Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Rylene- and Diaza-rylene-derived Cobalt Clusters for the Solid-State Pyrolysis towards Undoped and N-doped Carbon Nanoparticles

Simon Werner [a],Tobias Vollgraff [a], and Jörg Sundermeyer*[a]

[a] S. Werner, T. Vollgraff, Prof. Dr. J. Sundermeyer
Fachbereich Chemie and Materials Science Center
Philipps-Universität Marburg, Hans-Meerwein-Straße 4
35043 Marburg (Germany)
E-Mail: JSU@staff.uni-marburg.de

Contents

IR Spectra

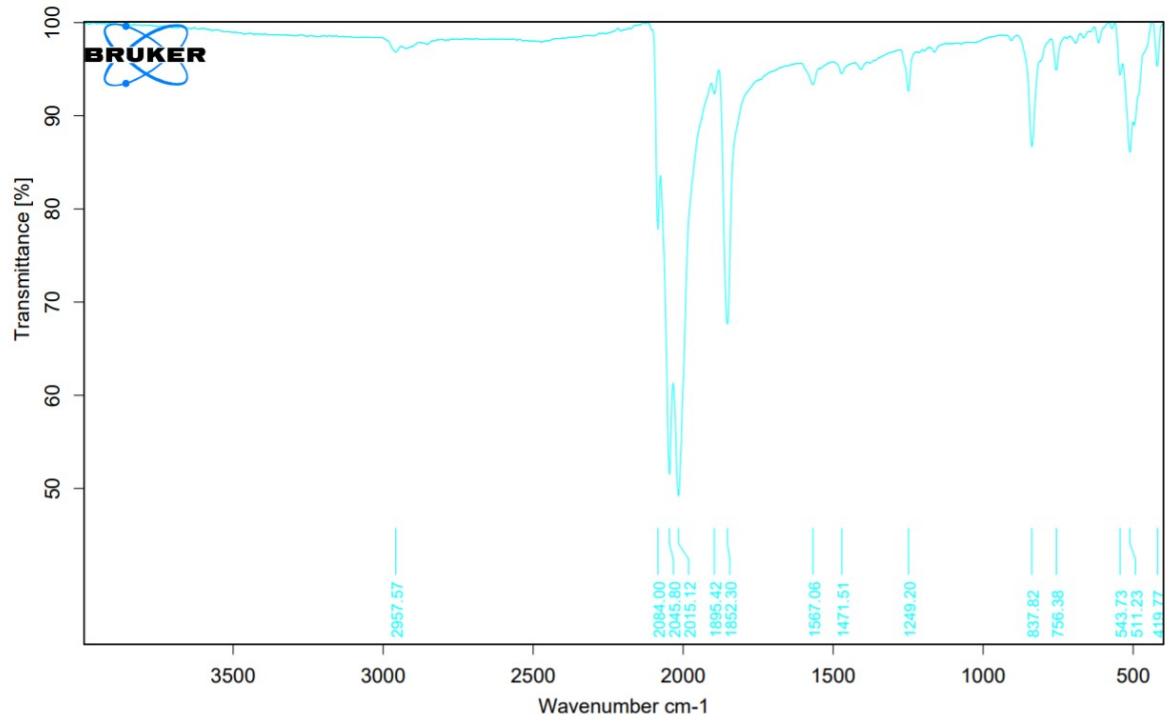


Figure S1. Measured ATR-FT-IR spectrum of compound **C1** (neat substance).

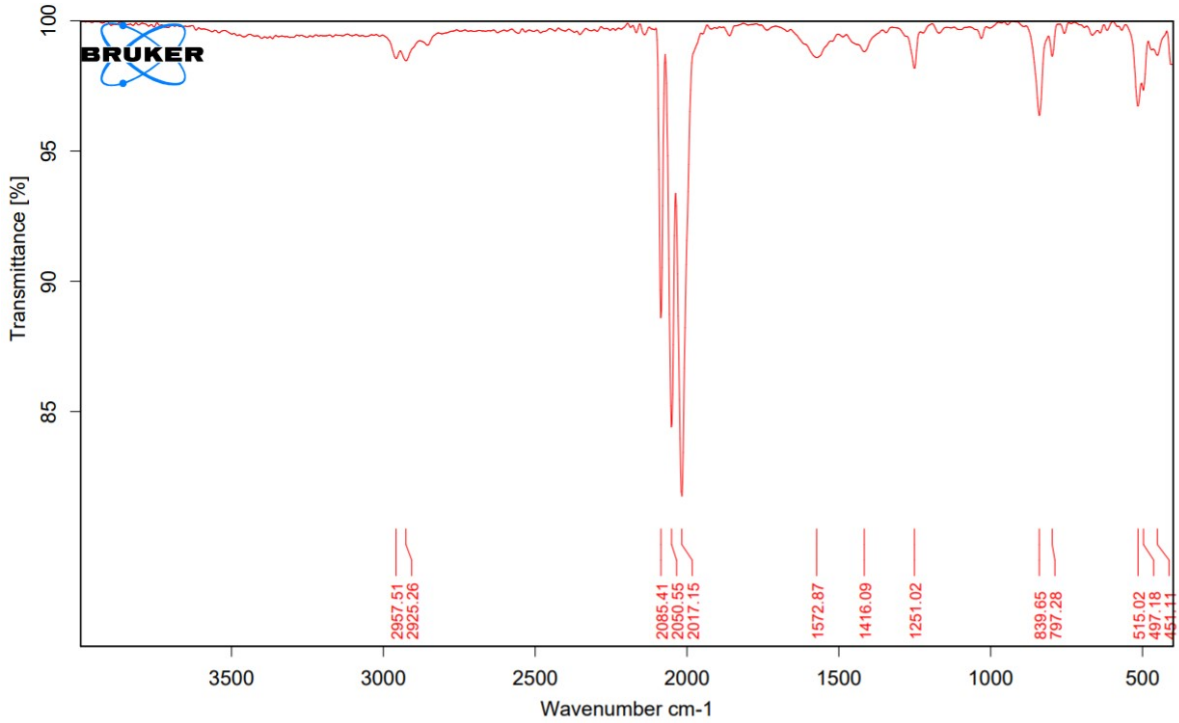


Figure S2. Measured ATR-FT-IR-spectrum of compound **C2** (neat substance).

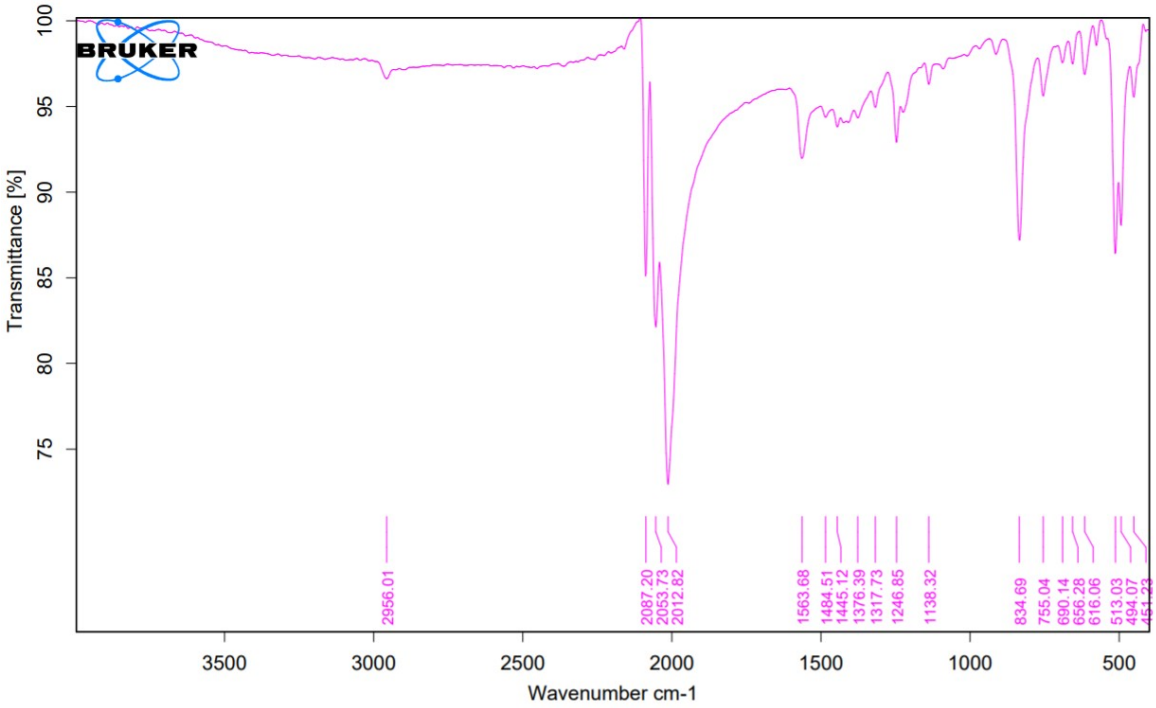


Figure S3. Measured ATR-FT-IR-spectrum of compound **N1** (neat substance).

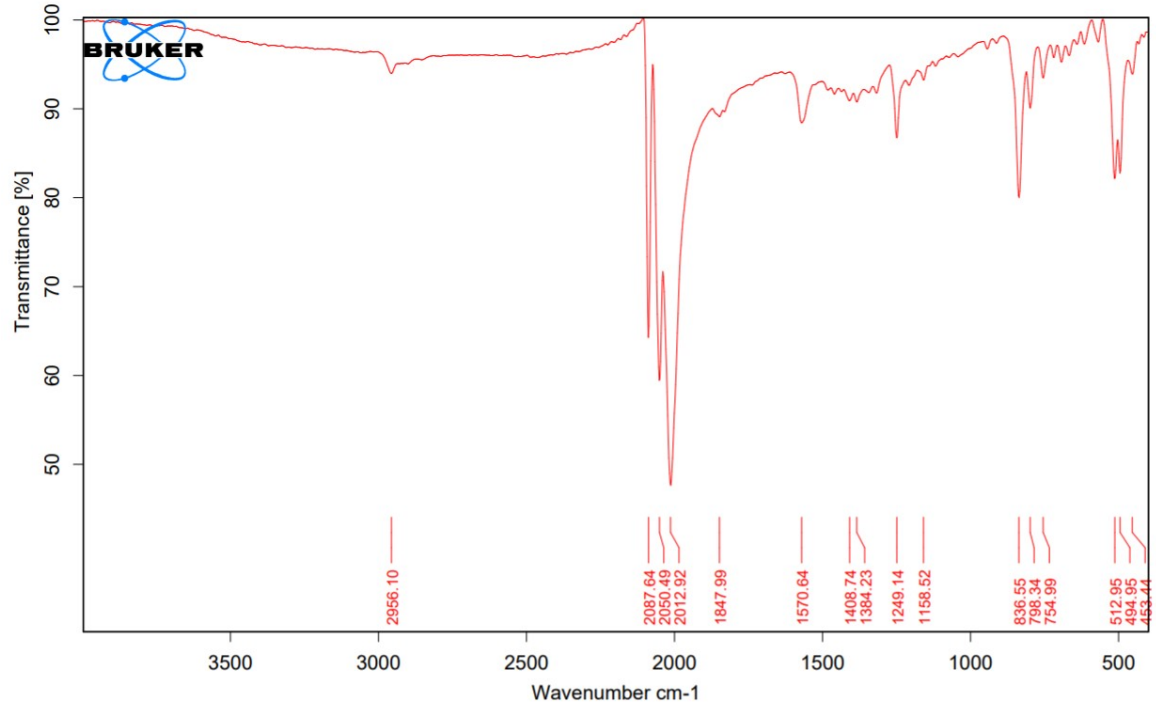


Figure S4. Measured ATR-FT-IR-spectrum of compound **N2** (neat substance).

Optimized geometries (DFT)

Table S1. Cartesian coordinates (XYZ) of DFT optimized geometry of the phenyl-model complex (def2-TZVPP/PBE).

C	3.184006000	0.515229000	1.788314000
C	3.852976000	-0.587923000	1.247346000
C	3.173378000	-1.461591000	0.395568000
C	1.833553000	-1.235832000	0.084804000
C	1.151289000	-0.128500000	0.624025000
C	1.846321000	0.743276000	1.480424000
C	-0.244419000	0.089127000	0.289101000
Co	-1.237174000	1.578188000	-0.550029000
C	-1.264981000	-0.414010000	-0.444859000
Co	-1.909949000	0.147192000	1.356203000
C	-3.704520000	0.195148000	1.155254000
C	-1.720759000	-1.377076000	2.229436000
C	-1.525790000	1.280841000	2.698072000
C	-2.871279000	1.982589000	-1.205252000
C	-0.244867000	1.784427000	-1.997100000
C	-0.701029000	3.032341000	0.361829000
O	-1.582505000	-2.372724000	2.795188000
O	-4.851271000	0.210880000	1.039699000
O	-1.272832000	1.989980000	3.571170000
O	0.412858000	1.911028000	-2.936221000
O	-3.906471000	2.250544000	-1.635364000
O	-0.343605000	3.970794000	0.928312000
Si	-1.823806000	-1.730282000	-1.636870000
C	-3.614772000	-1.455061000	-2.121890000
C	-1.632020000	-3.400694000	-0.787055000
C	-0.717899000	-1.636980000	-3.159074000
H	3.710089000	1.200401000	2.453531000
H	4.901107000	-0.764707000	1.489727000
H	3.689065000	-2.323320000	-0.029498000
H	1.300218000	-1.915609000	-0.579717000
H	1.325095000	1.603030000	1.901442000
H	-3.753998000	-0.490164000	-2.626961000
H	-3.938896000	-2.245518000	-2.814360000
H	-4.280800000	-1.480751000	-1.249445000
H	-0.604865000	-3.565491000	-0.433617000
H	-1.882220000	-4.210413000	-1.488071000
H	-2.302755000	-3.485866000	0.078460000
H	-0.963073000	-2.453472000	-3.853986000
H	-0.856297000	-0.687587000	-3.693476000
H	0.345698000	-1.723646000	-2.897662000

Table S2. Cartesian coordinates (XYZ) of DFT optimized geometry of the 1-pyridinyl-model complex (def2-TZVPP/PBE)

C	3.004925000	0.597290000	1.782018000
C	3.796615000	-0.462854000	1.326038000
C	3.215996000	-1.399159000	0.471835000
C	1.880274000	-1.240161000	0.110932000
C	1.164751000	-0.141912000	0.620638000
N	1.723845000	0.765528000	1.447188000
C	-0.231831000	0.045982000	0.261287000
Co	-1.203895000	1.540815000	-0.556558000
C	-1.252816000	-0.455254000	-0.470529000
Co	-1.873217000	0.102609000	1.343323000
C	-3.666145000	0.209997000	1.185659000
C	-1.730188000	-1.435318000	2.198189000
C	-1.401070000	1.209161000	2.690264000
C	-2.840908000	2.020168000	-1.139316000
C	-0.278651000	1.747244000	-2.045153000
C	-0.553130000	2.949222000	0.370890000

O	-1.622605000	-2.441549000	2.753002000
O	-4.814389000	0.261247000	1.094419000
O	-1.104853000	1.891589000	3.567764000
O	0.335529000	1.874972000	-3.013926000
O	-3.881634000	2.332283000	-1.525024000
O	-0.129603000	3.859908000	0.931390000
Si	-1.846784000	-1.751851000	-1.664227000
C	-3.631880000	-1.422068000	-2.135076000
C	-1.690320000	-3.431128000	-0.824455000
C	-0.745030000	-1.686011000	-3.191241000
H	3.425435000	1.351513000	2.452864000
H	4.838120000	-0.545814000	1.635478000
H	3.793907000	-2.241819000	0.090735000
H	1.384890000	-1.946999000	-0.554236000
H	-3.743885000	-0.446911000	-2.627400000
H	-3.986560000	-2.194024000	-2.833230000
H	-4.290519000	-1.435544000	-1.256619000
H	-0.664377000	-3.620675000	-0.479262000
H	-1.962776000	-4.231545000	-1.527858000
H	-2.356486000	-3.505908000	0.045391000
H	-1.021944000	-2.488305000	-3.890802000
H	-0.849403000	-0.728630000	-3.718842000
H	0.315616000	-1.814589000	-2.934250000

Additional SEM images of pyrolysis products of C2

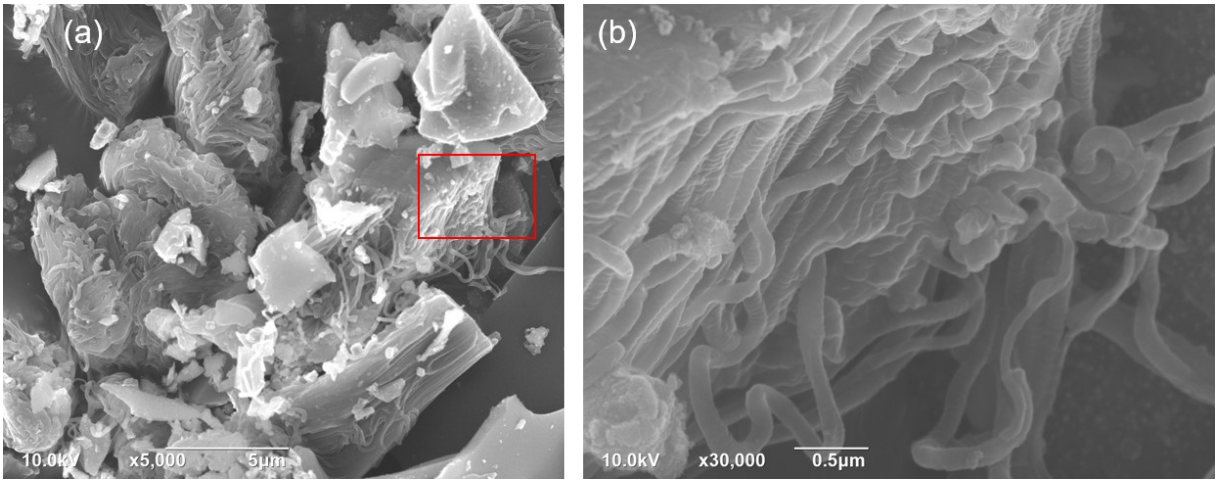


Figure S5. (a) and (b) Bundles of agglomerated carbon nanotubes obtained after SSP of **C2**.

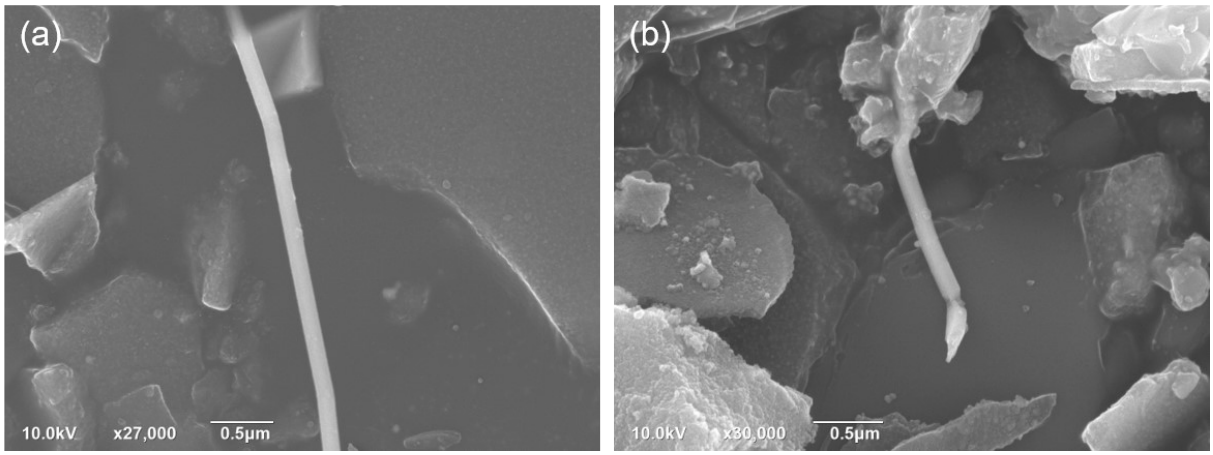


Figure S6. (a) and (b) Isolated larger fibrous-type carbon nanotubes after SSP of **C2**.

Low resolution TEM images of pyrolysis products of C2

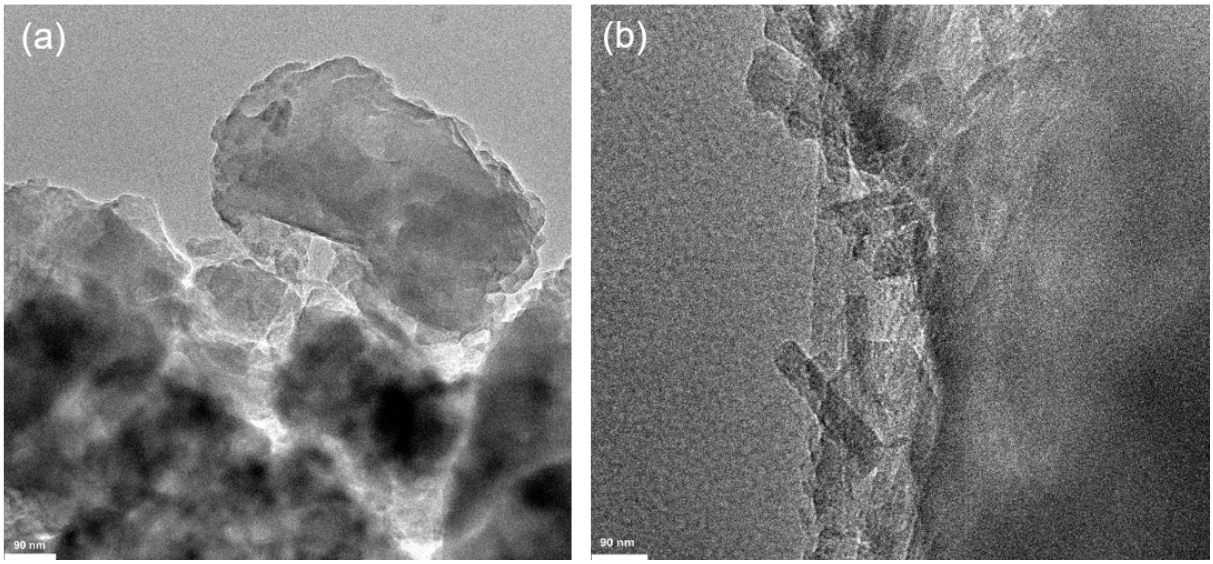


Figure S7. (a) and (b) Low resolution bright field TEM images of agglomerated carbon nanotubes and nanoparticlesobtained after SSP of **C2**.

FD mass spectra

Co-complex N1

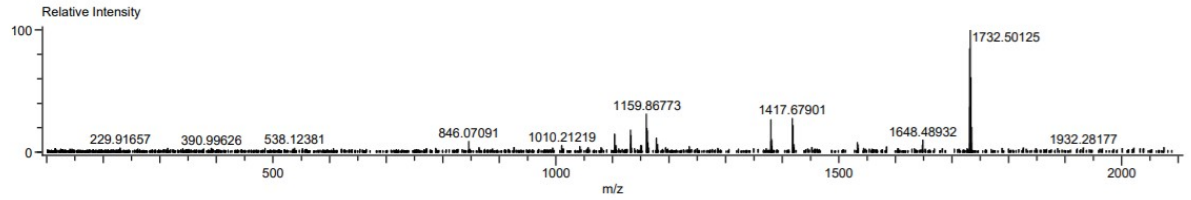


Figure S8. FD(+) MS spectrum of **N1**.

Co-complex N2

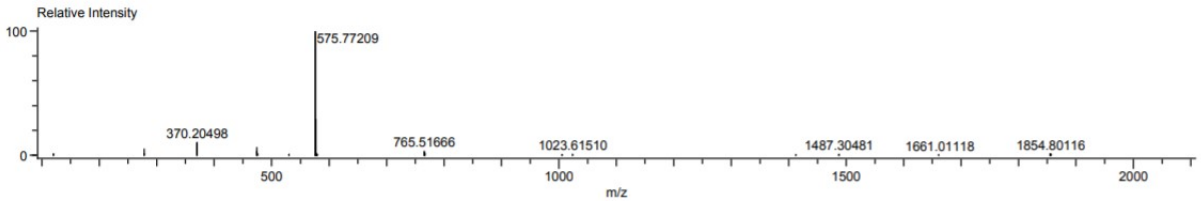
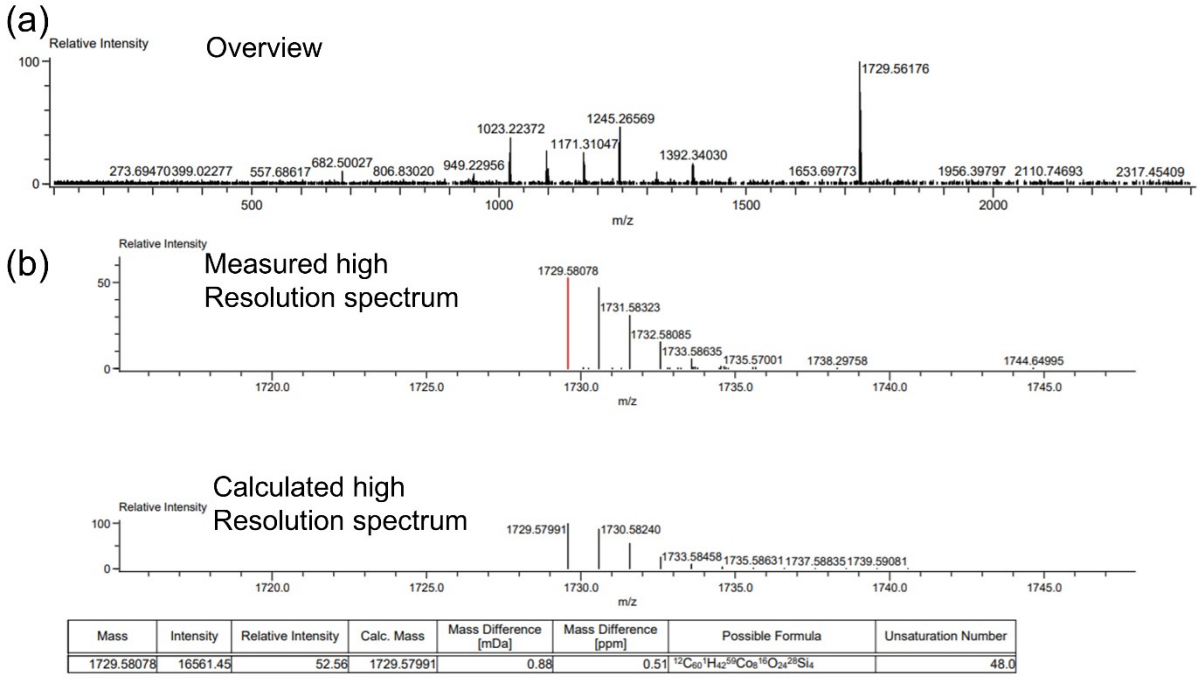


Figure S9. FD(+) MS spectrum of **N2**.

Co-complex C1



Mass	Intensity	Relative Intensity	Calc. Mass	Mass Difference [mDa]	Mass Difference [ppm]	Possible Formula	Unsaturation Number
1729.58078	16561.45	52.56	1729.57991	0.88	0.51	$^{12}C_{60}{}^{1}H_{42}{}^{59}Co_{8}{}^{16}O_{24}{}^{28}Si_{4}$	48.0

Figure S10. FD(+)-MS spectrum of **C1**: (a) Overview spectrum; (b) calculated and measured high resolution mass peak.

NMR Spectra

Co-complex C1

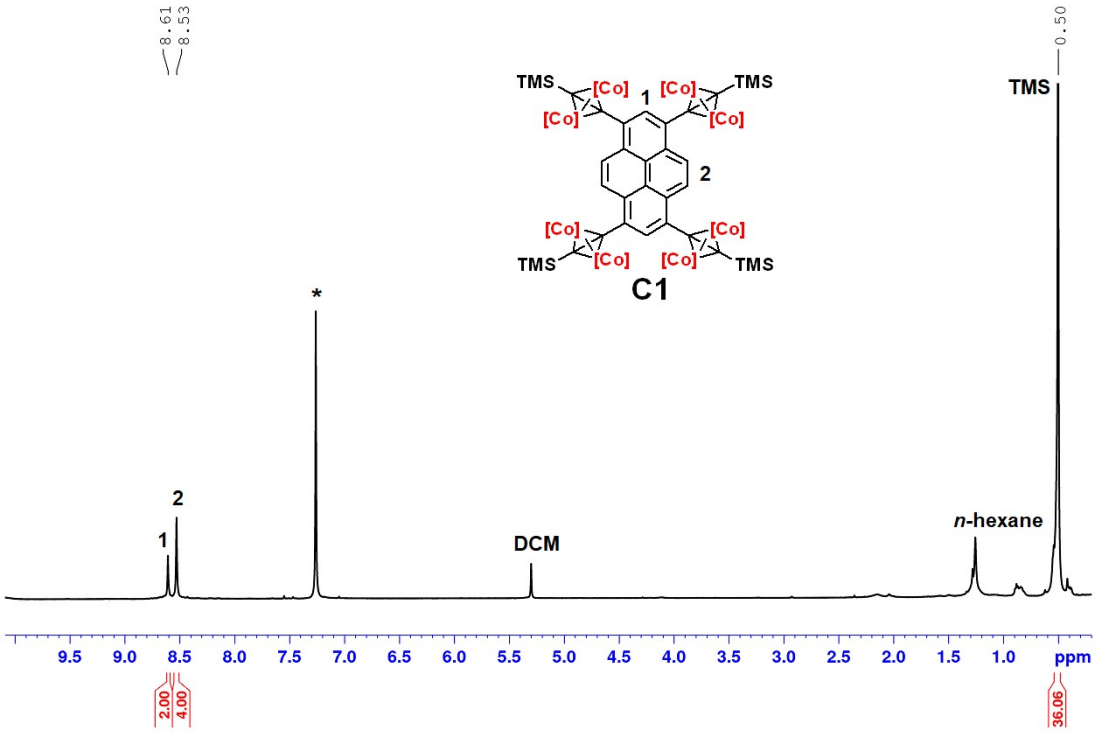


Figure S11. ^{1}H NMR (500.1 MHz, 298K, $CDCl_3$*) of **C1**. Contains solvent residues. The $[Co(CO)_3]$ units are abbreviated with [Co].

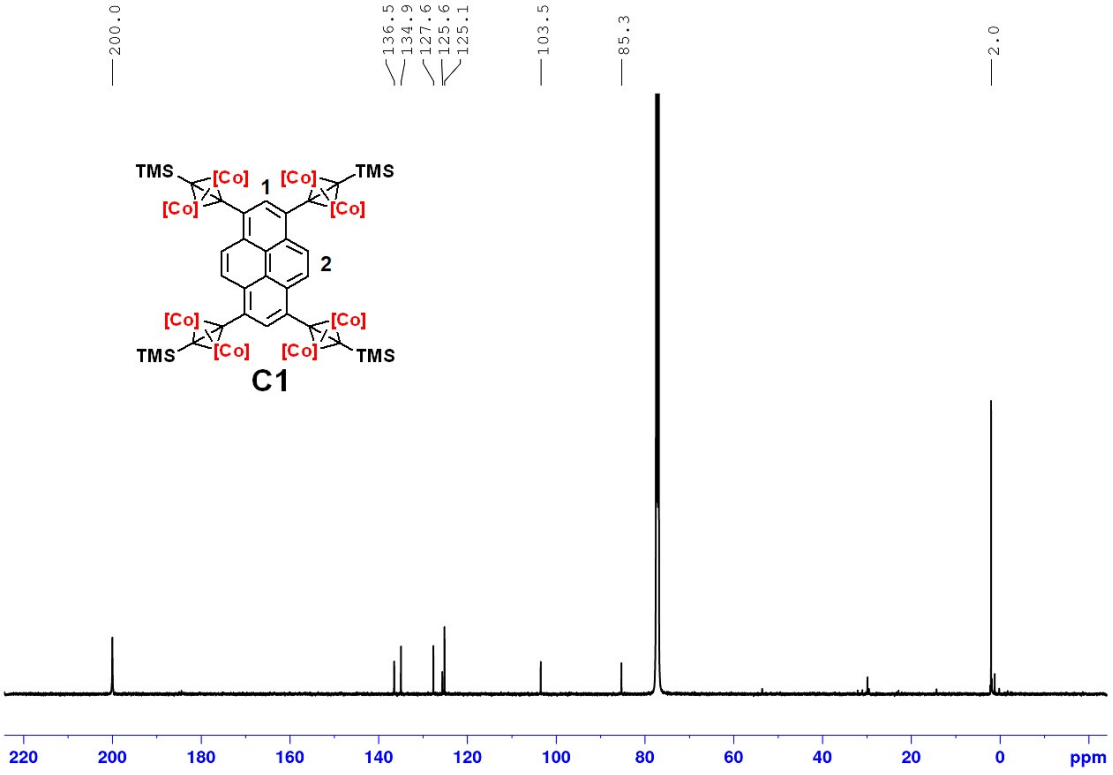


Figure S12. ^{13}C NMR (125.8 MHz, 298K, $CDCl_3$*) of **C1**. Contains solvent residues. The $[Co(CO)_3]$ units are abbreviated with [Co].

Co-complex C2

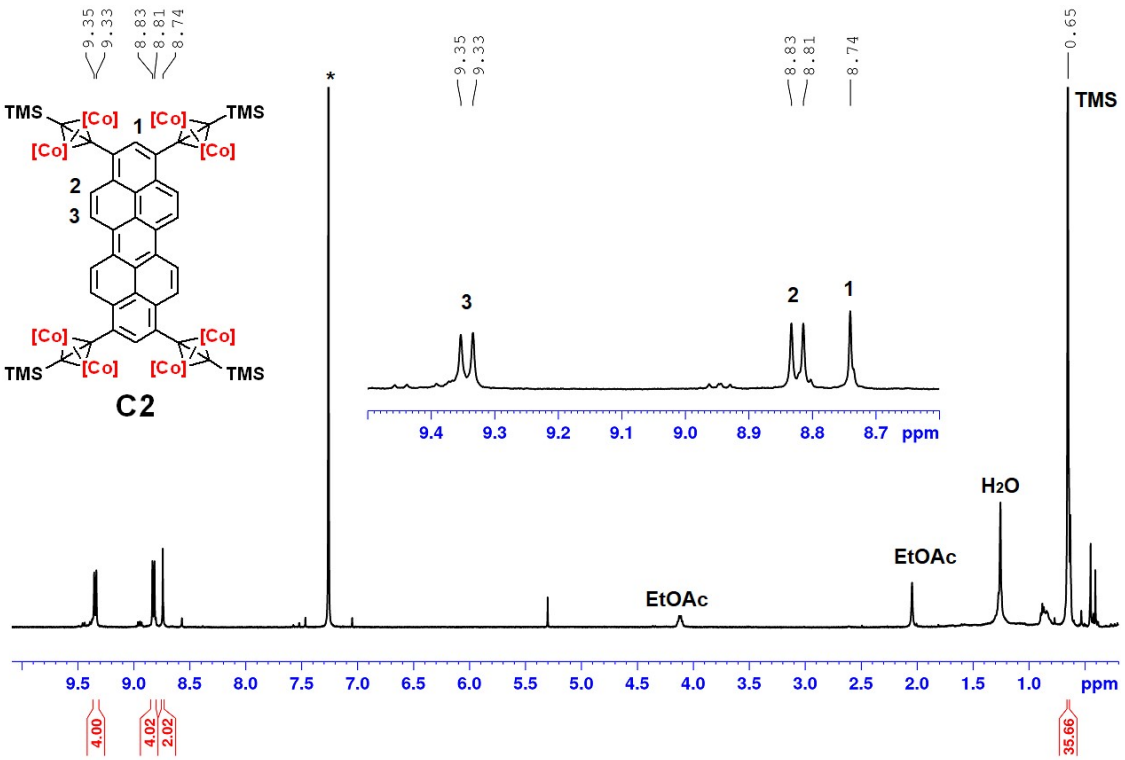


Figure S13. ^{1}H NMR (500.1 MHz, 298K, $CDCl_3$*) of **C2**. Contains solvent residues. The $[Co(CO)_3]$ units are abbreviated with [Co].

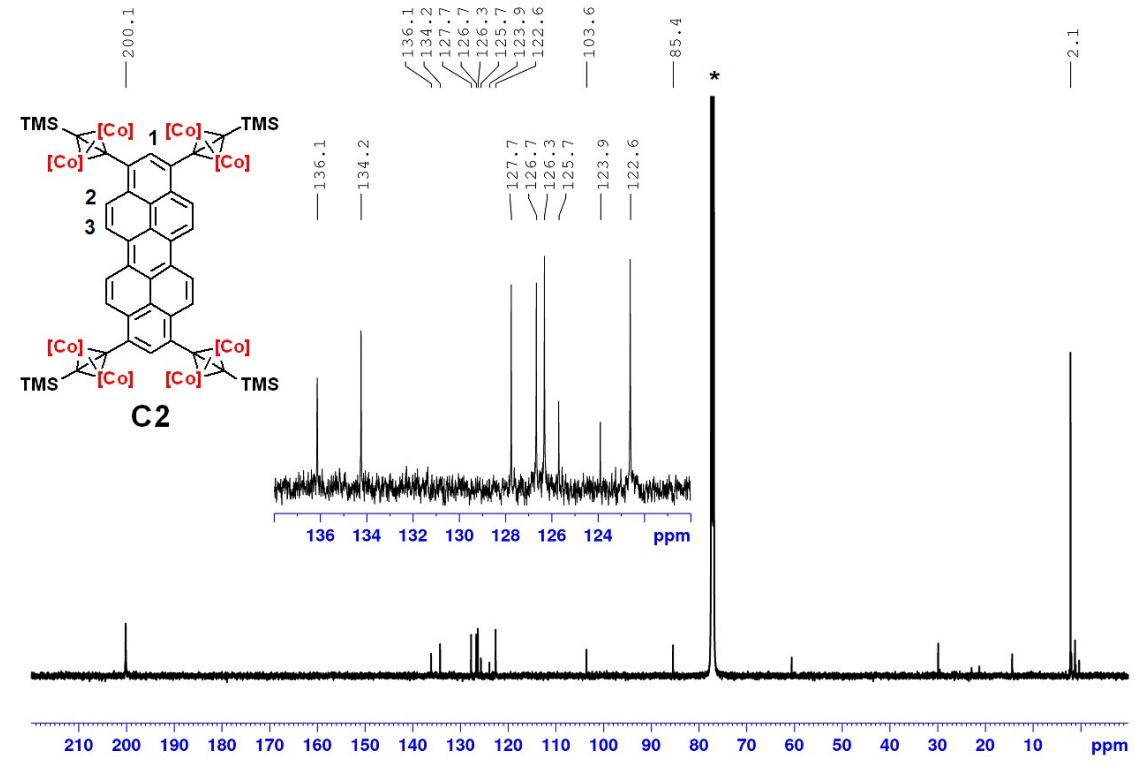


Figure S14. ^{13}C NMR (125.8 MHz, 298K, $CDCl_3$*) of **C2**. Contains solvent residues. The $[Co(CO)_3]$ units are abbreviated with [Co].

Co-complex N1

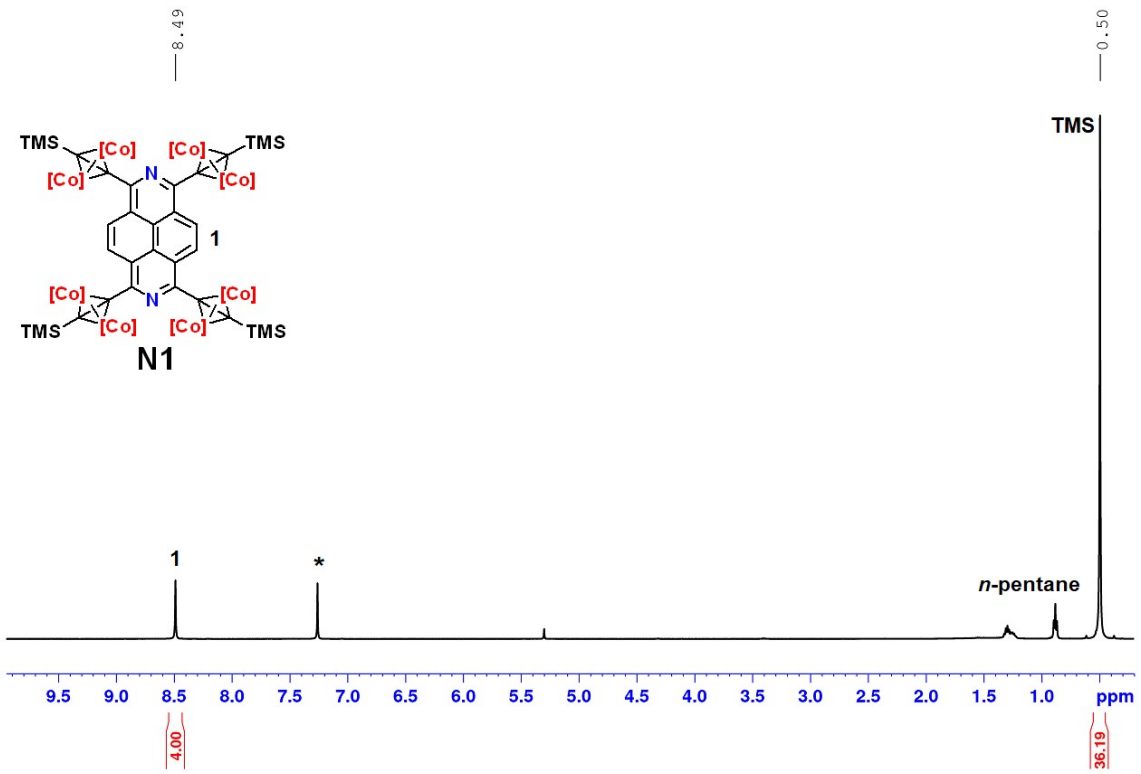


Figure S15. ^{1}H NMR (500.1 MHz, 298K, $CDCl_3$*) of **N1**. Contains solvent residues. The $[Co(CO)_3]$ units are abbreviated with [Co].

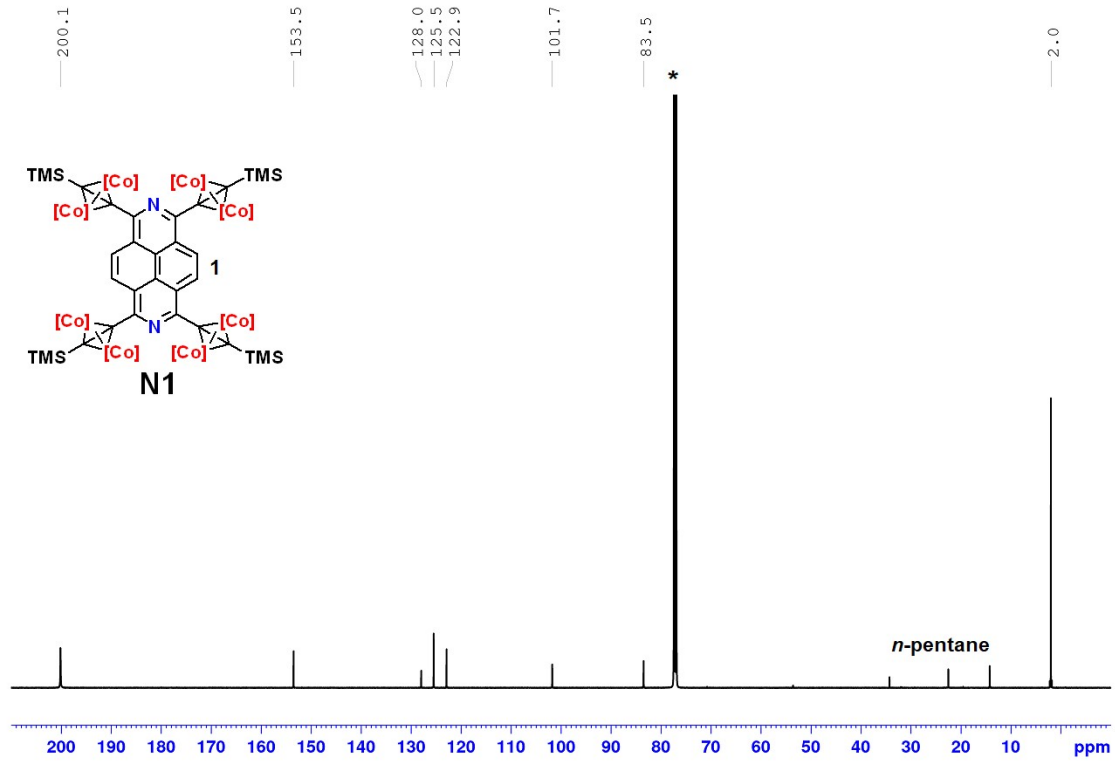


Figure S16. ^{13}C NMR (125.8 MHz, 298K, $CDCl_3$*) of **N1**. Contains solvent residues. The $[Co(CO)_3]$ units are abbreviated with [Co].

Co-complex N2

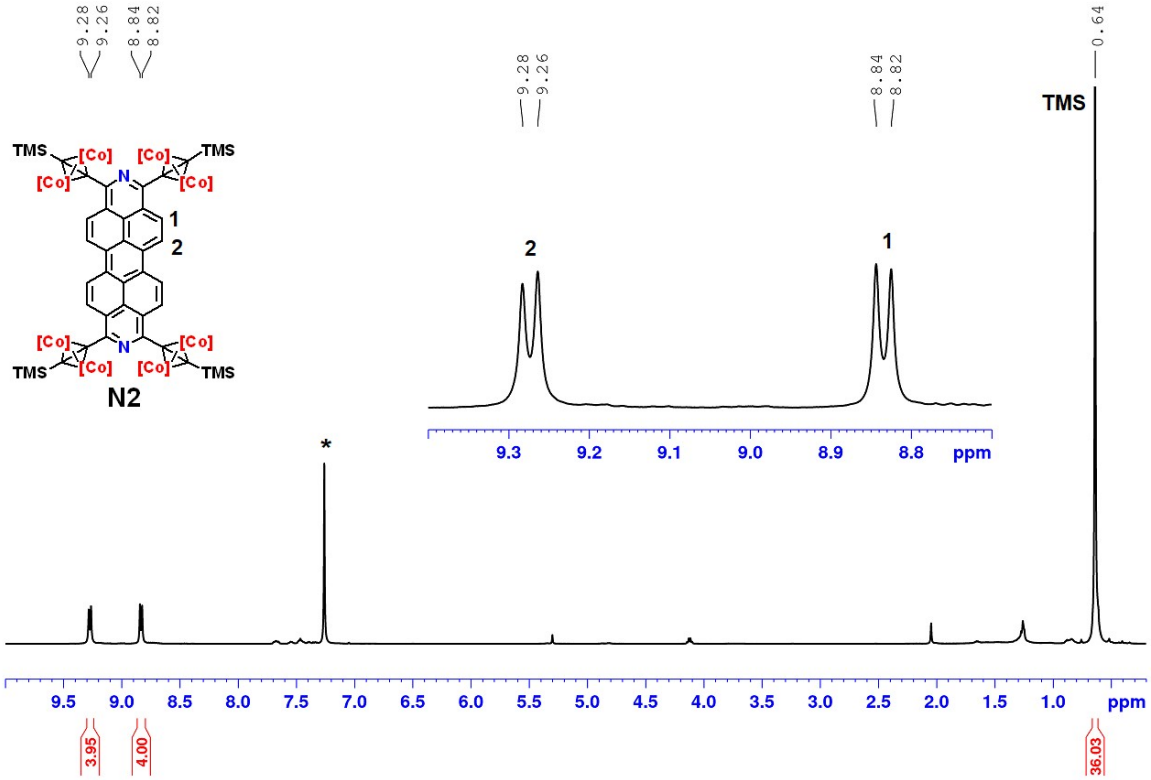


Figure S17. ^{1}H NMR (500.1 MHz, 298K, $CDCl_3$*) of **N2**. Contains solvent residues. The $[Co(CO)_3]$ units are abbreviated with [Co].

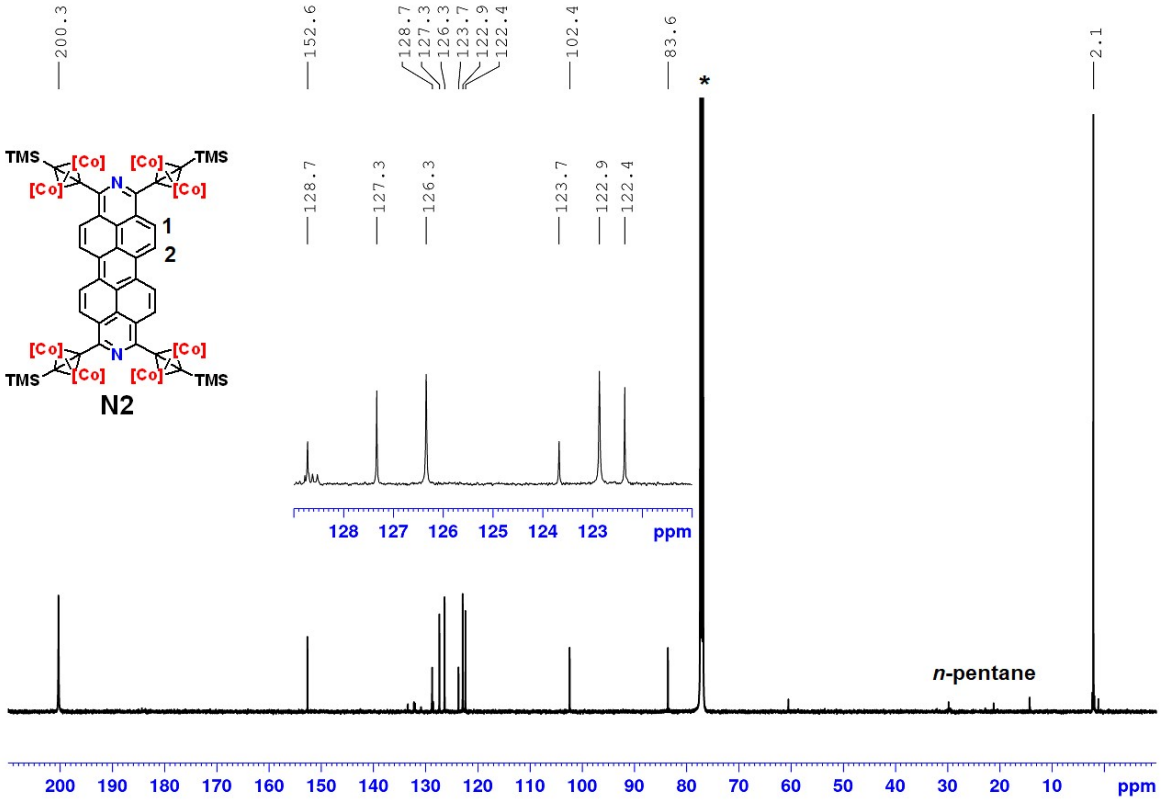


Figure S18. ^{13}C NMR (125.8 MHz, 298K, $CDCl_3$*) of **N2**. Contains solvent residues. The $[Co(CO)_3]$ units are abbreviated with [Co].

Single crystal X-ray structures

Crystal Data

Table 1. Crystal data and structure refinement for complex **N1**.

Identification code	SWP217_0m_a	
Empirical formula	C68 H64 Co8 N2 O24 Si4	
Formula weight	1877.01	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C 2/c	
Unit cell dimensions	a = 18.165(4) Å	a= 90°.
	b = 15.847(3) Å	b= 98.73(3)°.
	c = 28.456(6) Å	g = 90°.
Volume	8096(3) $Å^3$	
Z	4	
Density (calculated)	1.540 Mg/m^3	
Absorption coefficient	1.727 mm^{-1}	
F(000)	3800	
Crystal size	0.305 x 0.168 x 0.110 mm^3	
Theta range for data collection	2.130 to 25.752°.	
Index ranges	-22<=h<=22, -19<=k<=19, -34<=l<=34	
Reflections collected	145737	
Independent reflections	7743 [R(int) = 0.0562]	
Completeness to theta = 25.000°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7453 and 0.6979	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7743 / 37 / 517	
Goodness-of-fit on F^2	1.036	
Final R indices [I>2sigma(I)]	R1 = 0.0250, wR2 = 0.0529	
R indices (all data)	R1 = 0.0316, wR2 = 0.0550	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.546 and -0.421 $e.Å^{-3}$	

Table 2. Crystal data and structure refinement for complex **N2**.

Identification code	swp60_0m_a	
Empirical formula	C70 H48 Cl4 Co8 N2 O24 Si4	
Formula weight	2026.70	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 8.276(7) Å	a= 101.762(19)°.
	b = 14.505(12) Å	b= 99.807(18)°.
	c = 17.743(14) Å	g = 94.55(3)°.
Volume	2040(3) $Å^3$	
Z	1	
Density (calculated)	1.650 Mg/m^3	
Absorption coefficient	1.847 mm^{-1}	
F(000)	1014	
Crystal size	0.413 x 0.085 x 0.081 mm^3	
Theta range for data collection	2.389 to 25.253°.	
Index ranges	-9<=h<=9, -17<=k<=17, -20<=l<=21	
Reflections collected	44042	
Independent reflections	7323 [R(int) = 0.0793]	
Completeness to theta = 25.000°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7452 and 0.6048	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7323 / 490 / 557	
Goodness-of-fit on F^2	1.040	
Final R indices [I>2sigma(I)]	R1 = 0.0472, wR2 = 0.1026	
R indices (all data)	R1 = 0.0714, wR2 = 0.1120	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.174 and -0.905 $e.Å^{-3}$	

Molecular structures of the title compounds

Complex N1

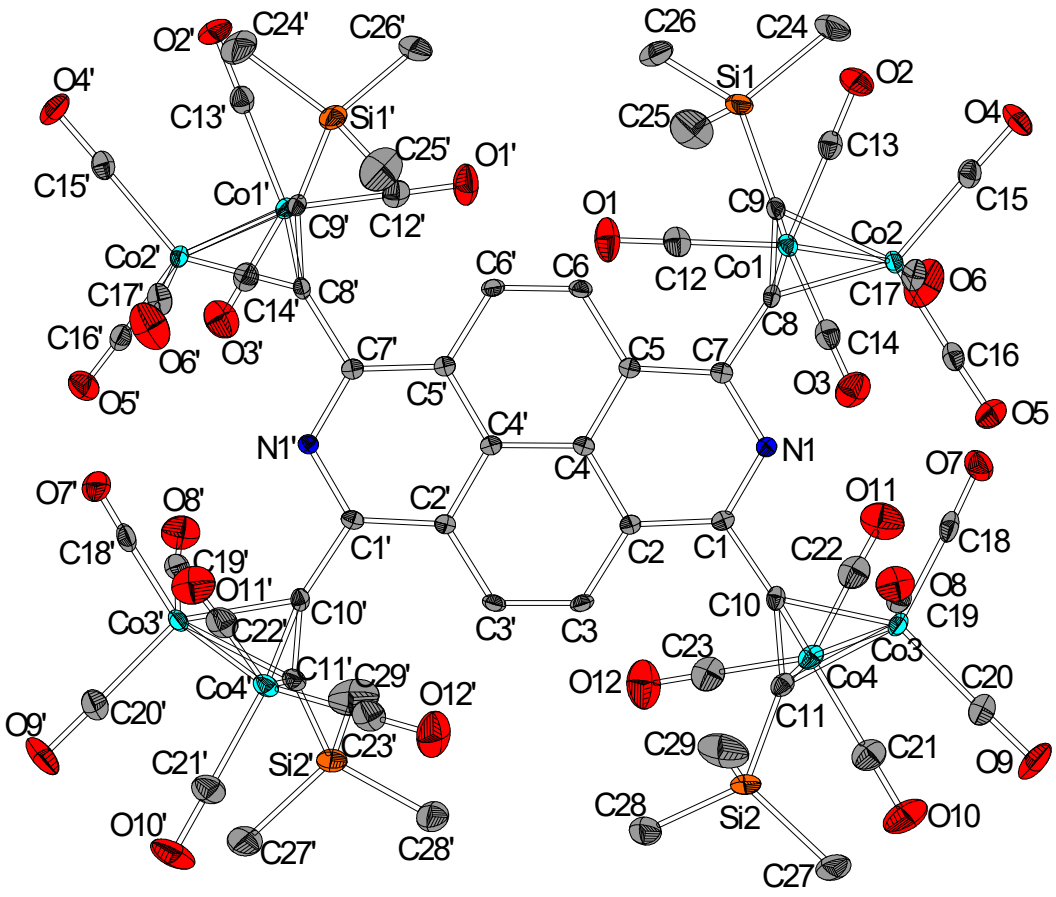


Figure S19. Reduced cell of the crystallographically determined molecular structure of **N1**. Protons are not shown. Symmetry transformations: 1 -x+1,y,-z+1/2

Table 3. Bond lengths [Å] and angles [°] **N1**.

C(1)-N(1)	1.346(2)
C(1)-C(2)	1.419(3)
C(1)-C(10)	1.465(3)
C(2)-C(4)	1.412(3)
C(2)-C(3)	1.427(3)
C(3)-C(3)#1	1.353(4)
C(3)-H(3)	0.9500
C(4)-C(5)	1.412(3)
C(4)-C(4)#1	1.430(4)
C(5)-C(7)	1.421(3)
C(5)-C(6)	1.429(3)
C(6)-C(6)#1	1.357(4)
C(6)-H(6)	0.9500
C(7)-N(1)	1.344(2)
C(7)-C(8)	1.464(3)
C(8)-C(9)	1.347(3)
C(8)-Co(2)	1.9425(19)
C(8)-Co(1)	1.9947(19)
C(9)-Si(1)	1.861(2)
C(9)-Co(2)	1.9858(19)
C(9)-Co(1)	1.9868(19)
C(10)-C(11)	1.346(3)

C(10)-Co(3)	1.9381(19)
C(10)-Co(4)	1.9930(19)
C(11)-Si(2)	1.861(2)
C(11)-Co(4)	1.988(2)
C(11)-Co(3)	1.997(2)
C(12)-O(1)	1.137(3)
C(12)-Co(1)	1.798(2)
C(13)-O(2)	1.132(2)
C(13)-Co(1)	1.820(2)
C(14)-O(3)	1.128(3)
C(14)-Co(1)	1.832(2)
C(15)-O(4)	1.135(2)
C(15)-Co(2)	1.822(2)
C(16)-O(5)	1.133(2)
C(16)-Co(2)	1.827(2)
C(17)-O(6)	1.134(3)
C(17)-Co(2)	1.797(2)
C(18)-O(7)	1.134(3)
C(18)-Co(3)	1.815(2)
C(19)-O(8)	1.134(3)
C(19)-Co(3)	1.796(2)
C(20)-O(9)	1.132(3)
C(20)-Co(3)	1.834(2)
C(21)-O(10)	1.135(3)
C(21)-Co(4)	1.820(2)
C(22)-O(11)	1.134(3)
C(22)-Co(4)	1.818(2)
C(23)-O(12)	1.134(3)
C(23)-Co(4)	1.803(2)
C(24)-Si(1)	1.860(2)
C(24)-H(24A)	0.9800
C(24)-H(24B)	0.9800
C(24)-H(24C)	0.9800
C(25)-Si(1)	1.864(3)
C(25)-H(25A)	0.9800
C(25)-H(25B)	0.9800
C(25)-H(25C)	0.9800
C(26)-Si(1)	1.868(3)
C(26)-H(26A)	0.9800
C(26)-H(26B)	0.9800
C(26)-H(26C)	0.9800
C(27)-Si(2)	1.849(2)
C(27)-H(27A)	0.9800
C(27)-H(27B)	0.9800
C(27)-H(27C)	0.9800
C(31)-C(30)	1.452(6)
C(31)-C(32)	1.534(4)
C(31)-C(36)	1.544(11)
C(31)-H(31A)	0.9900
C(31)-H(31B)	0.9900
C(32)-C(33)	1.471(4)
C(32)-H(32A)	0.9900
C(32)-H(32B)	0.9900
C(33)-C(34)	1.489(4)
C(33)-H(33A)	0.9900
C(33)-H(33B)	0.9900
C(34)-H(34A)	0.9800
C(34)-H(34B)	0.9800
C(34)-H(34C)	0.9800
Co(1)-Co(2)	2.4674(7)
Co(3)-Co(4)	2.4691(7)
Si(2)-C(37)	1.83(3)
Si(2)-C(28)	1.833(4)
Si(2)-C(29)	1.894(13)
Si(2)-C(35)	1.986(9)
C(28)-H(28A)	0.9800
C(28)-H(28B)	0.9800

C(28)-H(28C)	0.9800
C(29)-H(29A)	0.9800
C(29)-H(29B)	0.9800
C(29)-H(29C)	0.9800
C(30)-H(30A)	0.9800
C(30)-H(30B)	0.9800
C(30)-H(30C)	0.9800
C(35)-H(35A)	0.9800
C(35)-H(35B)	0.9800
C(35)-H(35C)	0.9800
C(36)-H(36A)	0.9800
C(36)-H(36B)	0.9800
C(36)-H(36C)	0.9800
C(37)-H(37A)	0.9800
C(37)-H(37B)	0.9800
C(37)-H(37C)	0.9800

N(1)-C(1)-C(2)	122.76(16)
N(1)-C(1)-C(10)	116.69(16)
C(2)-C(1)-C(10)	120.55(16)
C(4)-C(2)-C(1)	117.44(16)
C(4)-C(2)-C(3)	118.42(17)
C(1)-C(2)-C(3)	124.15(17)
C(3)#1-C(3)-C(2)	121.50(11)
C(3)#1-C(3)-H(3)	119.2
C(2)-C(3)-H(3)	119.2
C(5)-C(4)-C(2)	119.84(16)
C(5)-C(4)-C(4)#1	120.11(11)
C(2)-C(4)-C(4)#1	120.04(10)
C(4)-C(5)-C(7)	117.75(16)
C(4)-C(5)-C(6)	118.37(17)
C(7)-C(5)-C(6)	123.87(17)
C(6)#1-C(6)-C(5)	121.45(11)
C(6)#1-C(6)-H(6)	119.3
C(5)-C(6)-H(6)	119.3
N(1)-C(7)-C(5)	122.38(16)
N(1)-C(7)-C(8)	117.11(16)
C(5)-C(7)-C(8)	120.50(16)
C(9)-C(8)-C(7)	144.02(18)
C(9)-C(8)-Co(2)	71.69(11)
C(7)-C(8)-Co(2)	135.91(14)
C(9)-C(8)-Co(1)	69.91(11)
C(7)-C(8)-Co(1)	129.56(13)
Co(2)-C(8)-Co(1)	77.60(7)
C(8)-C(9)-Si(1)	149.97(15)
C(8)-C(9)-Co(2)	68.22(11)
Si(1)-C(9)-Co(2)	129.98(10)
C(8)-C(9)-Co(1)	70.54(11)
Si(1)-C(9)-Co(1)	131.76(10)
Co(2)-C(9)-Co(1)	76.79(7)
C(11)-C(10)-C(1)	145.04(18)
C(11)-C(10)-Co(3)	72.38(12)
C(1)-C(10)-Co(3)	132.38(14)
C(11)-C(10)-Co(4)	70.03(11)
C(1)-C(10)-Co(4)	131.68(13)
Co(3)-C(10)-Co(4)	77.81(7)
C(10)-C(11)-Si(2)	149.17(16)
C(10)-C(11)-Co(4)	70.44(11)
Si(2)-C(11)-Co(4)	134.45(11)
C(10)-C(11)-Co(3)	67.65(11)
Si(2)-C(11)-Co(3)	128.27(10)
Co(4)-C(11)-Co(3)	76.57(8)
O(1)-C(12)-Co(1)	179.8(2)
O(2)-C(13)-Co(1)	177.59(19)
O(3)-C(14)-Co(1)	179.6(2)
O(4)-C(15)-Co(2)	178.47(19)
O(5)-C(16)-Co(2)	178.02(18)

O(6)-C(17)-Co(2)	178.10(19)
O(7)-C(18)-Co(3)	177.32(19)
O(8)-C(19)-Co(3)	176.62(19)
O(9)-C(20)-Co(3)	178.7(2)
O(10)-C(21)-Co(4)	179.2(2)
O(11)-C(22)-Co(4)	178.3(2)
O(12)-C(23)-Co(4)	179.4(2)
Si(1)-C(24)-H(24A)	109.5
Si(1)-C(24)-H(24B)	109.5
H(24A)-C(24)-H(24B)	109.5
Si(1)-C(24)-H(24C)	109.5
H(24A)-C(24)-H(24C)	109.5
H(24B)-C(24)-H(24C)	109.5
Si(1)-C(25)-H(25A)	109.5
Si(1)-C(25)-H(25B)	109.5
H(25A)-C(25)-H(25B)	109.5
Si(1)-C(25)-H(25C)	109.5
H(25A)-C(25)-H(25C)	109.5
H(25B)-C(25)-H(25C)	109.5
Si(1)-C(26)-H(26A)	109.5
Si(1)-C(26)-H(26B)	109.5
H(26A)-C(26)-H(26B)	109.5
Si(1)-C(26)-H(26C)	109.5
H(26A)-C(26)-H(26C)	109.5
H(26B)-C(26)-H(26C)	109.5
Si(2)-C(27)-H(27A)	109.5
Si(2)-C(27)-H(27B)	109.5
H(27A)-C(27)-H(27B)	109.5
Si(2)-C(27)-H(27C)	109.5
H(27A)-C(27)-H(27C)	109.5
H(27B)-C(27)-H(27C)	109.5
C(30)-C(31)-C(32)	114.0(3)
C(32)-C(31)-C(36)	114.7(5)
C(30)-C(31)-H(31A)	108.8
C(32)-C(31)-H(31A)	108.8
C(30)-C(31)-H(31B)	108.8
C(32)-C(31)-H(31B)	108.8
H(31A)-C(31)-H(31B)	107.7
C(33)-C(32)-C(31)	115.0(3)
C(33)-C(32)-H(32A)	108.5
C(31)-C(32)-H(32A)	108.5
C(33)-C(32)-H(32B)	108.5
C(31)-C(32)-H(32B)	108.5
H(32A)-C(32)-H(32B)	107.5
C(32)-C(33)-C(34)	114.9(3)
C(32)-C(33)-H(33A)	108.5
C(34)-C(33)-H(33A)	108.5
C(32)-C(33)-H(33B)	108.5
C(34)-C(33)-H(33B)	108.5
H(33A)-C(33)-H(33B)	107.5
C(33)-C(34)-H(34A)	109.5
C(33)-C(34)-H(34B)	109.5
H(34A)-C(34)-H(34B)	109.5
C(33)-C(34)-H(34C)	109.5
H(34A)-C(34)-H(34C)	109.5
H(34B)-C(34)-H(34C)	109.5
C(12)-Co(1)-C(13)	100.18(9)
C(12)-Co(1)-C(14)	98.16(9)
C(13)-Co(1)-C(14)	106.24(9)
C(12)-Co(1)-C(9)	103.42(9)
C(13)-Co(1)-C(9)	100.12(8)
C(14)-Co(1)-C(9)	142.15(8)
C(12)-Co(1)-C(8)	102.01(8)
C(13)-Co(1)-C(8)	137.61(8)
C(14)-Co(1)-C(8)	105.76(8)
C(9)-Co(1)-C(8)	39.55(8)
C(12)-Co(1)-Co(2)	151.24(6)

C(13)-Co(1)-Co(2)	98.53(7)
C(14)-Co(1)-Co(2)	97.32(7)
C(9)-Co(1)-Co(2)	51.58(6)
C(8)-Co(1)-Co(2)	50.25(5)
C(17)-Co(2)-C(15)	100.67(10)
C(17)-Co(2)-C(16)	99.85(9)
C(15)-Co(2)-C(16)	101.59(9)
C(17)-Co(2)-C(8)	98.02(9)
C(15)-Co(2)-C(8)	144.02(8)
C(16)-Co(2)-C(8)	105.14(8)
C(17)-Co(2)-C(9)	99.72(9)
C(15)-Co(2)-C(9)	106.07(8)
C(16)-Co(2)-C(9)	142.24(8)
C(8)-Co(2)-C(9)	40.09(8)
C(17)-Co(2)-Co(1)	148.33(7)
C(15)-Co(2)-Co(1)	100.54(7)
C(16)-Co(2)-Co(1)	98.60(6)
C(8)-Co(2)-Co(1)	52.14(6)
C(9)-Co(2)-Co(1)	51.62(6)
C(19)-Co(3)-C(18)	100.21(9)
C(19)-Co(3)-C(20)	100.99(10)
C(18)-Co(3)-C(20)	105.65(10)
C(19)-Co(3)-C(10)	97.22(9)
C(18)-Co(3)-C(10)	100.57(9)
C(20)-Co(3)-C(10)	144.62(9)
C(19)-Co(3)-C(11)	99.45(9)
C(18)-Co(3)-C(11)	137.84(8)
C(20)-Co(3)-C(11)	106.66(9)
C(10)-Co(3)-C(11)	39.97(8)
C(19)-Co(3)-Co(4)	147.67(7)
C(18)-Co(3)-Co(4)	95.99(7)
C(20)-Co(3)-Co(4)	101.29(7)
C(10)-Co(3)-Co(4)	52.09(6)
C(11)-Co(3)-Co(4)	51.54(6)
C(23)-Co(4)-C(22)	98.15(10)
C(23)-Co(4)-C(21)	100.06(10)
C(22)-Co(4)-C(21)	104.02(10)
C(23)-Co(4)-C(11)	102.92(10)
C(22)-Co(4)-C(11)	143.22(9)
C(21)-Co(4)-C(11)	101.56(9)
C(23)-Co(4)-C(10)	103.16(9)
C(22)-Co(4)-C(10)	106.38(9)
C(21)-Co(4)-C(10)	138.27(9)
C(11)-Co(4)-C(10)	39.53(8)
C(23)-Co(4)-Co(3)	151.83(7)
C(22)-Co(4)-Co(3)	98.45(7)
C(21)-Co(4)-Co(3)	97.80(7)
C(11)-Co(4)-Co(3)	51.89(6)
C(10)-Co(4)-Co(3)	50.11(6)
C(7)-N(1)-C(1)	119.51(16)
C(24)-Si(1)-C(9)	110.35(10)
C(24)-Si(1)-C(25)	110.07(13)
C(9)-Si(1)-C(25)	108.37(11)
C(24)-Si(1)-C(26)	108.51(12)
C(9)-Si(1)-C(26)	108.25(10)
C(25)-Si(1)-C(26)	111.28(13)
C(37)-Si(2)-C(27)	119.4(8)
C(28)-Si(2)-C(27)	110.06(15)
C(37)-Si(2)-C(11)	109.3(10)
C(28)-Si(2)-C(11)	112.89(14)
C(27)-Si(2)-C(11)	110.42(11)
C(28)-Si(2)-C(29)	108.6(3)
C(27)-Si(2)-C(29)	108.1(3)
C(11)-Si(2)-C(29)	106.6(4)
C(37)-Si(2)-C(35)	111.5(6)
C(27)-Si(2)-C(35)	101.5(3)
C(11)-Si(2)-C(35)	103.4(3)

Si(2)-C(28)-H(28A)	109.5
Si(2)-C(28)-H(28B)	109.5
H(28A)-C(28)-H(28B)	109.5
Si(2)-C(28)-H(28C)	109.5
H(28A)-C(28)-H(28C)	109.5
H(28B)-C(28)-H(28C)	109.5
Si(2)-C(29)-H(29A)	109.5
Si(2)-C(29)-H(29B)	109.5
H(29A)-C(29)-H(29B)	109.5
Si(2)-C(29)-H(29C)	109.5
H(29A)-C(29)-H(29C)	109.5
H(29B)-C(29)-H(29C)	109.5
C(31)-C(30)-H(30A)	109.5
C(31)-C(30)-H(30B)	109.5
H(30A)-C(30)-H(30B)	109.5
C(31)-C(30)-H(30C)	109.5
H(30A)-C(30)-H(30C)	109.5
H(30B)-C(30)-H(30C)	109.5
Si(2)-C(35)-H(35A)	109.5
Si(2)-C(35)-H(35B)	109.5
H(35A)-C(35)-H(35B)	109.5
Si(2)-C(35)-H(35C)	109.5
H(35A)-C(35)-H(35C)	109.5
H(35B)-C(35)-H(35C)	109.5
C(31)-C(36)-H(36A)	109.5
C(31)-C(36)-H(36B)	109.5
H(36A)-C(36)-H(36B)	109.5
C(31)-C(36)-H(36C)	109.5
H(36A)-C(36)-H(36C)	109.5
H(36B)-C(36)-H(36C)	109.5
Si(2)-C(37)-H(37A)	109.5
Si(2)-C(37)-H(37B)	109.5
H(37A)-C(37)-H(37B)	109.5
Si(2)-C(37)-H(37C)	109.5
H(37A)-C(37)-H(37C)	109.5
H(37B)-C(37)-H(37C)	109.5

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

Complex N2

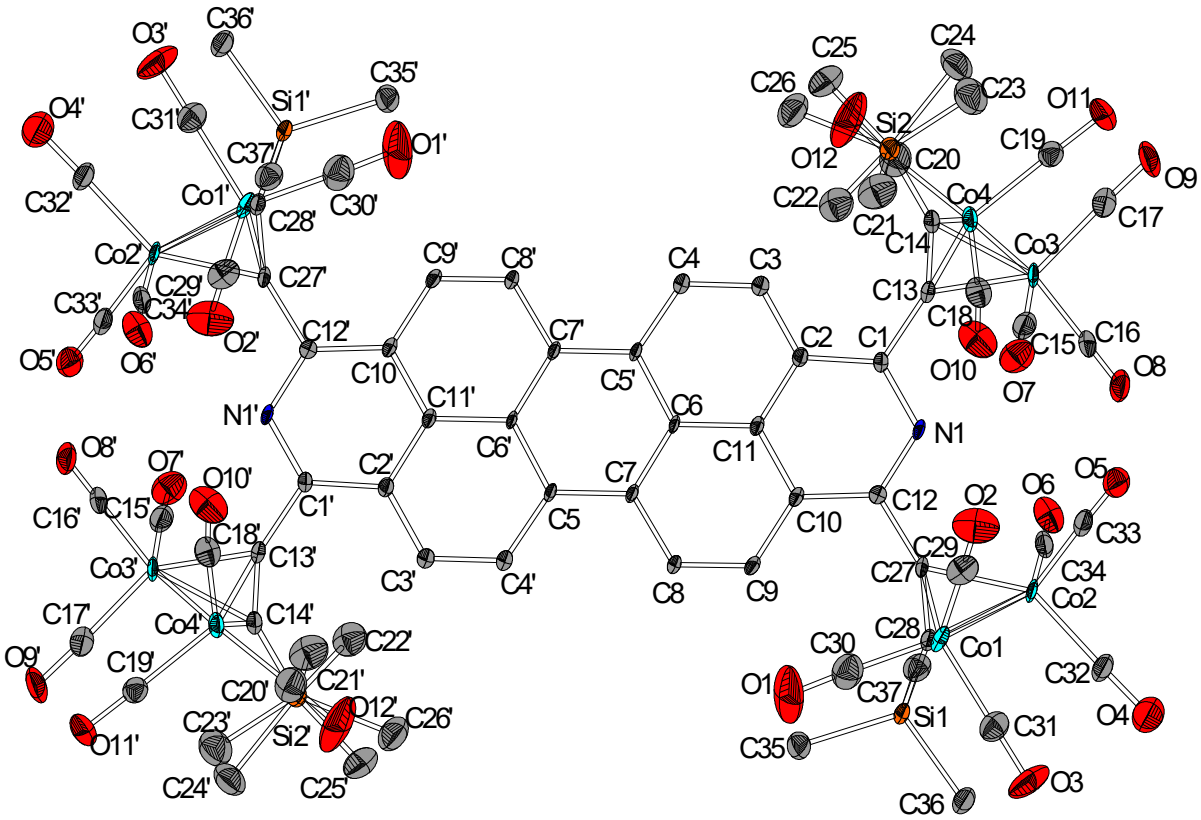


Figure S20. Reduced cell of the crystallographically determined molecular structure of **N2**. Protons and solvent molecules are not shown. Symmetry transformations: #1 -x,-y+1,-z+1

Table 4. Bond lengths [Å] and angles [°] for **N2**.

Co(1)-C(30)	1.786(6)
Co(1)-C(31)	1.810(5)
Co(1)-C(29)	1.823(5)
Co(1)-C(28)	1.982(4)
Co(1)-C(27)	1.988(4)
Co(1)-Co(2)	2.4724(18)
C(1)-N(1)	1.350(5)
C(1)-C(2)	1.417(6)
C(1)-C(13)	1.468(6)
N(1)-C(12)	1.342(5)
O(1)-C(30)	1.154(7)
Si(1)-C(28)	1.859(4)
Si(1)-C(37)	1.860(5)
Si(1)-C(36)	1.865(4)
Si(1)-C(35)	1.875(5)
Co(2)-C(34)	1.789(5)
Co(2)-C(33)	1.817(5)
Co(2)-C(32)	1.817(4)
Co(2)-C(27)	1.953(4)
Co(2)-C(28)	1.997(4)
C(2)-C(11)	1.410(6)
C(2)-C(3)	1.423(5)
O(2)-C(29)	1.129(6)
Si(2)-C(25)	1.841(12)
Si(2)-C(22)	1.847(13)
Si(2)-C(21)	1.851(10)
Si(2)-C(23)	1.855(14)
Si(2)-C(24)	1.858(10)

Si(2)-C(14)	1.861(4)
Si(2)-C(26)	1.887(10)
Co(4)-C(20)	1.784(5)
Co(4)-C(19)	1.812(5)
Co(4)-C(18)	1.832(5)
Co(4)-C(13)	1.983(4)
Co(4)-C(14)	1.998(4)
Co(4)-Co(3)	2.4669(19)
C(4)-C(3)	1.369(6)
C(4)-C(5)#1	1.422(6)
C(4)-H(4)	0.9500
O(4)-C(32)	1.139(5)
Co(3)-C(15)	1.795(5)
Co(3)-C(16)	1.815(5)
Co(3)-C(17)	1.827(5)
Co(3)-C(13)	1.956(4)
Co(3)-C(14)	1.991(4)
C(3)-H(3)	0.9500
O(3)-C(31)	1.140(6)
O(8)-C(16)	1.142(5)
C(8)-C(9)	1.356(6)
C(8)-C(7)	1.439(5)
C(8)-H(8)	0.9500
O(7)-C(15)	1.136(6)
C(7)-C(6)	1.409(6)
C(7)-C(5)	1.424(5)
O(6)-C(34)	1.135(5)
C(6)-C(5)#1	1.431(5)
C(6)-C(11)	1.437(5)
O(5)-C(33)	1.133(5)
O(9)-C(17)	1.140(6)
C(9)-C(10)	1.415(6)
C(9)-H(9)	0.9500
O(10)-C(18)	1.135(6)
C(10)-C(12)	1.415(6)
C(10)-C(11)	1.417(5)
O(11)-C(19)	1.140(6)
O(12)-C(20)	1.136(6)
C(12)-C(27)	1.474(5)
C(13)-C(14)	1.340(6)
C(27)-C(28)	1.347(6)
C(35)-H(35A)	0.9800
C(35)-H(35B)	0.9800
C(35)-H(35C)	0.9800
C(36)-H(36A)	0.9800
C(36)-H(36B)	0.9800
C(36)-H(36C)	0.9800
C(37)-H(37A)	0.9800
C(37)-H(37B)	0.9800
C(37)-H(37C)	0.9800
C(22)-H(22A)	0.9800
C(22)-H(22B)	0.9800
C(22)-H(22C)	0.9800
C(23)-H(23A)	0.9800
C(23)-H(23B)	0.9800
C(23)-H(23C)	0.9800
C(25)-H(25A)	0.9800
C(25)-H(25B)	0.9800
C(25)-H(25C)	0.9800
C(21)-H(21A)	0.9800
C(21)-H(21B)	0.9800
C(21)-H(21C)	0.9800
C(24)-H(24A)	0.9800
C(24)-H(24B)	0.9800
C(24)-H(24C)	0.9800
C(26)-H(26A)	0.9800
C(26)-H(26B)	0.9800

C(26)-H(26C)	0.9800
Cl(1)-C(39)	1.782(12)
Cl(2)-C(39)	1.762(12)
C(39)-H(39A)	0.9900
C(39)-H(39B)	0.9900
C(38)-Cl(3)	1.702(10)
C(38)-Cl(4)	1.742(12)
C(38)-H(38A)	0.9900
C(38)-H(38B)	0.9900

C(30)-Co(1)-C(31)	98.4(2)
C(30)-Co(1)-C(29)	100.0(2)
C(31)-Co(1)-C(29)	108.6(2)
C(30)-Co(1)-C(28)	102.2(2)
C(31)-Co(1)-C(28)	102.23(19)
C(29)-Co(1)-C(28)	138.5(2)
C(30)-Co(1)-C(27)	106.9(2)
C(31)-Co(1)-C(27)	137.36(19)
C(29)-Co(1)-C(27)	100.2(2)
C(28)-Co(1)-C(27)	39.68(16)
C(30)-Co(1)-Co(2)	153.37(17)
C(31)-Co(1)-Co(2)	93.84(17)
C(29)-Co(1)-Co(2)	98.27(17)
C(28)-Co(1)-Co(2)	51.86(12)
C(27)-Co(1)-Co(2)	50.51(11)
N(1)-C(1)-C(2)	123.2(4)
N(1)-C(1)-C(13)	116.4(3)
C(2)-C(1)-C(13)	120.4(3)
C(12)-N(1)-C(1)	118.1(3)
C(28)-Si(1)-C(37)	106.3(2)
C(28)-Si(1)-C(36)	109.4(2)
C(37)-Si(1)-C(36)	111.6(2)
C(28)-Si(1)-C(35)	111.6(2)
C(37)-Si(1)-C(35)	110.8(2)
C(36)-Si(1)-C(35)	107.1(2)
C(34)-Co(2)-C(33)	99.4(2)
C(34)-Co(2)-C(32)	100.0(2)
C(33)-Co(2)-C(32)	101.4(2)
C(34)-Co(2)-C(27)	96.17(19)
C(33)-Co(2)-C(27)	106.44(18)
C(32)-Co(2)-C(27)	145.0(2)
C(34)-Co(2)-C(28)	100.50(19)
C(33)-Co(2)-C(28)	142.40(18)
C(32)-Co(2)-C(28)	106.2(2)
C(27)-Co(2)-C(28)	39.86(17)
C(34)-Co(2)-Co(1)	147.07(14)
C(33)-Co(2)-Co(1)	97.55(15)
C(32)-Co(2)-Co(1)	104.12(17)
C(27)-Co(2)-Co(1)	51.78(13)
C(28)-Co(2)-Co(1)	51.30(13)
C(11)-C(2)-C(1)	118.2(3)
C(11)-C(2)-C(3)	118.6(4)
C(1)-C(2)-C(3)	123.2(4)
C(25)-Si(2)-C(22)	111.4(6)
C(25)-Si(2)-C(23)	110.7(6)
C(22)-Si(2)-C(23)	109.6(7)
C(21)-Si(2)-C(24)	110.4(5)
C(25)-Si(2)-C(14)	111.5(4)
C(22)-Si(2)-C(14)	105.5(4)
C(21)-Si(2)-C(14)	109.9(3)
C(23)-Si(2)-C(14)	108.0(4)
C(24)-Si(2)-C(14)	108.2(3)
C(21)-Si(2)-C(26)	107.8(5)
C(24)-Si(2)-C(26)	106.7(5)
C(14)-Si(2)-C(26)	113.8(3)
C(20)-Co(4)-C(19)	98.9(2)
C(20)-Co(4)-C(18)	101.2(2)

C(19)-Co(4)-C(18)	106.7(2)
C(20)-Co(4)-C(13)	111.1(2)
C(19)-Co(4)-C(13)	139.15(19)
C(18)-Co(4)-C(13)	94.3(2)
C(20)-Co(4)-C(14)	97.3(2)
C(19)-Co(4)-C(14)	111.86(19)
C(18)-Co(4)-C(14)	133.7(2)
C(13)-Co(4)-C(14)	39.36(17)
C(20)-Co(4)-Co(3)	148.38(17)
C(19)-Co(4)-Co(3)	89.46(15)
C(18)-Co(4)-Co(3)	105.50(16)
C(13)-Co(4)-Co(3)	50.73(12)
C(14)-Co(4)-Co(3)	51.68(12)
C(3)-C(4)-C(5)#1	122.1(4)
C(3)-C(4)-H(4)	118.9
C(5)#1-C(4)-H(4)	118.9
C(15)-Co(3)-C(16)	101.6(2)
C(15)-Co(3)-C(17)	98.8(2)
C(16)-Co(3)-C(17)	104.9(2)
C(15)-Co(3)-C(13)	97.6(2)
C(16)-Co(3)-C(13)	101.78(19)
C(17)-Co(3)-C(13)	144.99(19)
C(15)-Co(3)-C(14)	101.31(19)
C(16)-Co(3)-C(14)	137.38(18)
C(17)-Co(3)-C(14)	106.45(19)
C(13)-Co(3)-C(14)	39.69(17)
C(15)-Co(3)-Co(4)	148.52(15)
C(16)-Co(3)-Co(4)	92.65(14)
C(17)-Co(3)-Co(4)	104.47(16)
C(13)-Co(3)-Co(4)	51.70(13)
C(14)-Co(3)-Co(4)	51.91(12)
C(4)-C(3)-C(2)	121.0(4)
C(4)-C(3)-H(3)	119.5
C(2)-C(3)-H(3)	119.5
C(9)-C(8)-C(7)	121.7(4)
C(9)-C(8)-H(8)	119.1
C(7)-C(8)-H(8)	119.1
C(6)-C(7)-C(5)	120.3(3)
C(6)-C(7)-C(8)	118.1(4)
C(5)-C(7)-C(8)	121.6(4)
C(7)-C(6)-C(5)#1	120.9(4)
C(7)-C(6)-C(11)	119.8(3)
C(5)#1-C(6)-C(11)	119.2(4)
C(4)#1-C(5)-C(7)	123.1(3)
C(4)#1-C(5)-C(6)#1	118.1(4)
C(7)-C(5)-C(6)#1	118.8(4)
C(8)-C(9)-C(10)	121.5(4)
C(8)-C(9)-H(9)	119.2
C(10)-C(9)-H(9)	119.2
C(12)-C(10)-C(9)	123.7(4)
C(12)-C(10)-C(11)	117.8(4)
C(9)-C(10)-C(11)	118.5(4)
C(2)-C(11)-C(10)	118.9(4)
C(2)-C(11)-C(6)	120.8(3)
C(10)-C(11)-C(6)	120.3(4)
N(1)-C(12)-C(10)	123.7(3)
N(1)-C(12)-C(27)	116.1(4)
C(10)-C(12)-C(27)	120.2(4)
C(14)-C(13)-C(1)	145.1(4)
C(14)-C(13)-Co(3)	71.6(2)
C(1)-C(13)-Co(3)	131.8(3)
C(14)-C(13)-Co(4)	70.9(3)
C(1)-C(13)-Co(4)	132.3(3)
Co(3)-C(13)-Co(4)	77.57(16)
C(13)-C(14)-Si(2)	148.2(3)
C(13)-C(14)-Co(3)	68.7(2)
Si(2)-C(14)-Co(3)	129.2(2)

C(13)-C(14)-Co(4)	69.7(2)
Si(2)-C(14)-Co(4)	134.8(2)
Co(3)-C(14)-Co(4)	76.41(15)
O(7)-C(15)-Co(3)	177.7(4)
O(9)-C(17)-Co(3)	177.8(4)
O(8)-C(16)-Co(3)	176.7(4)
O(10)-C(18)-Co(4)	174.3(4)
O(11)-C(19)-Co(4)	178.5(4)
O(12)-C(20)-Co(4)	178.5(6)
C(28)-C(27)-C(12)	144.4(4)
C(28)-C(27)-Co(2)	71.8(2)
C(12)-C(27)-Co(2)	132.6(3)
C(28)-C(27)-Co(1)	69.9(2)
C(12)-C(27)-Co(1)	132.8(3)
Co(2)-C(27)-Co(1)	77.70(14)
C(27)-C(28)-Si(1)	148.6(3)
C(27)-C(28)-Co(1)	70.4(2)
Si(1)-C(28)-Co(1)	135.3(2)
C(27)-C(28)-Co(2)	68.3(2)
Si(1)-C(28)-Co(2)	127.3(2)
Co(1)-C(28)-Co(2)	76.84(15)
O(2)-C(29)-Co(1)	178.2(4)
O(1)-C(30)-Co(1)	178.2(5)
O(3)-C(31)-Co(1)	177.8(5)
O(4)-C(32)-Co(2)	178.4(5)
O(5)-C(33)-Co(2)	177.8(4)
O(6)-C(34)-Co(2)	177.0(4)
Si(1)-C(35)-H(35A)	109.5
Si(1)-C(35)-H(35B)	109.5
H(35A)-C(35)-H(35B)	109.5
Si(1)-C(35)-H(35C)	109.5
H(35A)-C(35)-H(35C)	109.5
H(35B)-C(35)-H(35C)	109.5
Si(1)-C(36)-H(36A)	109.5
Si(1)-C(36)-H(36B)	109.5
H(36A)-C(36)-H(36B)	109.5
Si(1)-C(36)-H(36C)	109.5
H(36A)-C(36)-H(36C)	109.5
H(36B)-C(36)-H(36C)	109.5
Si(1)-C(37)-H(37A)	109.5
Si(1)-C(37)-H(37B)	109.5
H(37A)-C(37)-H(37B)	109.5
Si(1)-C(37)-H(37C)	109.5
H(37A)-C(37)-H(37C)	109.5
H(37B)-C(37)-H(37C)	109.5
Si(2)-C(22)-H(22A)	109.5
Si(2)-C(22)-H(22B)	109.5
H(22A)-C(22)-H(22B)	109.5
Si(2)-C(22)-H(22C)	109.5
H(22A)-C(22)-H(22C)	109.5
H(22B)-C(22)-H(22C)	109.5
Si(2)-C(23)-H(23A)	109.5
Si(2)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23B)	109.5
Si(2)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5
Si(2)-C(25)-H(25A)	109.5
Si(2)-C(25)-H(25B)	109.5
H(25A)-C(25)-H(25B)	109.5
Si(2)-C(25)-H(25C)	109.5
H(25A)-C(25)-H(25C)	109.5
H(25B)-C(25)-H(25C)	109.5
Si(2)-C(21)-H(21A)	109.5
Si(2)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
Si(2)-C(21)-H(21C)	109.5

H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5
Si(2)-C(24)-H(24A)	109.5
Si(2)-C(24)-H(24B)	109.5
H(24A)-C(24)-H(24B)	109.5
Si(2)-C(24)-H(24C)	109.5
H(24A)-C(24)-H(24C)	109.5
H(24B)-C(24)-H(24C)	109.5
Si(2)-C(26)-H(26A)	109.5
Si(2)-C(26)-H(26B)	109.5
H(26A)-C(26)-H(26B)	109.5
Si(2)-C(26)-H(26C)	109.5
H(26A)-C(26)-H(26C)	109.5
H(26B)-C(26)-H(26C)	109.5
Cl(2)-C(39)-Cl(1)	107.5(7)
Cl(2)-C(39)-H(39A)	110.2
Cl(1)-C(39)-H(39A)	110.2
Cl(2)-C(39)-H(39B)	110.2
Cl(1)-C(39)-H(39B)	110.2
H(39A)-C(39)-H(39B)	108.5
Cl(3)-C(38)-Cl(4)	115.6(7)
Cl(3)-C(38)-H(38A)	108.4
Cl(4)-C(38)-H(38A)	108.4
Cl(3)-C(38)-H(38B)	108.4
Cl(4)-C(38)-H(38B)	108.4
H(38A)-C(38)-H(38B)	107.4

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