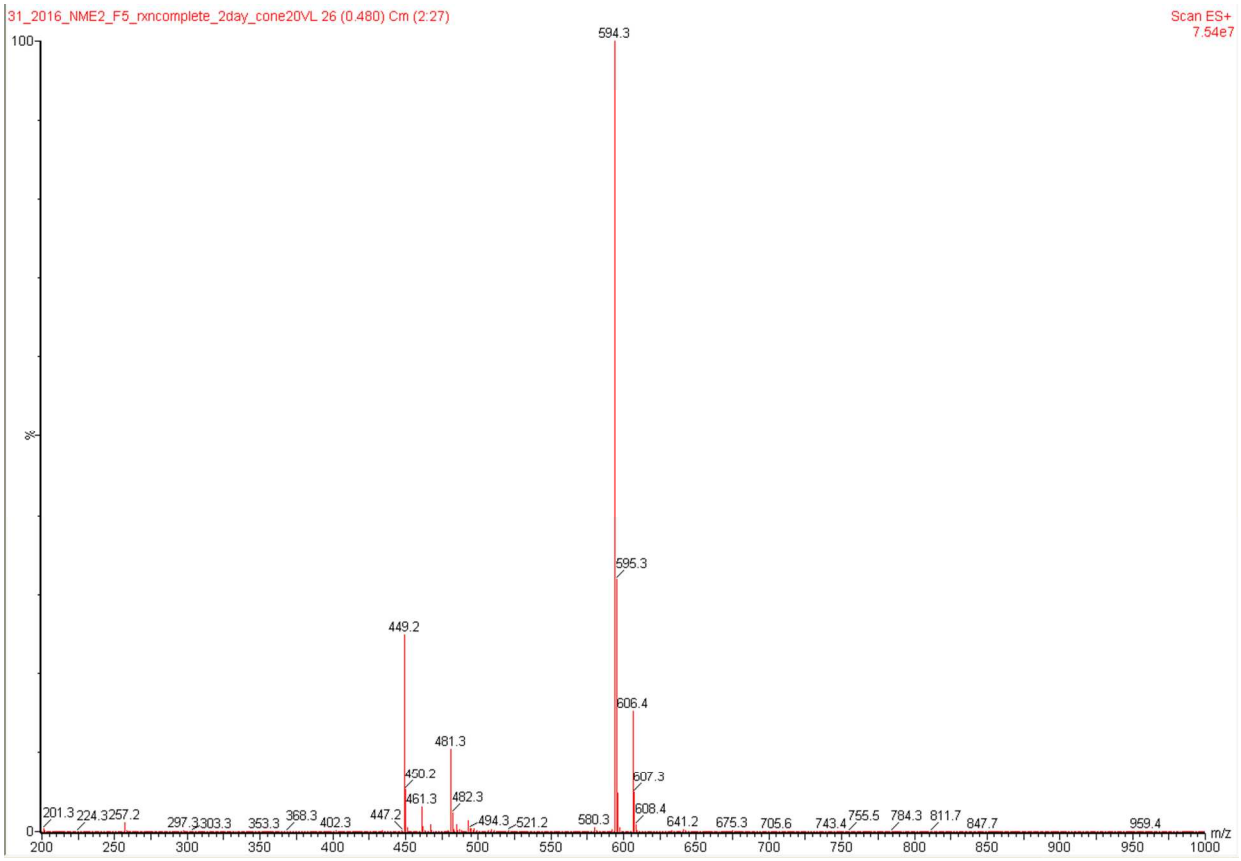


Figure S6. MS data for the reaction mixture of **4** after 24h shows no observable scrambling of acetylides as is the case of lithium reagents. No peaks corresponding to **3** (m/z = 547) or *trans*-$[Co(cyclam)(C_2C_6F_5)_2]^+$ (calculated to be at m/z = 641) are present.

Crystal structures

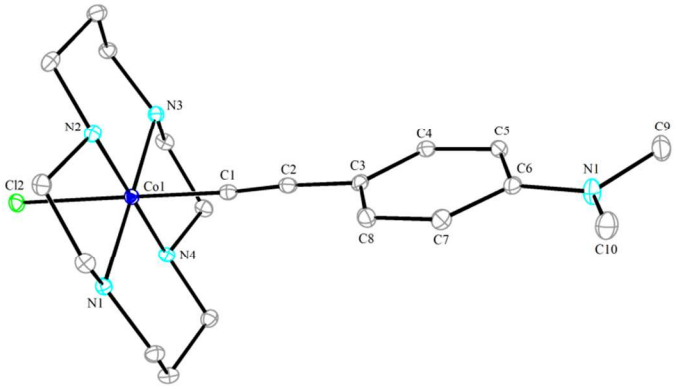


Figure S7. ORTEP plot of $\mathbf{1}^+$ at 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Co1-N_{av}, 1.979[2]; Co1-Cl2, 2.3177(4); Co1-C1, 1.890(2); C1-C2, 1.201(2); C2-C3, 1.444(2); C6-N1, 1.376(2); Cl1-Co1-C1, 178.42(4); C2-C1-Co1, 172.3(2); C1-C2-C3, 174.2(2); C6-N1-C9, 121.3(2).

Crystallographic Details:

General Procedures. X-ray diffraction data for **1-4** were collected using a Nonius Kappa CCD diffractometer with Mo-Kα radiation (λ = 0.71073 Å), or a Rigaku Rapid II curved image plate diffractometer with Cu-Kα (λ = 1.54178 Å). The Nonius Kappa CCD instrument features a fine focus sealed tube X-ray source with graphite monochromator. The Rigaku Rapid II diffractometer is equipped with an X-ray microsources with a laterally graded multilayers (Goebel) mirror for monochromatization. Single crystals were mounted on Mitegen micromesh or loop mounts using a trace of mineral oil and cooled in-situ to 100(2) K for data collection. Data on the Kappa CCD diffractometer were collected using the Nonius Collect software[4]. Data obtained from the Rigaku Rapid II instrument were collected using the dtrek option of CrystalClear.[5] and processed using HKL3000[5]. Both kinds of data sets were processed using HKL3000[6] and data were corrected for absorption and scaled using Scalepack[6]. The space groups were assigned and the structures were solved by direct methods using XPREP within the SHELXTL suite of programs[7] and refined by full matrix least squares against F^2 with all

reflections using Shelxl2013 or 2014[8] using the graphical interface Shelxle[9]. If not specified otherwise H atoms attached to carbon and nitrogen atoms and hydroxyl hydrogens 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, and 0.98 Å for aliphatic C-H and CH_3 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 $U_{eq}(C)$ with 1.5 for CH_3, and 1.2 for C-H units, respectively. Non meroheric twinning was handled using the programs Rotax[10] and WinGX[11].

In compound **2** one of the two triflate anions is disordered over one major and two minor orientations. The three 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 the occupancy rates refined to 0.817(2), 0.058(2) and 0.1249(18).

In compound **3** the crystal under investigation was found to be slightly twinned by non-merohedry. Programs compatible with the Nonius KappaCCD diffractometer and HKL3000 lack the ability to simultaneously integrate more than one twin domain. With no data set obtainable through simultaneous integration of both twin domains, the data were instead handled as if not twinned, with only the major domain integrated, and converted into an hklf 5 type format hkl file after integration using the "Make HKLF5 File" routine as implemented in WinGX. The twin law and matrix were obtained using the program ROTAX as implemented in WinGX. The twin operation was identified as a 180 degree rotation around 1 0 0 in the reciprocal lattice direction, the twin matrix as 1 0.591 0.293, 0 -1 0, 0 0 -1. The Overlap R1 and R2 values in the "Make HKLF5 File" routine used were 0.18, i.e. reflections with a discriminator function less or equal to overlap radius of 0.18 were counted as overlapped, all others as single. The discriminator function used was the "delta function on index non-integrality". No reflections were omitted.

The structure was solved using direct methods with all reflections of component 1. The structure was refined using the hklf 5 routine with all reflections of component 1 (including the verlapping ones) as obtained from WinGX, resulting in a BASF value of 0.0607(9). No R_{int} value is obtainable for the hklf 5 type file using the WinGX routine.

Disorder is observed in the structure, affecting the triflate anions, the solvate ether and acetonitrile molecules, as well as one of the dimethyl amine substituents of one of the four crystallographically independent cations. The two triflate cations are disordered by rotation. The molecule of S1A was refined as disordered over two orientations. That of S1B as disordered over three orientations. All five triflate moieties were restrained to have similar geometries (SAME command in Skelxl). U^{ij} components of ADPs of atoms at each site were restrained to be similar if closer than 1.7 Å. Subject to these conditions the occupancy rates refined to 0.667(9) and 0.333(9) for the moieties of S1A and S1C, and to 0.513(4), 0.364(3) and 0.122(2) for the moieties of S1B, S1D and S1E. One of the dimethyl amine substituents was refined as disordered by inversion at the nitrogen. The two moieties were restrained to have similar geometries, and U^{ij} components of ADPs were restrained to be similar if closer than 1.7 Å. Subject to these conditions the occupancy rates refined to 0.55(3) and 0.45(3).

Solvate acetonitrile and ether molecules are extensively disordered, with one site occupied by mostly acetonitrile, and a neighboring site by mostly ether. The latter site is in close proximity to an inversion center, and part of the disordered ether molecules are incompatible with their own symmetry equivalent counterparts. Due to the extensive disorder and overlap of neighboring disordered molecules no attempts were made to ensure exact full occupancy for each site. All ether molecules and all acetonitrile molecules were each restrained to have similar geometries. For the acetonitrile molecules the N-C triple bond length was restrained to approximately 1.15(2) Angstrom, the 1,3 N...C distance to at least 2.50(2) Å. U^{ij} components of ADPs were restrained to be similar if closer than 1.7 Å. Subject to these conditions the occupancy rates refined to 0.396(7), 0.220(6) and 0.076(6) for the three ether molecule moieties, and to 0.400(14), 0.299(14), 0.150(8) and 0.184(10) for the four acetonitrile moieties. The forth of these moieties does overlap mostly with the ether molecules, the other three take up the other solvate occupied site.

TableS1. Experimental details

	1	**2**
Crystal data		
Chemical formula	$C_{20}H_{34}ClCoN_5 \cdot 2(CH_4O) \cdot Cl$	$C_{22}H_{37}CoN_6 \cdot 2(CF_3O_3S)$
M_r	538.43	742.64
Temperature (K)	100	100
Crystal system, space group	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/n$
a, b, c (Å)	10.3649 (2), 19.2578 (5), 12.8446 (3)	9.2529 (1), 23.1380 (3), 15.0659 (2)
α, β, γ (°)	90, 97.7118 (19), 90	90, 95.7595 (5), 90
V (Å^3)	2540.66 (10)	3209.23 (7)
Z	4	4
F(000)	1144	1536
D_x (Mg m^{-3})	1.408	1.537
Radiation type	Mo $K\alpha$	Mo $K\alpha$
No. of reflections for cell measurement	25671	83733
θ range (°) for cell measurement	1.9–30.5	2.4–30.0
μ (mm^{-1})	0.91	0.75
Crystal shape	Rod	Rod
Colour	Red	Red
Crystal size (mm)	0.35 × 0.19 × 0.18	0.55 × 0.20 × 0.11
Data collection		
Diffractometer	Nonius Kappa CCD diffractometer	Nonius Kappa CCD diffractometer
Radiation source	fine focus X-ray tube	fine focus X-ray tube
Monochromator	Graphite	Graphite
Scan method	ω and ϕ scans	ω and ϕ scans
Absorption correction	multi-scan, *SCALEPACK* (Otwinowski & Minor, 1997)	multi-scan, *SCALEPACK* (Otwinowski & Minor, 1997)
T_{min}, T_{max}	0.697, 0.853	0.693, 0.922
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	25661, 6771, 5288	83733, 8632, 6980
R_{int}	0.051	0.039
θ values (°)	θ_{max} = 30.5, θ_{min} = 1.9	θ_{max} = 30.0, θ_{min} = 2.4
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.714	0.704
Range of h, k, l	h = -11→13, k = -23→26, l = -13→16	h = -12→12, k = -31→31, l = -20→19
Refinement		

$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.031, 0.076, 1.06	0.033, 0.087, 1.05
No. of reflections	6771	8632
No. of parameters	296	557
No. of restraints	0	1123
	$w = 1/[\sigma^2(F_o^2) + (0.0341P)^2 + 0.2295P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0405P)^2 + 1.607P]$ where $P = (F_o^2 + 2F_c^2)/3$
H-atom treatment	H-atom parameters were constrained	H-atom parameters were constrained
$(\Delta/\sigma)_{max}$	0.002	0.001
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.46, -0.45	0.41, -0.53

	3	**4**
Crystal data		
Chemical formula	$C_{30}H_{44}CoN_6 \cdot CF_3O_3S \cdot 0.346(C_4H_{10}O) \cdot 0.516(C_2H_3N)$	$C_{28}H_{34}CoF_5N_5 \cdot CF_3O_3S$
M_r	743.49	743.60
Temperature (K)	100	100
Crystal system, space group	Triclinic, $P\overline{1}$	Orthorhombic, *Pbca*
a, *b*, *c* (Å)	13.6550 (3), 16.9720 (3), 17.1983 (5)	22.9383 (13), 12.1841 (8), 23.0305 (18)
α, β, γ (°)	93.6056 (8), 99.2916 (8), 110.8429 (9)	90, 90, 90
V (Å^3)	3644.62 (15)	6436.6 (8)
Z	4	8
F(000)	1567.4	3056
D_x (Mg m^{-3})	1.355	1.535
Radiation type	Mo *K*α	Cu *K*α
No. of reflections for cell measurement	37807	50866
θ range (°) for cell measurement	1.8–28.3	5.3–72.8
μ (mm^{-1})	0.59	5.56
Crystal shape	Plate	Plate
Colour	Orange	Orange
Crystal size (mm)	0.45 × 0.43 × 0.20	0.41 × 0.31 × 0.01
Data collection		
Diffractometer	Nonius Kappa CCD diffractometer	Rigaku Rapid II curved image plate diffractometer
Radiation source	fine focus X-ray tube	microfocus X-ray tube
Monochromator	Graphite	Laterally graded multilayer (Goebel) mirror
Scan method	ω and ϕ scans	ω scans
Absorption correction	multi-scan, *SCALEPACK* (Otwinowski & Minor, 1997)	multi-scan, *SCALEPACK* (Otwinowski & Minor, 1997)
T_{min}, T_{max}	0.606, 0.892	0.300, 0.946
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	37807, 37807, 27588	50866, 6189, 3633
R_{int}	n/a (non-merohedric twin)	0.162
θ values (°)	θ_{max} = 28.3, θ_{min} = 1.8	θ_{max} = 72.8, θ_{min} = 5.3
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.667	0.619
Range of *h*, *k*, *l*	*h* = -17→18, *k* = -22→22, *l* = -22→22	*h* = -27→27, *k* = -14→14, *l* = -26→28

Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.060, 0.175, 1.01	0.097, 0.289, 1.04
No. of reflections	37807	6189
No. of parameters	1337	426
No. of restraints	1696	0
	$w = 1/[\sigma^2(F_o^2) + (0.0939P)^2 + 4.1876P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.1049P)^2 + 30.4873P]$ where $P = (F_o^2 + 2F_c^2)/3$
H-atom treatment	H-atom parameters were constrained	H-atom parameters were constrained
$(\Delta/\sigma)_{max}$	0.003	< 0.001
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.59, -0.49	0.68, -1.27

Computer programs: Nonius Collect (Nonius, 1998), *CrystalClear*-SM Expert 2.1 b32 (Rigaku, 2014), *HKL-3000* (Otwinowski & Minor, 1997), *SHELXS97* (Sheldrick, 2008), *SHELXL2014*/7 (Sheldrick, 2014), SHELXLE Rev714 (Hübschle *et al.*, 2011).

Cyclic voltammograms

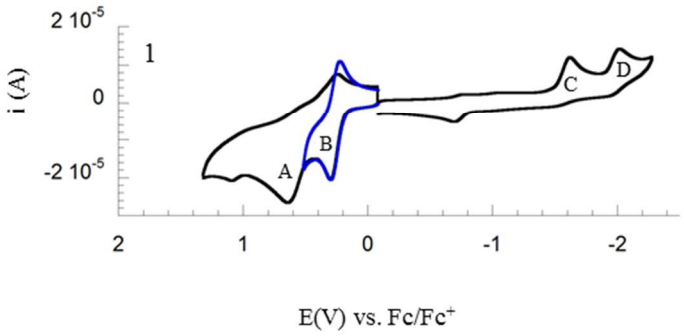


Figure S8: Cyclic voltammagrams of **1** in 0.1 M MeCN solution of Bu_4NPF_6 at a scan rate of 0.10 V/s (black trace). Anodic scan of **1** to 0.6 V, showing improved reversibility of **B** (blue trace) at lower potentials.

Differential pulse voltammogram

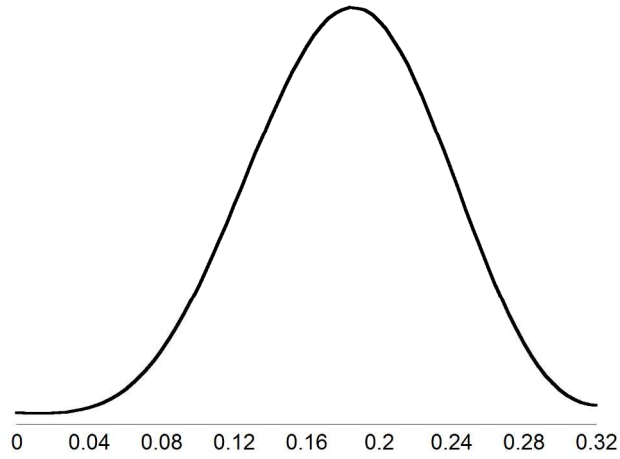


Figure S9. Differential pulse voltammagram showing the 1st oxidation $(NMe_2\text{-}NMe_2)^+$ of [**3**]**(OTf)** in DCM with 0.1M NBu_4PF_6 under Taube-Richardson conditions (pulse amplitude = 10 mV).

Computational Details

The geometries of [**3'**]$^+$, and [**4'**]$^+$ 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. The calculation was accomplished by using the Gaussian03 program package.[4]

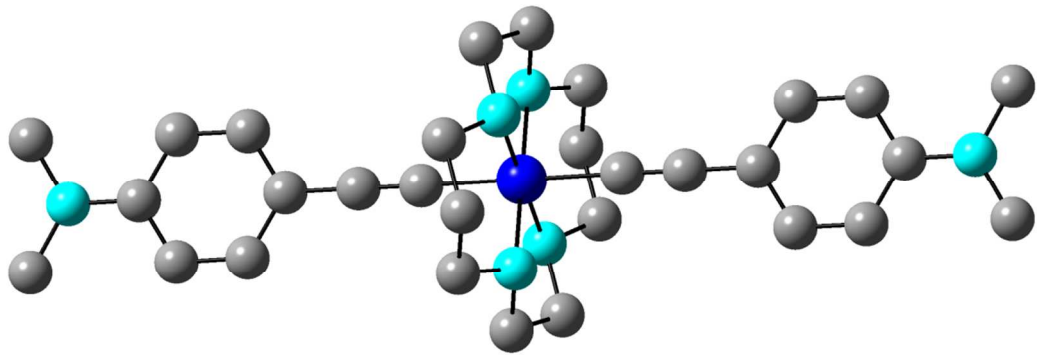


Figure S10. Fully optimized structure of [**3'**]$^+$ using DFT method at the LanL2DZ level.

Table S2. Relevant bond length (Å) and angles (deg) computed for [**3'**]$^+$.

Co1-N1	2.01822
Co1-N2	2.01700
Co1-N3	2.01822
Co1-N4	2.01700
Co1-C1	1.95550
C1-C2	1.24466
C2-C3	1.44008
C3-C4	1.41912

C3-C8	1.41894
C4-C5	1.39765
C5-C6	1.42833
C6-C7	1.42831
C7-C8	1.39773
C6-N5	1.39027
C9-N5	1.46832
C10-N5	1.46831
C1-Co-C1’	180.00000
Co1-C1-C2	176.24215
C2-C3-C4	121.51154
C6-N5-C9	120.19868

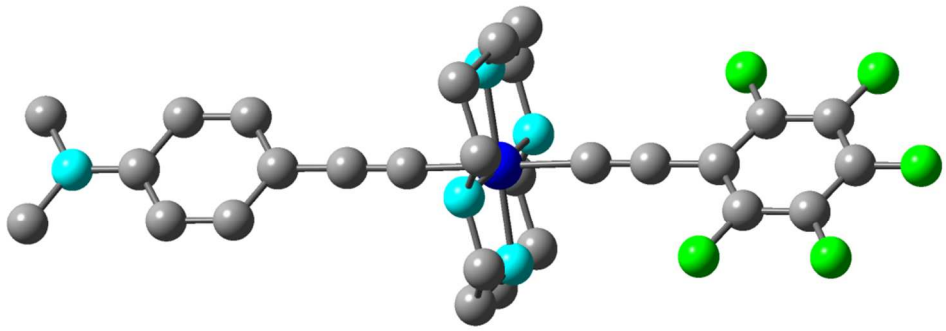


Figure S11. Fully optimized structure of [**4'**]$^{+}$ using DFT method at the LanL2DZ level.

Table S3. Relevant bond length (Å) and angles (deg) computed for [**4'**]$^{+}$.

Co1-N1	2.01754
Co1-N2	2.01649
Co1-N3	2.02140
Co1-N4	2.02176
Co1-C1	1.95147
C1-C2	1.24031
C2-C3	1.42788
C3-C4	1.41236
C3-C8	1.41224
C4-C5	1.39727
C5-C6	1.40216
C6-C7	1.40212
C7-C8	1.39733
Co1-C9	1.94413
C9-C10	1.24401
C10-C11	1.43953
C11-C12	1.41918
C11-C16	1.41924
C12-C13	1.39714
C13-C14	1.42899

C14-C15	1.42900
C15-C16	1.39707
C14-N5	1.38868
N5-C17	1.46903
N5-C18	1.46907
C1-Co-C9	179.66673
Co1-C1-C2	175.93343
C1-C2-C3	179.04337
C2-C3-C4	121.93349
Co1-C9-C10	175.65246
C9-C10-C11	179.01916
C10-C11-C12	121.45834
C14-N5-C17	120.22733

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