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Supplementary Information

for

Diisocyanoarene-linked pentacarbonylvanadate(I-) ions as building blocks in a supramolecular charge-transfer framework assembled through noncovalent π-π and contact ion interactions

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A. SYNTHESES AND CHARACTERIZATION OF 1a, 1b, and 2

A1. General Procedures, Starting Materials and Equipment. Unless specified otherwise, all operations were performed under an atmosphere of 99.5% argon further purified by passage through columns of activated BASF catalyst and molecular sieves. All connections involving the gas purification systems were made of glass, metal, or other materials impermeable to air. Solutions were transferred via stainless steel needles (cannulas) whenever possible. Standard Schlenk techniques were employed with a double manifold vacuum line. Both CH_3CN and CD_3CN, as well as CH_2Cl_2, were distilled over CaH_2. Diethyl ether and THF were distilled from Na/benzophenone. Heptane and pentane were distilled from Na/benzophenone dissolved in a minimum amount of diglyme. DMSO was distilled over P_2O_5. Following purification, all solvents, including deuterated solvents, were stored under argon.

Infrared spectra were recorded on a PerkinElmer Spectrum 100 FTIR spectrometer with samples sealed in 0.1 mm NaCl cells or between NaCl disks. NMR samples were analyzed on Bruker Avance 400 or 500 spectrometers. ^1H and ^{13}C NMR chemical shifts are given with reference to residual solvent resonances relative to $SiMe_4$. ^{51}V NMR chemical shifts are referenced to neat $VOCl_3$. A solution of $[Et_4N][V(CO)_6]$ in CD_3CN was used as an external ^{51}V NMR reference ($\delta(^{51}V) = -1955.0$ ppm vs. neat $VOCl_3$). UV-Vis spectra were recorded in CH_2Cl_2 or CH_3CN at 24 °C using a CARY 100 spectrophotometer.

Cyclic voltammetry (CV) experiments on *ca.* 2×10^{-3} M solutions of **1a**, **1b**, and **2** in CH_3CN were conducted at room temperature using an EPSILON (Bioanalytical Systems Inc., West Lafayette, IN) electrochemical workstation. The electrochemical cell was placed in an argon-filled Vacuum Atmospheres dry-box. Tetrabutylammonium hexafluorophosphate (0.1 M solution in CH_3CN) was used as a supporting electrolyte. Cyclic voltammograms were recorded at 22 ± 2 °C using a three component system consisting of a platinum working electrode, a platinum wire auxiliary electrode, and a glass encased non-aqueous silver/silver chloride reference electrode. The reference Ag/Ag^+ electrode was monitored with the ferrocenium/ferrocene couple. IR compensation was achieved before each CV run by measuring the uncompensated solution resistance followed by incremental compensation and circuit stability testing. Background cyclic voltammograms of the electrolyte solution were recorded before adding the analytes. The half-wave potentials ($E_{1/2}$) were determined as averages of the cathodic and anodic peak potentials of reversible/partially reversible couples and are referenced to the external FcH^+/FcH couple.[1]

Melting points are uncorrected and were determined for samples in capillary tubes sealed under argon. Elemental analyses were carried out by Desert Analytics (now Columbia Analytical Services), Tucson, Arizona.

Compounds $[Et_4N][V(CO)_6]$,[2] $[Cp_2Co][V(CO)_6]$,[3] $V(CO)_6$,[4] $[Cp_2Co][BF_4]$,[5] 1,4-CNC_6Me_4NC,[6] and CNXyl (Xyl = 2,6-dimethylphenyl)[7] were prepared according to literature procedures. Complex $[Et_4N][V(CO)_5(DMSO)]$, generated in THF by the method of Rehder,[8] was used *in situ*. Other reagents were obtained from commercial sources and used as received.

A2. Synthesis of 1a. A yellow solution of $[Et_4N][V(CO)_6]$ (0.3466 g, 0.9924 mmol) and DMSO (0.4 mL, 5.6 mmol) in 80 mL of THF was irradiated using a Hanovia Hg 450 W immersion lamp for 4 hrs at 22 °C with stirring. 1,4-Diisocyanodurene (0.0914g, 0.4962 mmol) dissolved in 20 mL of THF was added to the above solution and the mixture was stirred for 15 hrs. Then, the reaction mixture was concentrated to about 20 mL and stirred for an additional 2-hour period. Pentane (30mL) was added to the reaction flask and the mixture was vigorously stirred for 30 min. An oily dark red precipitate formed, which was washed with toluene (2×20 mL). The toluene washings were carefully removed via cannula. After addition of 50 mL of pentane with stirring, the solution/slurry was filtered. The filter-cake was dissolved in THF. This THF solution was filtered; the filtrate was layered with 150 mL of pentane and stored at -35 °C for 3 hrs. The magenta precipitate was filtered off, washed with pentane (2×10 mL) and dried at 10^{-2} torr to provide **1a** (0.2523 g, 0.3052 mmol) in a 62% yield as a free-flowing magenta solid. Mp 82-84 °C. Anal. Calcd. for $C_{38}H_{52}N_4O_{10}V_2$: C, 55.21; H, 6.34; N, 6.78. Found: C, 54.18; H, 6.30; N, 7.14. IR (CH_3CN): ν_{CN} 2061 w, ν_{CO} 1951 m, 1831 vs cm^{-1}. ^1H NMR (500 MHz, CD_3CN, 25°C): δ 1.20 (t, 24H, CH_2CH_3, $^3J_{H-H}$ = 7 Hz), 2.32 (s, 12H, CH_3), 3.16 (q, 16H, CH_2CH_3, $^3J_{H-H}$ = 7 Hz) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, CD_3CN, 25°C): δ 7.7 (CH_2CH_3), 16.4 (CH_3), 53.2 (CH_2CH_3) ppm. ^{51}V NMR (131.6 MHz, CD_3CN, 25°C): δ -1903.9 ppm; two ^{13}CO satellite doublets of the relative intensities 4:1 were also observed at -1904.2 ppm with $^1J(^{13}C-^{51}V)$ = 116.8 Hz and -1903.9 ppm with $^1J(^{13}C-^{51}V)$ = 167.5 Hz, respectively, as well a $C^{18}O$ satellite singlet at -1904.0 ppm. UV-Vis (CH_3CN, λ_{max} ($\varepsilon\times10^{-3}$ M^{-1} cm^{-1}), 24 °C): 489 (1.02) nm.

A3. Synthesis of 1b from $V(CO)_6$. A colourless solution of diisocyanodurene, 1,4-CNC_6Me_4NC (0.0716 g, 0.3886 mmol), in 100 mL of heptane was added to a cold (-70°C) canary yellow solution of hexacarbonylvanadium(0) (0.1702 g, 0.7772 mmol) in 200 mL of heptane in the dark with stirring. The reaction mixture was stirred at -70°C for 2 hours while acquiring a pale tangerine colour and then warmed to 0°C. FTIR of the solution/slurry in the ν_{CN} and ν_{CO} regions indicated essentially complete consumption of the starting materials. Then, an orange-brown solution of cobaltocene (0.1470 g, 0.7772 mmol) in 20 mL of CH_2Cl_2 was transferred to the reaction mixture in one portion at 0 °C and the mixture was vigorously stirred for 30 min. The resulting dark solid was filtered off, washed with CH_2Cl_2 (100 mL) and pentane (50 mL), recrystallized from CH_3CN/Et_2O, and dried at 10^{-2} torr to afford dark violet, nearly black, **1b** (0.3020 g, 0.3198 mmol) in a 73% yield. Compound **1b** decomposes without melting at 138°C. Anal. Calcd. for $C_{42}H_{32}Co_2N_2O_{10}V_2$: C, 53.41; H, 3.42; N, 2.97. Found: C, 52.89; H, 3.60; N, 3.38. IR (CH_3CN): ν_{CN} 2041 w br, ν_{CO} 1926 m br, 1847 s sh, 1839 vs, 1824 m sh cm^{-1}. UV-vis (CH_3CN, λ_{max} ($\varepsilon\times10^{-3}$ M^{-1} cm^{-1}), 24 °C): 484 (3.23) nm.

A4. Cation metathesis 1a → 1b. A mixture of cobaltocenium tetrafluoroborate (0.0818 g, 0.2963 mmol) and **1a** (0.1225 g, 0.1482 mmol) was dissolved in 80 mL of CH_2Cl_2. The resulting solution was stirred at 22 °C for 48 h to form a dark violet precipitate. After addition of *less* than 100 mL of heptane, the solid was filtered off, washed with 50 mL of heptane, and dried at 10^{-2} torr. Recrystallization from CH_3CN/Et_2O (20/150 mL) followed by drying of the product at 10^{-2} torr afforded a 53% yield of **1b** (0.0738g 0.0781 mmol), which was spectroscopically (FTIR, ^{1}H NMR) identical to *bona fide* **1b** described above in section A3.

A5. Synthesis of 1b from [Cp$_2$Co][V(CO)$_6$]. A solution of [Cp$_2$Co][V(CO)$_6$] (0.1573 g, 0.3855 mmol) and DMSO (0.2 mL, 2.8 mmol) in 80 mL of THF was irradiated using a Hanovia Hg 450 W immersion lamp for 4 h at 22 °C with stirring. Then, the red-orange reaction mixture was concentrated to about 20 mL under vacuum. 1,4-Diisocyanodurene (0.0355g, 0.1927 mmol) dissolved in 20 mL of THF was added to the above concentrated solution. The mixture was stirred for 10 hrs, concentrated to about 10 mL, and stirred for an additional 8-hour period. An oily black precipitate formed. Pentane (30 mL) was added to the reaction flask and the mixture was vigorously stirred for 30 min. Then, 20 mL of toluene was added with stirring, and the solution/slurry was allowed to settle. The solution was carefully removed by cannula, and the residue was washed with toluene (2×20 mL). The resulting dark violet, nearly black solid was washed with 50 mL of pentane and then triturated with an additional 50 mL of pentane. Filtration followed by drying at 10^{-2} torr provided crude **1b** as a dark violet powder. Recrystallization of this solid from CH_3CN/Et_2O gave microcrystalline **1b** (0.0572g, 0.0606 mmol) in a 31% yield. The product was spectroscopically (FTIR, NMR) identical to *bona fide* **1b** described above in section A3.

A6. Synthesis of 2. A colourless solution of 2,6-dimethylphenyl isocyanide (0.1970 g, 1.5019 mmol), in 70 mL of heptane was added to a yellow-green solution of hexacarbonylvanadium(0) (0.3325 g, 1.5183 mmol) in 100 mL of heptane at room temperature. The reaction mixture rapidly acquired a mustard colour. After stirring for 2 h, an orange-brown solution of cobaltocene (0.3234 g, 1.7100 mmol) was added to the reaction mixture at 22 °C to result in the formation of dark aqua-coloured slurry. This mixture was stirred for 1 hr and then filtered. The filter-cake was washed with heptane (2×30 mL) and recrystallized from THF/Et_2O to afford microcrystalline dark turquoise (bluish green) **2** (0.5425 g, 1.0610 mmol) in two crops in a 71% combined yield. Mp 104-106 °C (dec). Anal. Calcd. for $C_{18}H_{19}CoNO_5V$: C, 56.38; H, 3.75; N, 2.74. Found: C, 56.43; H, 4.01; N, 2.61. IR (CH_3CN): ν_{CN} 2053 w, ν_{CO} 1943 m, 1849 s sh, 1837 vs cm^{-1}. ^{1}H NMR (400 MHz, CD_3CN, 21 °C): δ 2.36 (s, 6H, CH_3), 5.35 (s, 10H, C_5H_5), 7.02 (t, 1H, *p*-H, $^3J_{H\text{-}H}$ = 8 Hz), 7.05 (d, 2H, *m*-H, $^3J_{H\text{-}H}$ = 8 Hz) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, CD_3CN, 21°C): δ 19.1 (CH_3), 88.9 (C_5H_5), 126.7, 128.6, 134.4 (aromatic *C*) ppm. UV-vis (CH_3CN, λ_{max} ($\varepsilon \times 10^{-3}$ M^{-1} cm^{-1}), 24 °C): 483 (1.75) nm.

B. X-RAY CHRYSTALLOGRAPHIC CHARACTERIZATION OF 1b

B1. Experimental

Black needle-shaped crystals of **1b** were grown by layering Et_2O over a nearly saturated solution of **1b** in CH_3CN at room temperature and then cooling the sample to +4 °C for several days. All manipulations with the crystals prior to transfer to the goniometer were performed in argon atmosphere. A full hemisphere of diffracted intensities (1850 10-second frames with an ω scan width of 0.30°) was measured for a single-domain specimen using graphite-monochromated MoKα radiation ($\lambda = 0.71073$ Å) on a Bruker SMART APEX CCD Single Crystal Diffraction System.[9] X-rays were provided by a fine-focus sealed x-ray tube operated at 50kV and 30mA. Lattice constants were determined with the Bruker SAINT software package using peak centers for 8659 reflections. A total of 41416 integrated reflection intensities having $2\theta < 60.20°$ were produced using the Bruker program SAINT.[10] The intensity data were corrected empirically for variable absorption effects using equivalent reflections.[11] The Bruker software package SHELXTL Version 6.10 was used to solve the structure using "direct methods" techniques. All stages of weighted full-matrix least-squares refinement were conducted using F_o^2 data with the SHELXTL software package.[12] A region of the unit cell containing disordered solvent molecules of crystallization (presumably acetonitrile) was modeled using the Squeeze option in PLATON.[13]

The final structural model incorporated anisotropic thermal parameters for all nonhydrogen atoms and isotropic thermal parameters for all hydrogen atoms. The two crystallographically-independent methyl groups in the dianion were included in the structural model as rigid groups (using idealized sp^3-hybridized geometry and a C-H bond length of 0.98 Å) which were allowed to rotate about their C-C bonds in least-squares refinement cycles. The remaining hydrogen atoms were included in the structural model as idealized atoms (assuming sp^2-hybridization of the carbon atoms and a C-H bond length of 0.95 Å). The isotropic thermal parameters of all idealized hydrogen atoms were fixed at values 1.2 (non-methyl) or 1.5 (methyl) times the equivalent isotropic thermal parameter of the carbon atom to which they are covalently bonded.

Thermal ellipsoid plots were made using ORTEP III program.[14] The displacement ellipsoids are drawn at the 50% probability level. Crystal data, data collection, solution, and refinement information for **1b** are summarized in Table S1. Tables S2 through S6 contain atomic coordinates, as well as metric and displacement parameters for **1b**.

Table S1. Crystal data and structure refinement for **1b**.

Empirical formula	$C_{42}H_{32}Co_2N_2O_{10}V_2$	
Formula weight	944.44	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Tetragonal	
Space group	$P4_2/n – C_{4h}^{4}$ (No. 86)	
Unit cell dimensions	**a** = 23.719 (1) Å	α= 90.000°
	b = 23.719 (1) Å	β= 90.000°
	c = 7.1617(8) Å	γ= 90.000°
Volume	4029.2(6) $Å^3$	
Z	4 molecular units	
Density (calculated)	1.557 Mg/m^3	
Absorption coefficient	1.319 mm^{-1}	
F(000)	1912	
Crystal size	0.46 x 0.16 x 0.10 mm^3	
Theta range for data collection	2.43° to 30.10°	
Index ranges	$-33 \le h \le 33$, $-33 \le k \le 33$, $-10 \le l \le 9$	
Reflections collected	41416	
Independent reflections	5907 [$R_{int} = 0.051$]	
Completeness to theta = 30.10°	99.6 %	
Absorption correction	SADABS	
Max. and min. transmission	1.000 and 0.746	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5907 / 0 / 264	
Goodness-of-fit on F^2	1.069	
Final R indices [I>2sigma(I)]	$R_1 = 0.050$, $wR_2 = 0.120$	
R indices (all data)	$R_1 = 0.070$, $wR_2 = 0.129$	
Largest diff. peak and hole	1.25 and -0.28 $e^-/Å^3$	

Table S2. Atomic coordinates and equivalent isotropic displacement parameters for **1b**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
V	174(1)	6565(1)	-1147(1)	24(1)
O(10)	-972(1)	5945(1)	-1053(3)	51(1)
O(11)	405(1)	6044(1)	-5060(2)	37(1)
O(12)	-340(1)	7588(1)	-3258(3)	47(1)
O(13)	-92(1)	7075(1)	2749(2)	37(1)
O(14)	603(1)	5490(1)	881(3)	52(1)
N(1)	1414(1)	7098(1)	-1177(3)	31(1)
C(1)	957(1)	6908(1)	-1158(3)	29(1)
C(2)	1962(1)	7302(1)	-1196(3)	25(1)
C(3)	2405(1)	6911(1)	-1193(3)	25(1)
C(4)	2043(1)	7887(1)	-1214(3)	25(1)
C(5)	2292(1)	6284(1)	-1170(4)	36(1)
C(6)	1554(1)	8286(1)	-1231(4)	35(1)
C(10)	-543(1)	6191(1)	-1113(3)	34(1)
C(11)	331(1)	6236(1)	-3613(3)	28(1)
C(12)	-141(1)	7216(1)	-2453(3)	32(1)
C(13)	15(1)	6889(1)	1315(3)	29(1)
C(14)	462(1)	5894(1)	131(3)	33(1)
Co	-693(1)	8565(1)	932(1)	28(1)
C(21)	-215(1)	9200(1)	1954(5)	45(1)
C(22)	17(1)	8668(1)	2462(4)	44(1)
C(23)	140(1)	8376(1)	785(4)	34(1)
C(24)	-14(1)	8728(1)	-724(4)	34(1)
C(25)	-235(1)	9231(1)	0(4)	40(1)
C(31)	-1459(1)	8600(1)	2193(4)	43(1)
C(32)	-1210(1)	8060(1)	2437(4)	44(1)
C(33)	-1115(1)	7829(1)	640(4)	37(1)
C(34)	-1304(1)	8223(1)	-713(4)	36(1)
C(35)	-1514(1)	8701(1)	245(4)	38(1)

Table S3. Bond lengths [Å] for **1b**.

V-C(10)	1.919(3)	Co-C(22)	2.022(3)
V-C(12)	1.953(3)	Co-C(32)	2.025(3)
V-C(14)	1.959(3)	Co-C(33)	2.025(3)
V-C(13)	1.960(3)	Co-C(23)	2.028(2)
V-C(11)	1.967(3)	Co-C(25)	2.030(3)
V-C(1)	2.027(2)	Co-C(31)	2.031(3)
O(10)-C(10)	1.174(3)	Co-C(35)	2.034(3)
O(11)-C(11)	1.145(3)	Co-C(24)	2.036(2)
O(12)-C(12)	1.155(3)	Co-C(34)	2.037(3)
O(13)-C(13)	1.146(3)	C(21)-C(25)	1.402(4)
O(14)-C(14)	1.148(3)	C(21)-C(22)	1.425(4)
N(1)-C(1)	1.173(3)	C(22)-C(23)	1.416(4)
N(1)-C(2)	1.388(3)	C(23)-C(24)	1.414(4)
C(2)-C(4)	1.401(3)	C(24)-C(25)	1.403(4)
C(2)-C(3)	1.401(3)	C(31)-C(35)	1.421(4)
C(3)-C(4)#1	1.394(3)	C(31)-C(32)	1.422(4)
C(3)-C(5)	1.512(3)	C(32)-C(33)	1.417(4)
C(4)-C(3)#1	1.394(3)	C(33)-C(34)	1.419(4)
C(4)-C(6)	1.498(3)	C(34)-C(35)	1.416(4)
Co-C(21)	2.022(3)		

Symmetry transformations used to generate equivalent atoms: #1 -x+1/2,-y+3/2,z.

Table S4. Bond angles [°] for **1b.**

C(10)-V-C(12)	91.87(11)	C(22)-Co-C(32)	106.65(13)
C(10)-V-C(14)	85.79(11)	C(21)-Co-C(33)	163.23(13)
C(12)-V-C(14)	177.55(11)	C(22)-Co-C(33)	124.83(12)
C(10)-V-C(13)	89.99(10)	C(32)-Co-C(33)	40.96(12)
C(12)-V-C(13)	92.71(10)	C(21)-Co-C(23)	68.79(11)
C(14)-V-C(13)	88.02(10)	C(22)-Co-C(23)	40.94(11)
C(10)-V-C(11)	89.71(10)	C(32)-Co-C(23)	119.11(11)
C(12)-V-C(11)	87.53(10)	C(33)-Co-C(23)	106.59(10)
C(14)-V-C(11)	91.73(10)	C(21)-Co-C(25)	40.49(13)
C(13)-V-C(11)	179.63(10)	C(22)-Co-C(25)	68.89(12)
C(10)-V-C(1)	176.02(11)	C(32)-Co-C(25)	163.61(12)
C(12)-V-C(1)	91.84(10)	C(33)-Co-C(25)	154.46(12)
C(14)-V-C(1)	90.49(10)	C(23)-Co-C(25)	68.55(10)
C(13)-V-C(1)	91.27(10)	C(21)-Co-C(31)	108.05(12)
C(11)-V-C(1)	89.01(9)	C(22)-Co-C(31)	119.91(13)
C(1)-N(1)-C(2)	177.7(3)	C(32)-Co-C(31)	41.04(11)
N(1)-C(1)-V	178.9(2)	C(33)-Co-C(31)	68.81(11)
N(1)-C(2)-C(4)	118.2(2)	C(23)-Co-C(31)	154.63(12)
N(1)-C(2)-C(3)	118.2(2)	C(25)-Co-C(31)	126.36(12)
C(4)-C(2)-C(3)	123.56(19)	C(21)-Co-C(35)	120.40(11)
C(4)#1-C(3)-C(2)	118.4(2)	C(22)-Co-C(35)	155.31(12)
C(4)#1-C(3)-C(5)	120.3(2)	C(32)-Co-C(35)	69.06(12)
C(2)-C(3)-C(5)	121.2(2)	C(33)-Co-C(35)	68.77(11)
C(3)#1-C(4)-C(2)	118.0(2)	C(23)-Co-C(35)	162.68(12)
C(3)#1-C(4)-C(6)	120.6(2)	C(25)-Co-C(35)	108.02(11)
C(2)-C(4)-C(6)	121.4(2)	C(31)-Co-C(35)	40.93(12)
O(10)-C(10)-V	177.4(2)	C(21)-Co-C(24)	68.08(12)
O(11)-C(11)-V	177.8(2)	C(22)-Co-C(24)	68.60(12)
O(12)-C(12)-V	177.6(2)	C(32)-Co-C(24)	154.28(11)
O(13)-C(13)-V	178.2(2)	C(33)-Co-C(24)	119.65(11)
O(14)-C(14)-V	176.5(2)	C(23)-Co-C(24)	40.71(10)
C(21)-Co-C(22)	41.28(12)	C(25)-Co-C(24)	40.36(11)
C(21)-Co-C(32)	125.98(14)	C(31)-Co-C(24)	163.42(11)

C(35)-Co-C(24)	125.85(11)	C(25)-C(24)-Co	69.57(15)
C(21)-Co-C(34)	154.83(12)	C(23)-C(24)-Co	69.31(14)
C(22)-Co-C(34)	162.41(12)	C(21)-C(25)-C(24)	108.2(2)
C(32)-Co-C(34)	68.97(12)	C(21)-C(25)-Co	69.45(16)
C(33)-Co-C(34)	40.90(11)	C(24)-C(25)-Co	70.07(14)
C(23)-Co-C(34)	125.07(11)	C(35)-C(31)-C(32)	108.1(2)
C(25)-Co-C(34)	120.04(11)	C(35)-C(31)-Co	69.64(15)
C(31)-Co-C(34)	68.71(12)	C(32)-C(31)-Co	69.27(15)
C(35)-Co-C(34)	40.70(11)	C(33)-C(32)-C(31)	107.7(3)
C(24)-Co-C(34)	107.52(11)	C(33)-C(32)-Co	69.52(15)
C(25)-C(21)-C(22)	108.3(2)	C(31)-C(32)-Co	69.69(15)
C(25)-C(21)-Co	70.06(15)	C(32)-C(33)-C(34)	108.3(2)
C(22)-C(21)-Co	69.38(16)	C(32)-C(33)-Co	69.52(16)
C(23)-C(22)-C(21)	107.2(3)	C(34)-C(33)-Co	69.99(15)
C(23)-C(22)-Co	69.73(15)	C(35)-C(34)-C(33)	107.9(3)
C(21)-C(22)-Co	69.34(16)	C(35)-C(34)-Co	69.53(15)
C(24)-C(23)-C(22)	107.8(2)	C(33)-C(34)-Co	69.11(15)
C(24)-C(23)-Co	69.97(14)	C(34)-C(35)-C(31)	108.0(2)
C(22)-C(23)-Co	69.33(14)	C(34)-C(35)-Co	69.77(14)
C(25)-C(24)-C(23)	108.5(2)	C(31)-C(35)-Co	69.42(14)

Symmetry transformations used to generate equivalent atoms: #1 -x+1/2,-y+3/2,z.

Table S5. Anisotropic displacement parameters (Å^2 x 10^3) for **1b**. The anisotropic displacement factor exponent takes the form: $-2\pi^2$ [$h^2 a^{*2}U_{11}$+ ... + 2 h k a* b* U_{12}].

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
V	22(1)	26(1)	25(1)	0(1)	-1(1)	0(1)
O(10)	40(1)	75(2)	38(1)	0(1)	-3(1)	-23(1)
O(11)	44(1)	35(1)	31(1)	-2(1)	2(1)	5(1)
O(12)	71(1)	36(1)	34(1)	-3(1)	-7(1)	18(1)
O(13)	46(1)	38(1)	27(1)	-2(1)	0(1)	4(1)
O(14)	75(2)	48(1)	34(1)	7(1)	2(1)	23(1)
N(1)	27(1)	40(1)	26(1)	-2(1)	1(1)	-7(1)
C(1)	29(1)	32(1)	25(1)	-2(1)	0(1)	0(1)
C(2)	23(1)	35(1)	17(1)	-2(1)	2(1)	-7(1)
C(3)	29(1)	31(1)	15(1)	-1(1)	0(1)	-7(1)
C(4)	26(1)	33(1)	15(1)	0(1)	1(1)	-1(1)
C(5)	41(1)	29(1)	37(1)	-3(1)	-1(1)	-7(1)
C(6)	32(1)	40(1)	34(1)	-1(1)	3(1)	3(1)
C(10)	34(1)	44(1)	25(1)	0(1)	-2(1)	-4(1)
C(11)	25(1)	26(1)	33(1)	3(1)	-3(1)	0(1)
C(12)	38(1)	32(1)	26(1)	-7(1)	-1(1)	2(1)
C(13)	26(1)	28(1)	32(1)	5(1)	-4(1)	-1(1)
C(14)	36(1)	34(1)	28(1)	-1(1)	4(1)	4(1)
Co	26(1)	26(1)	31(1)	2(1)	3(1)	5(1)
C(21)	39(1)	41(2)	56(2)	-18(1)	3(1)	-2(1)
C(22)	36(1)	59(2)	37(2)	0(1)	-7(1)	0(1)
C(23)	22(1)	32(1)	48(2)	3(1)	3(1)	3(1)
C(24)	29(1)	36(1)	39(1)	3(1)	7(1)	-4(1)
C(25)	34(1)	28(1)	58(2)	6(1)	0(1)	-2(1)
C(31)	30(1)	49(2)	50(2)	-5(1)	11(1)	5(1)
C(32)	35(1)	47(2)	49(2)	15(1)	12(1)	2(1)
C(33)	32(1)	29(1)	52(2)	5(1)	6(1)	1(1)
C(34)	33(1)	34(1)	40(1)	2(1)	-3(1)	-1(1)
C(35)	28(1)	35(1)	53(2)	3(1)	-2(1)	5(1)

Table S6. Hydrogen coordinates (× 10^4) and isotropic displacement parameters (Å^2 × 10^3) for **1b**.

	x	y	z	U(eq)
H(5A)	2493	6111	-120	53
H(5B)	2423	6116	-2343	53
H(5C)	1886	6217	-1031	53
H(6A)	1613	8572	-2201	53
H(6B)	1523	8471	-11	53
H(6C)	1206	8078	-1493	53
H(21)	-336	9486	2795	54
H(22)	77	8533	3695	53
H(23)	298	8009	691	41
H(24)	25	8639	-2010	41
H(25)	-374	9540	-710	48
H(31)	-1569	8850	3162	51
H(32)	-1123	7886	3596	52
H(33)	-953	7470	385	45
H(34)	-1291	8175	-2030	43
H(35)	-1664	9031	-316	46

C. DFT CALCULATIONS

C1. Experimental

Density Functional Theory (DFT) calculations on 1,4-diisocyanodurene and 2,6-dimethylphenyl isocyanide were performed using the Orca (v.2.8.0) program.[15] Geometric optimizations were performed spin-restricted using the BP86 functional[16] with a TZVP basis set.[17] The resolution of identity approximation (RI) was used along with the SV/J auxiliary basis set.[18] Single point energy calculations were performed using the B3LYP functional[19] with a TZVP basis set to obtain orbital energies. Orbital pictures were produced using the Molekel (v.5.4.0.8) program with isodensity values set at ±0.05.[20] The following tables contain Cartesian coordinates for the optimized compounds.

Table S7. Cartesian coordinates (Å) for the optimized structure of 1,4-diisocyanodurene.

Atom	x	y	z
C	-0.017504	0.055012	0.000010
C	0.796565	1.323120	0.000003
C	2.202156	1.320808	-0.000104
C	2.870100	2.569195	-0.000096
C	2.200524	3.816708	0.000002
C	0.794940	3.812583	0.000106
C	0.131384	2.567420	0.000098
N	-1.255058	2.566515	0.000195
C	-2.439848	2.565748	0.000276
C	-0.020763	5.079635	0.000213
H	0.609147	5.973938	0.000295
H	-0.678109	5.124537	-0.881447
H	-0.678123	5.124381	0.881868
C	2.975421	5.111849	-0.000004
H	4.055348	4.934823	-0.000109
H	2.734384	5.718217	-0.886221
H	2.734544	5.718132	0.886315
N	4.258686	2.570101	-0.000187
C	5.443031	2.570868	-0.000266
C	2.978738	0.026681	-0.000221
H	4.058431	0.205116	-0.000309
H	2.738645	-0.579988	0.886044
H	2.738488	-0.579921	-0.886488
H	0.613569	-0.838479	0.000017
H	-0.674798	0.009342	0.881664
H	-0.674791	0.009330	-0.881650

Table S8. Cartesian coordinates (Å) for the optimized structure of 2,6-dimethylphenyl isocyanide.

Atom	**x**	**y**	**z**
C	-0.010178	0.007214	0.000002
C	-0.740912	1.325988	0.000109
C	-2.140892	1.356911	0.000209
C	-2.838302	2.565488	0.000310
C	-2.142467	3.774974	0.000309
C	-0.742529	3.807714	0.000211
C	-0.060209	2.567295	0.000112
N	1.328739	2.568195	0.000013
C	2.512577	2.568954	-0.000071
C	-0.013510	5.127437	0.000214
H	1.074486	5.001018	0.000120
H	-0.287395	5.721067	-0.885255
H	-0.287252	5.720985	0.885782
H	-2.690854	4.719191	0.000387
H	-3.929694	2.564771	0.000389
H	-2.688058	0.411982	0.000209
H	1.077650	0.135049	-0.000072
H	-0.283161	-0.586763	0.885516
H	-0.283289	-0.586690	-0.885522

D. FIGURES

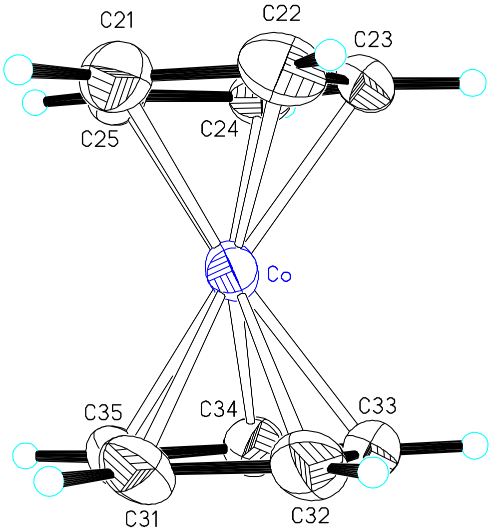

Figure S1. Thermal ellipsoid plot for the cobaltocenium cations in **1b** (all $[Cp_2Co]^+$ cations are mutually symmetry equivalent).

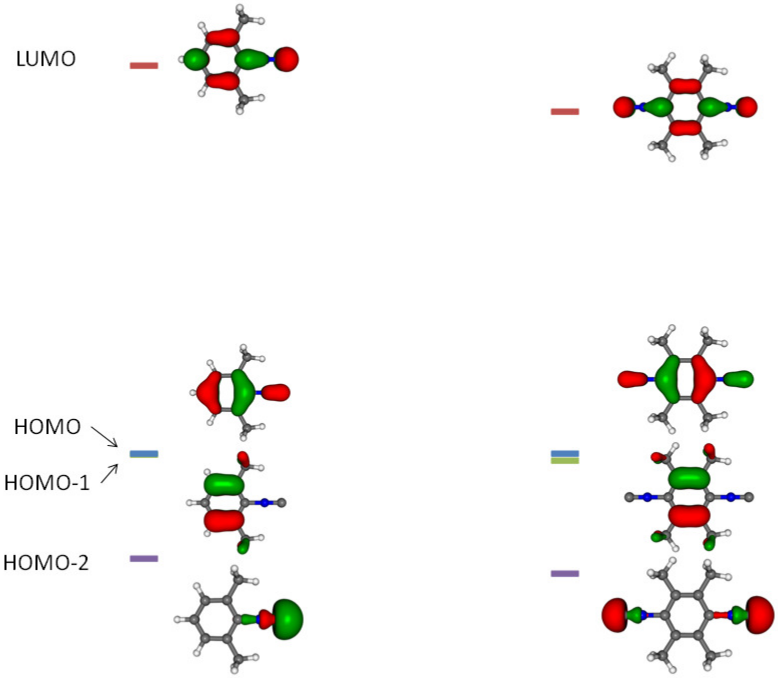

Figure S2. Frontier molecular orbitals for 2,6-dimethylphenyl isocyanide (left) and 1,4-diisocyanodurene (right).

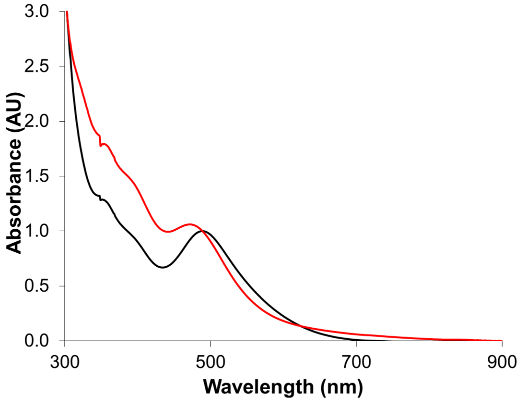

Figure S3. UV-Vis spectra of **1a** in CH_2Cl_2 (red) and CH_3CN (black) at 24 °C.

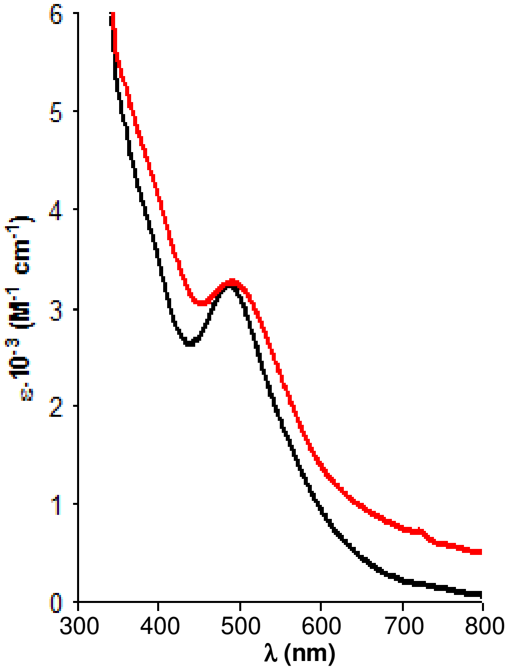

Figure S4. UV-Vis spectra of **1b** in CH_2Cl_2 (red) and CH_3CN (black) at 24 °C.

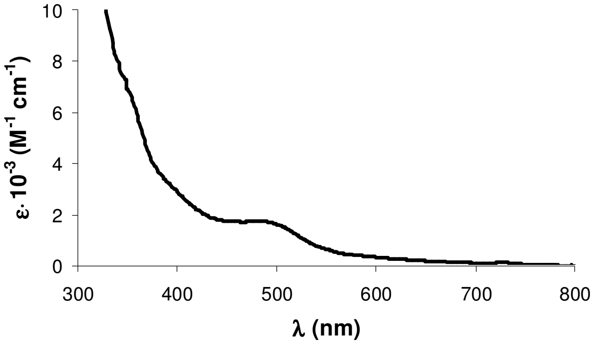

Figure S5. UV-Vis spectrum of **2** in CH_3CN at 24 °C.

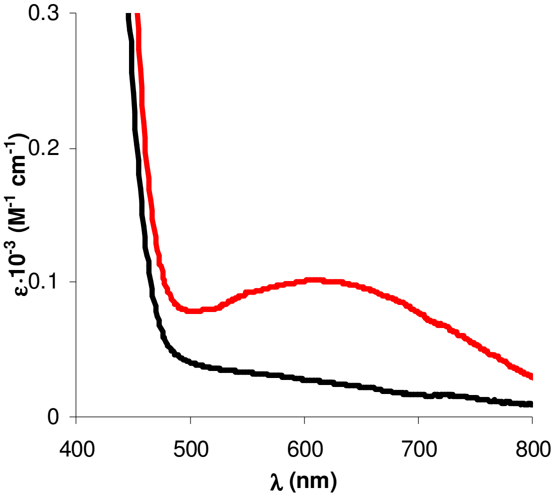

Figure S6. Electronic absorption spectra (visible region) of $[Cp_2Co][V(CO)_6]$ in CH_2Cl_2 (red) and CH_3CN (black) at 24 °C. The vanadium-to-cobalt contact ion pair charge transfer occurs at $\lambda_{max} = 620$ nm in CH_2Cl_2.[21]

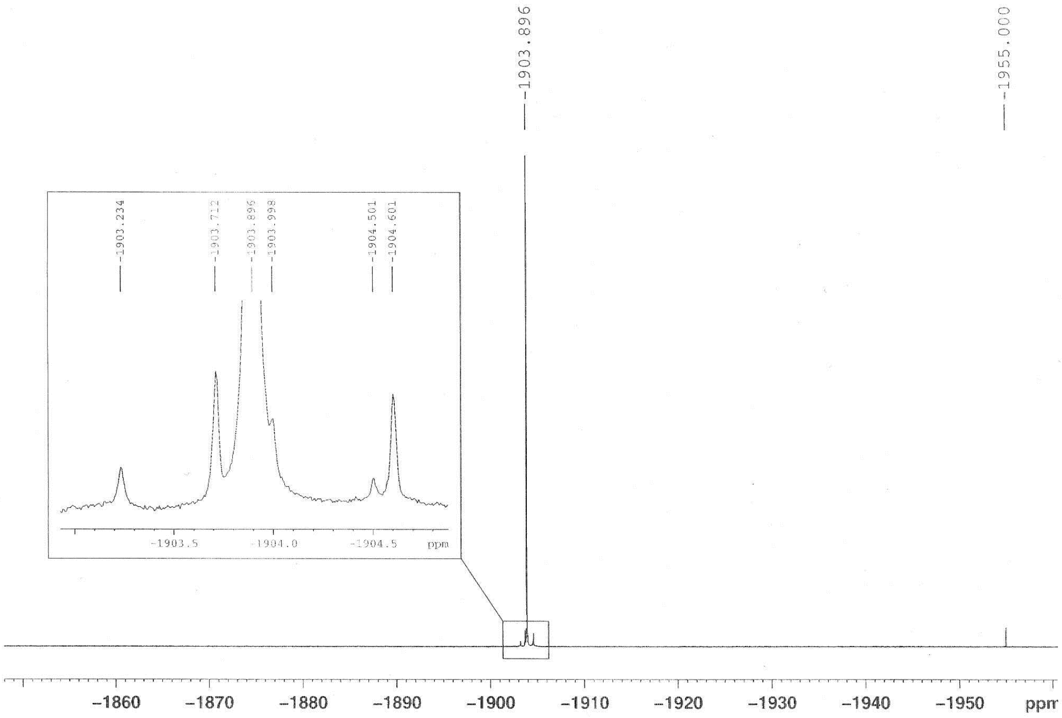

Figure S7. ^{51}V NMR (131.6 MHz, CD_3CN, 25°C) spectrum of **1a** in CD_3CN at 25 °C referenced to neat $VOCl_3$. A very small peak at -1955.0 ppm corresponds to trace contamination of the sample with $[Et_4N][V(CO)_6]$, which is a common and persistent impurity associated with photolytic substitution reactions of $[Et_4N][V(CO)_6]$.

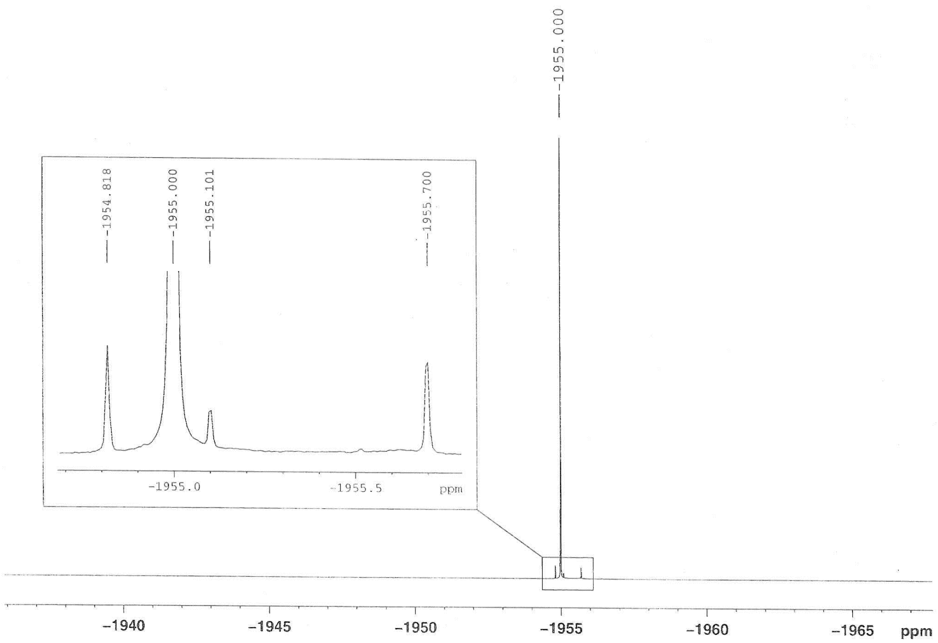

Figure S8. ^{51}V NMR (131.6 MHz, CD_3CN, 25°C) spectrum of $[Et_4N][V(CO)_6]$ in CD_3CN at 25 °C referenced to neat $VOCl_3$.

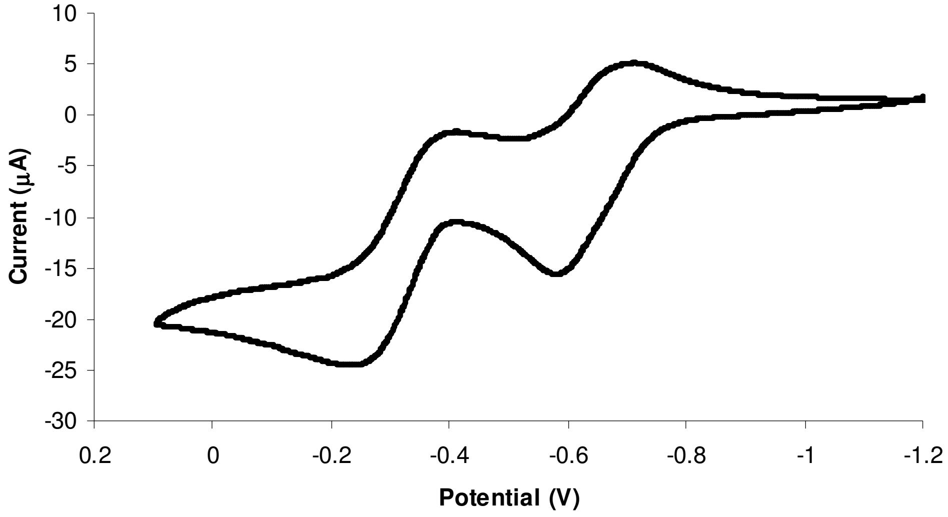

Figure S9. Cyclic voltammogram for **1a** in CH_3CN at 22 °C at 100 mV/s. Potentials are referenced to the $Cp_2Fe^{0/+}$ couple.

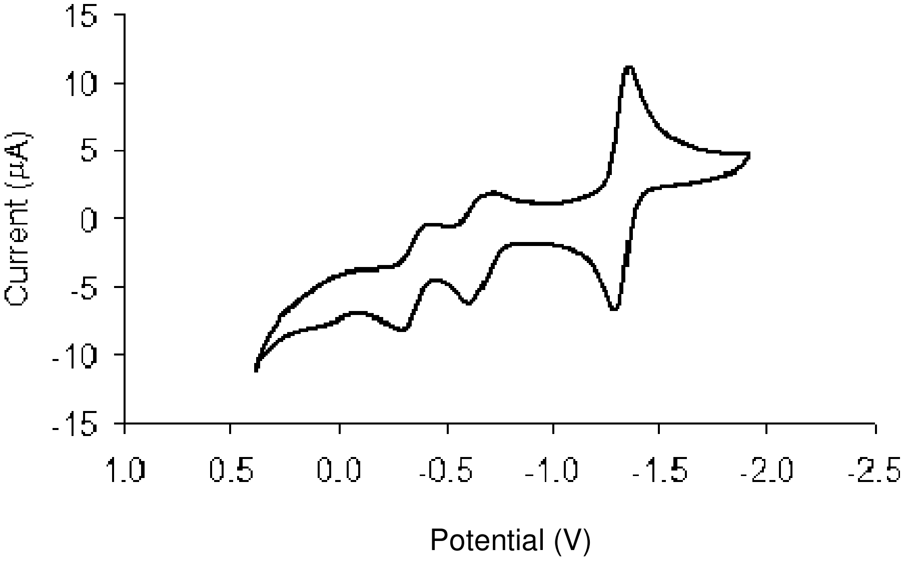

Figure S10. Cyclic voltammogram for **1b** in CH_3CN at 22 °C at 100 mV/s. Potentials are referenced to the $Cp_2Fe^{0/+}$ couple.

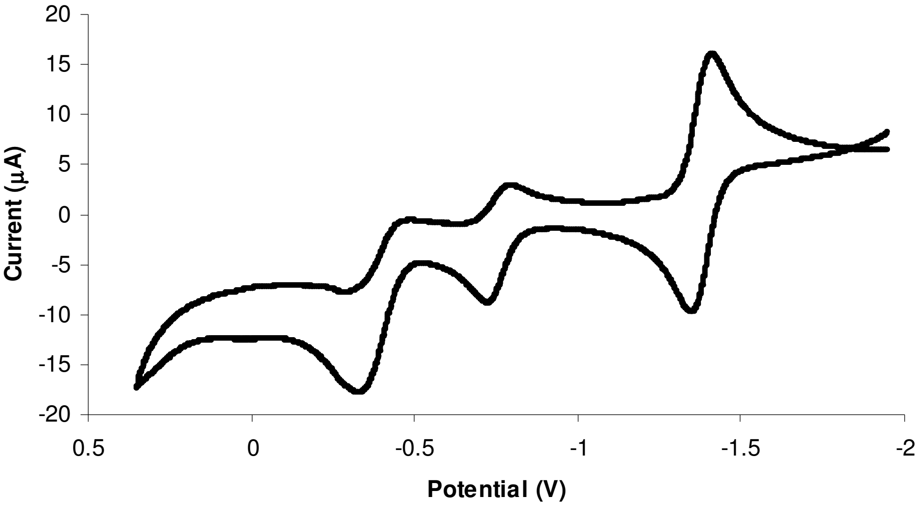

Figure S11. Cyclic voltammogram for **2** in CH_3CN at 22 °C at 100 mV/s. Potentials are referenced to the $Cp_2Fe^{0/+}$ couple.

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