Electronic Supplementary Material (ESI) for Chemical Communications.

An Elusive Vinyl Radical Isolated as an Appended Unit in a Five-Coordinate Co(III)–Bis(Iminobenzosemiquinone) Complex Formed *via* Ligand–Centered C–S Bond Cleavage

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EXPERIMENTAL SECTION:

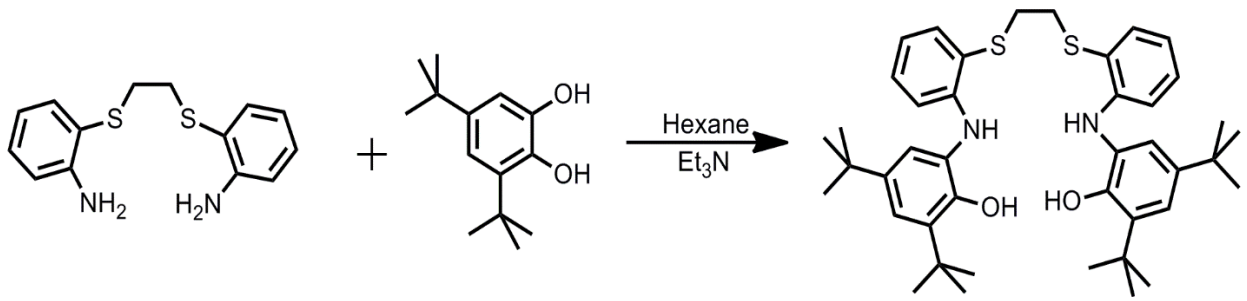
Materials: All the chemicals and solvents were obtained from commercial sources and were used as supplied, unless noted otherwise. 3,5–di–*tert*–butylcatechol, 2-aminothiophenol, and 1,2-dibromoethane were purchased from Sigma–Aldrich. Solvents were obtained from Merck (India). Mass spectra were measured in HPLC grade acetonitrile solution.

Physical methods: X–ray crystallographic data were collected using Super Nova, Single source at offset, Eos diffractometer. The data refinement and cell reductions were carried out by CrysAlisPro.[1a] Structures were solved by direct methods using SHELXS–97 and refined by the full matrix least squares method using SHELXL 2014[1b] present in the program suite WinGX (version 2014.1)[1c]. All the non–hydrogen atoms were refined anisotropically. All hydrogen atoms (except H22A/H22B) were positioned geometrically and refined isotropically using a riding model with U_{iso}(H) = 1.2Ueq[C], U_{iso}(H) = 1.5Ueq (methyl groups). C22A/C22B - bound H atoms were located using difference Fourier maps, but in the final refinement their distances were constrained at 0.97 Å (DFIX). IR spectra were recorded on a Perkin Elmer Instrument at normal temperature with KBr pellet by grinding the sample with KBr (IR Grade). ^{1}H–, and ^{13}C–NMR spectra of the ligand were recorded in BRUKER 600 MHz NMR machine. UV–Vis spectra were recorded on a Perkin Elmer, Lamda 750, UV/VIS/NIR spectrometer by preparing a known concentration of the samples in HPLC Grade CH_2Cl_2 at room temperature (25 °C) using a cuvette of 1 cm width. Mass spectral (MS) data were obtained from quadrupole time–of–flight (QTOF)–MS spectrometer ('Waters, Model: Q–Tof Premier') and peaks are given in *m/z* (% of basis peak). Magnetic susceptibility of the complex in solution was measured using Evan's method at 400 MHz NMR machine (Varian, Model: Mercury plus). Variable temperature magnetic susceptibility measurements for the complex were performed using superconducting quantum interference device (SQUID) magnetometer at 1 T. Simulations of the experimentally obtained magnetic measurements were performed using *julX* programme developed by Dr. E. Bill, Max-Planck Institute, Muelheim an der Ruhr, Germany.

Computational Details: All DFT calculations are performed using Gaussian09[2] program suit. The initial geometry optimization is performed at M06[3]/6-31+G(d,p) and subjected for further optimization using the PBE functional (exchange and correlation) (PBEPBE)[4] in conjunction with an uncontracted Ahlrichs def2-TZVP[5] basis set. Subsequently, frequency calculations are also performed at the same level (*i.e.*, PBEPBE/def2-TZVP). The natural bond orbital (NBO) analysis[6] is performed to understand the bonding nature of the atoms as implemented in Gaussian09.

Syntheses:

Synthesis of 1,2-Bis(2-aminophenylthio)ethane: Same as previously been reported.[7]



Synthesis of [$C_{42}H_{56}N_2O_2S_2$], $H_4Pra^{edt(AP/AP)}$: To a solution of 1,2-bis(aminophenylthio)ethane (1.10 gm, 4 mmol) and 3,5-di-*tert*-butylcatechol (2.22 g, 10 mmol) in hexane (30 mL), Et_3N (0.1 mL) was added. The solution was refluxed for 24 h. During this period a brown color precipitate was appeared. The resulting suspension was further stirred at room temperature (25 °C) for 2 h. Thus formed precipitate was filtered and washed with methanol thoroughly. The solid was dried under high vacuum. Yield: 1.947 g, 71%. FTIR (KBr pellet cm^{-1}): 3379, 3297, 2955, 2907, 2867, 1586, 1476, 1448, 1420, 1362, 1310, 1222, 1201, 1157, 1126, 1117, 1057, 1035, 974, 881, 823, 810, 754, 676, 620. ^{1}H NMR ($CDCl_3$, 600MHz): δ 7.44 (s, 2H), 7.24 (d, *J* = 2.2 Hz, 2H), 7.13 (t, *J* = 7.7 Hz, 2H), 6.97 (d, *J* = 2.1 Hz, 2H), 6.77 (t, *J* = 7.5 Hz, 2H), 6.47 (d, *J* = 7.6 Hz, 2H), 6.38 (s, 2H), 6.20 (s, 2H), 3.02 (s, 4H), 1.44 (s, 18H), 1.25 (s, 18H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 149.66, 148.72, 142.56, 136.15, 135.62, 130.62, 127.55, 122.47, 121.82, 119.8, 118.04, 114.13, 77.43, 77.22, 77.01, 35.22, 34.95, 34.57, 31.78, 29.71. ESI-MS (+) *m/z* for $[C_{42}H_{56}N_2O_2S_2+H]^+$: calcd, 685.3855; found, 685.3983.

Synthesis of [$C_{42}H_{50}N_2O_2S_2Co$]: To the stirred solution of $H_4Pra^{edt(AP/AP)}$ (154 mg, 0.225 mmol) in methanol (15 mL), $Co(OAc)_2•2H_2O$ (56 mg, 0.225 mmol) was added followed by dropwise addition of Et_3N (0.1 mL). The resulting solution was stirred at room temperature (25 °C) for 24 h under air. A deep violet precipitate appeared which was filtered and washed thoroughly with methanol. Recrystallization of the solid from a $CHCl_3$:MeOH (4:1) solvent mixture provided crystalline compound, which was suitable for single crystal X-ray analysis. Yield: 98 mg, 51% (including $1CHCl_3$). FTIR (KBr pellet cm^{-1}): 3434, 3050, 2955, 2905, 2866, 1587, 1523, 1461, 1386, 1361, 1328, 1265, 1249, 1201, 1174, 1110, 1060, 1025, 996, 885, 859, 822, 756, 741, 665, 647, 538. ESI-MS (+) *m/z* for $[C_{42}H_{50}N_2O_2S_2Co+H]^+$: calcd, 738.27; found, 738.14. Anal. Calcd for $C_{42}H_{50}N_2O_2S_2Co•1CHCl_3•2.6H_2O$: C, 56.95; H, 5.88; N, 2.88. Found: C, 57.20; H, 6.27; N, 3.10.

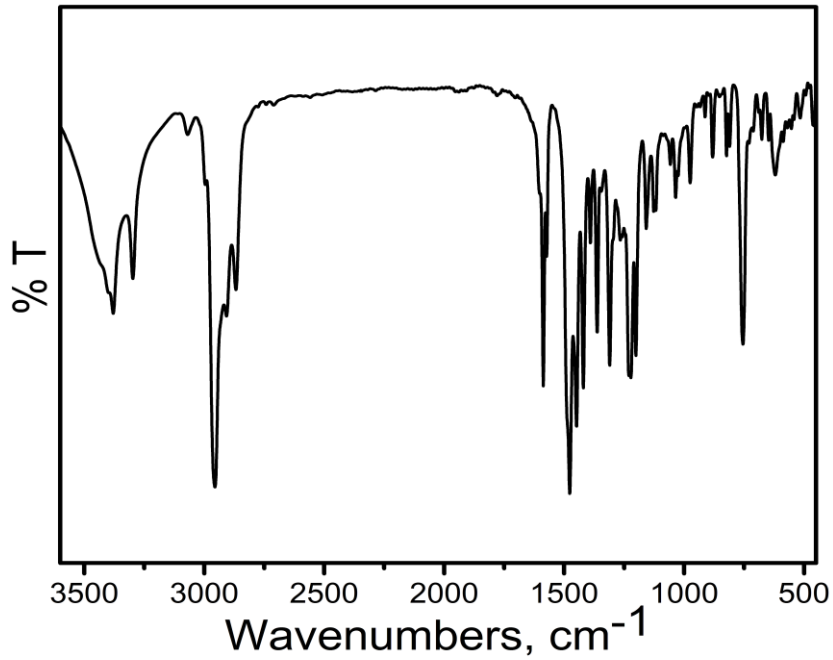


Figure S1: IR spectrum of $H_4Pra^{edt(AP/AP)}$.

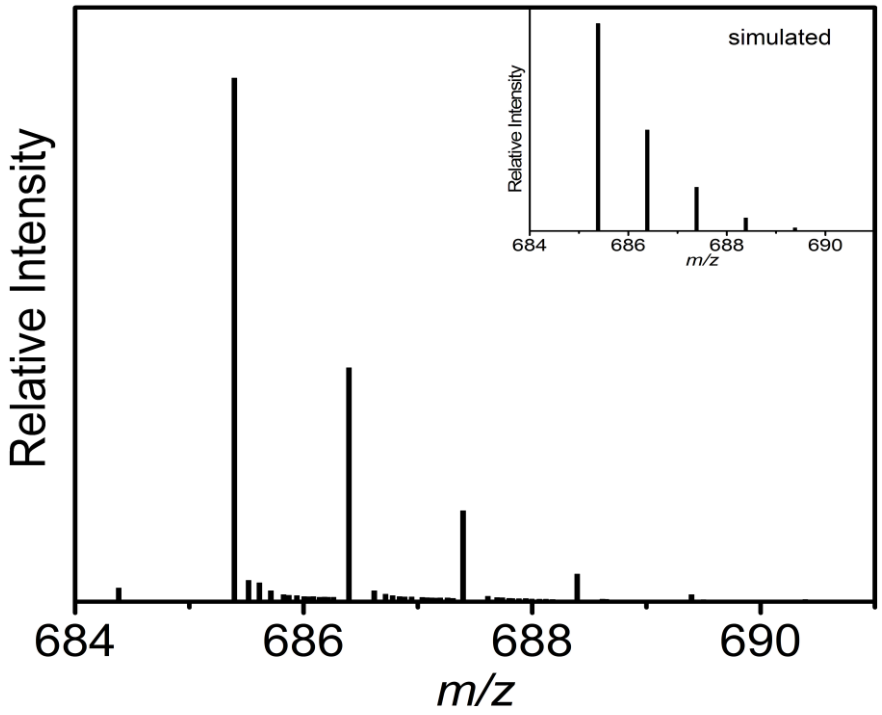


Figure S2. Experimental and simulated mass spectra for $H_4Pra^{edt(AP/AP)}$+ H = $[C_{40}H_{52}N_2O_2S_2+H]^+$ have been shown.

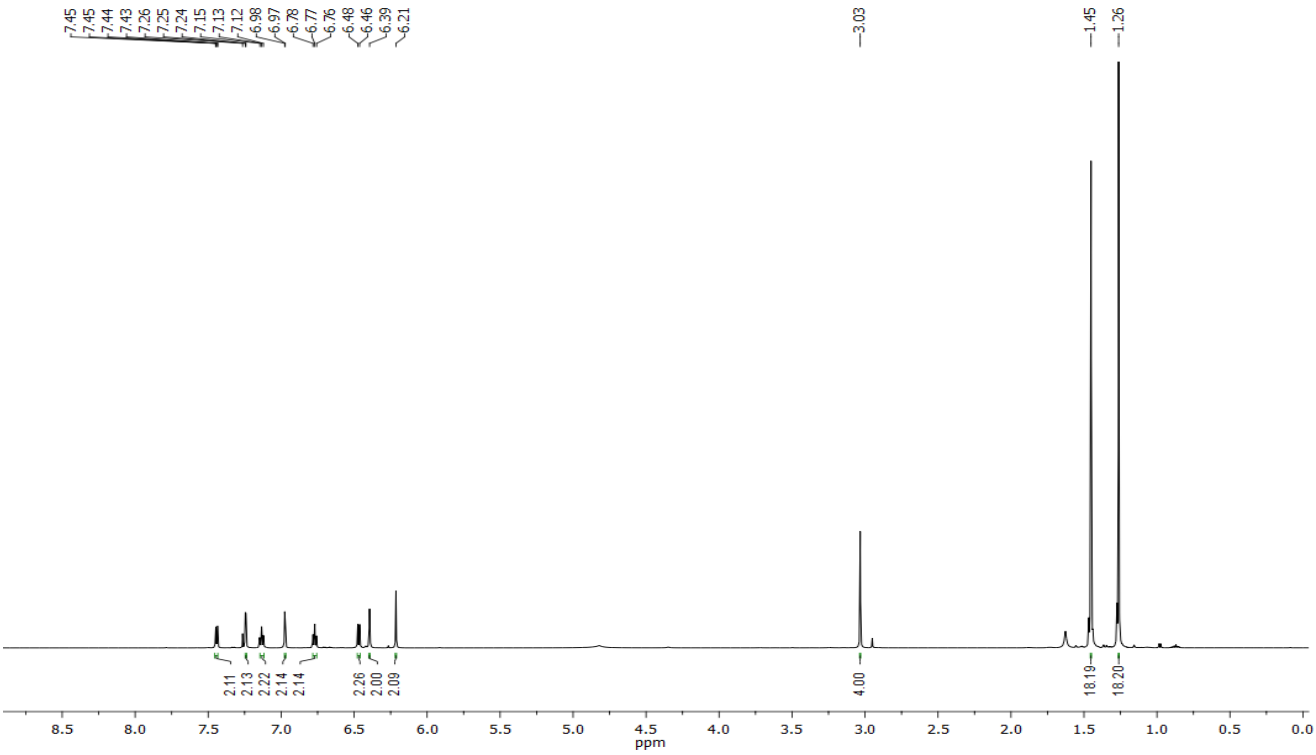


Figure S3: ^{1}H-NMR spectrum of $H_4Pra^{edt(AP/AP)}$.

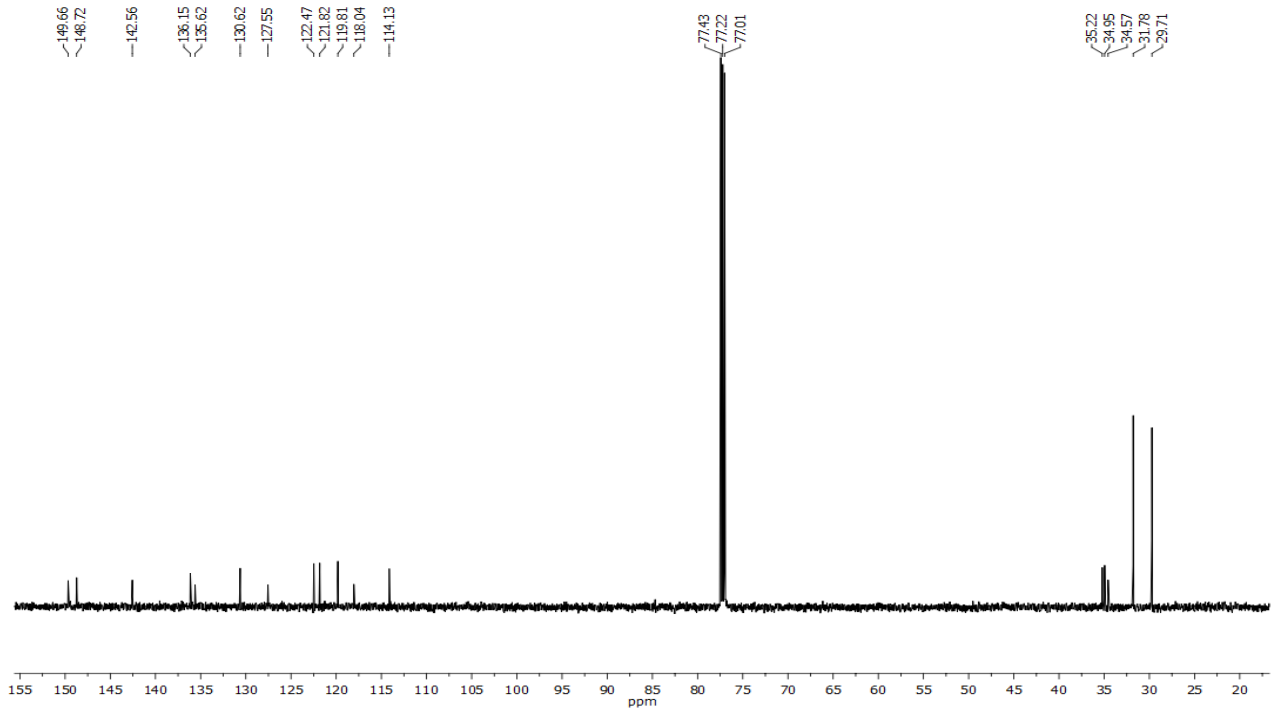


Figure S4: ^{13}C NMR spectrum of $H_4Pra^{edt(AP/AP)}$.

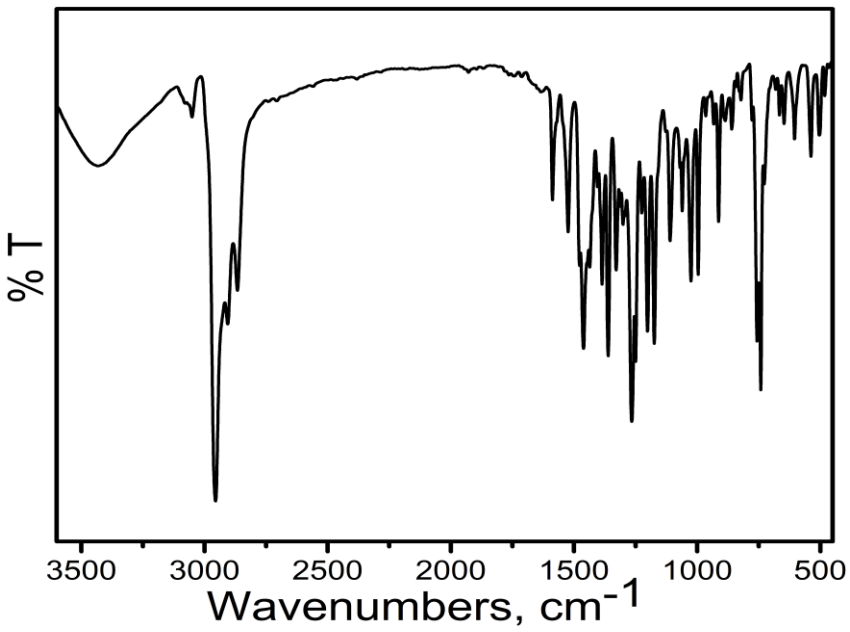


Figure S5: IR spectrum of complex **1**, $C_{42}H_{50}N_2O_2S_2Co$.

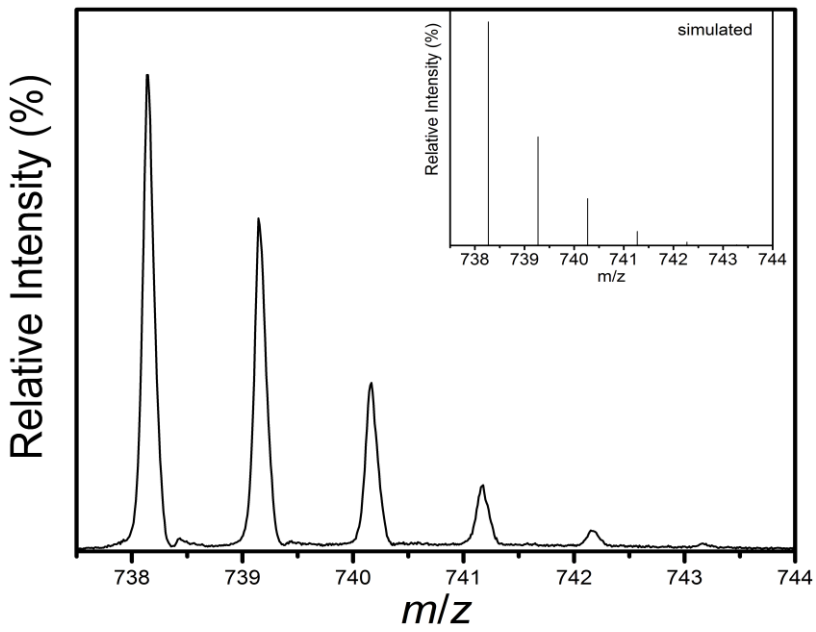


Figure S6. Experimental and simulated mass spectra for complex **1**+H = $[C_{42}H_{50}N_2O_2S_2Co+H]^+$ have been shown.

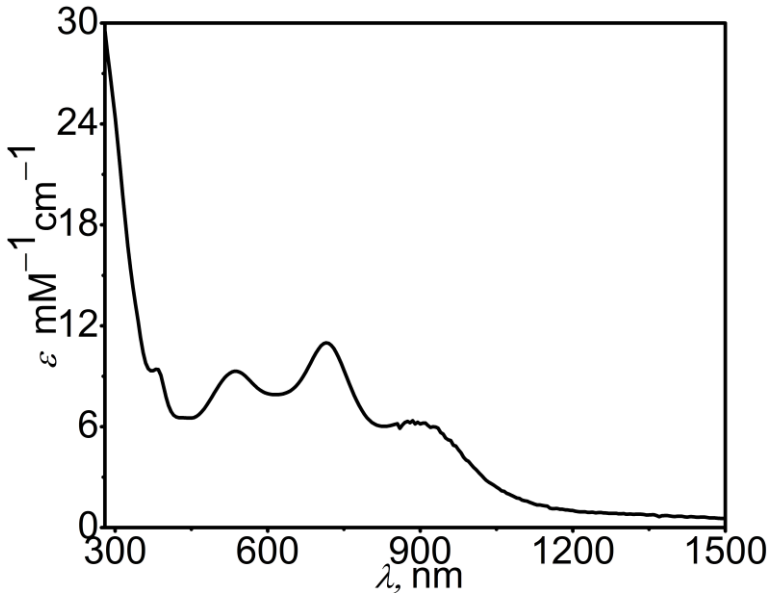


Figure S7: UV spectrum of complex **1** in CH_2Cl_2 at 25 °C.

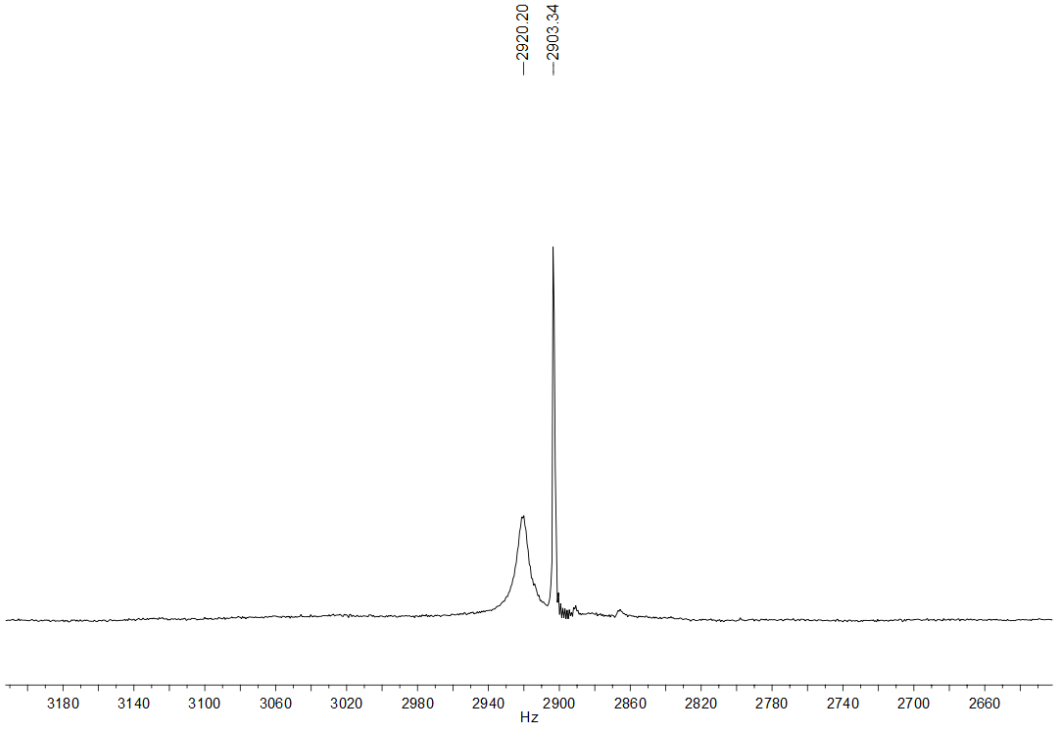


Figure S8: Showing NMR shift in solvent peak ($CDCl_3$) during Evan's method magnetic susceptibility measurement of complex 1•1$CHCl_3$ at 25 °C. c = 15 mg/mL.

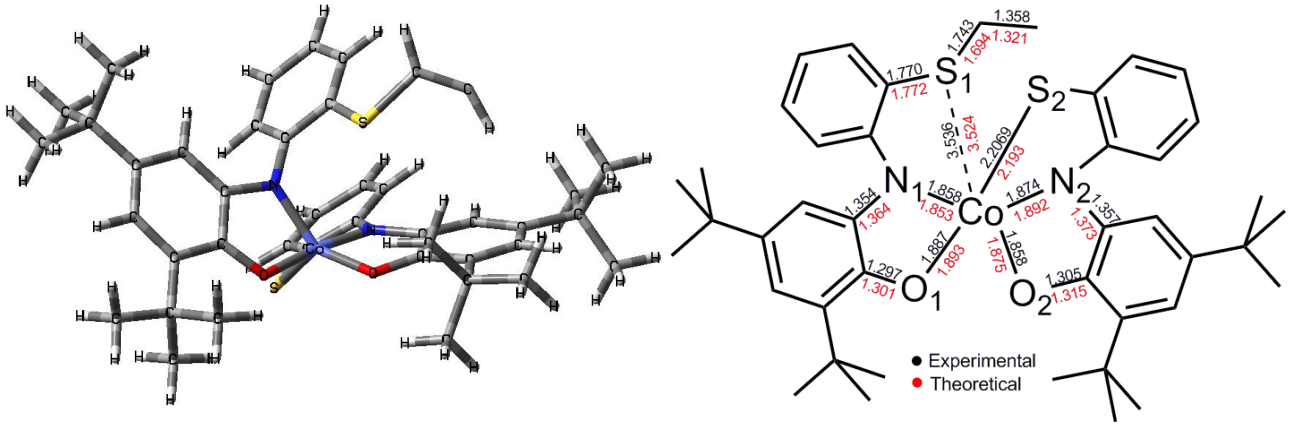


Figure S9: Optimized structure of the complex at PBEPBE/def2-TZVP level.

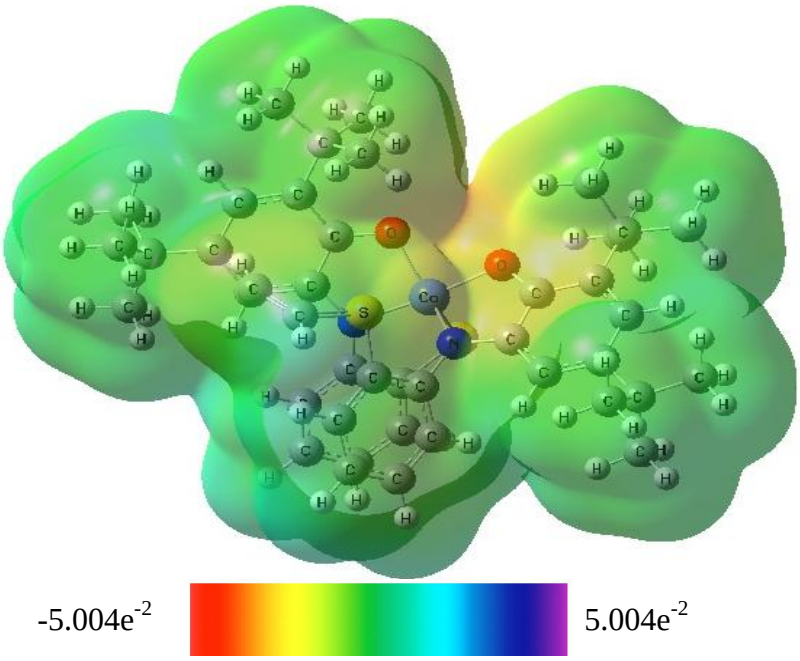


Figure S10: Electrostatic potential plot computed at PBEPBE/def2-TZVP level (Iso-value = 0.03).

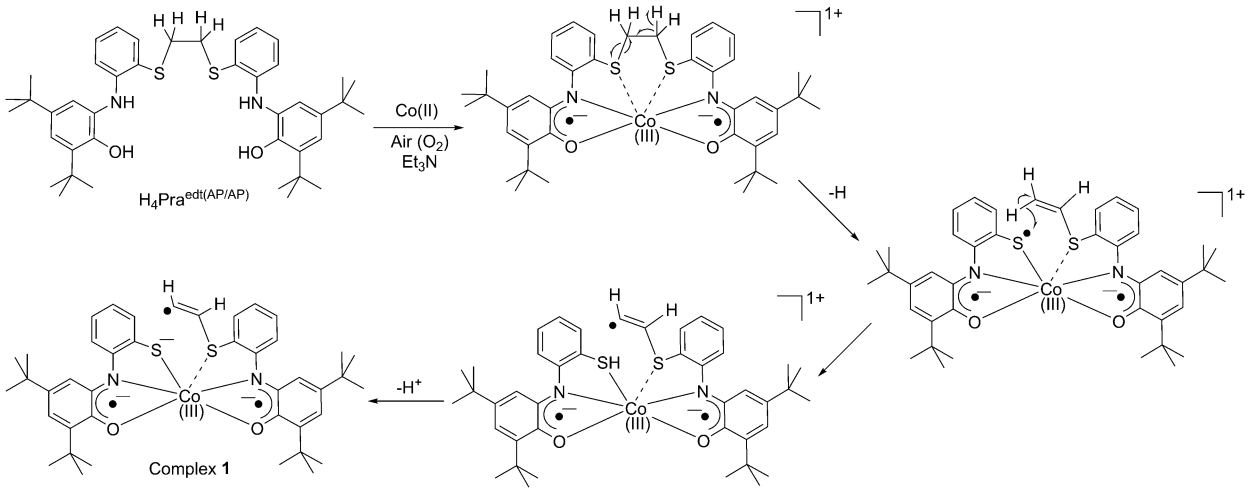


Figure S11: Showing proposed mechanism for the formation of complex **1**.

Table S1: Selected bond distances (Å) and bond angles (°) for complex **1**.

Co1–N1	1.858(3)	O1–C2	1.297(4)
Co1–O2	1.858(2)	O2–C28	1.305(4)
Co1–N2	1.874(3)	N2–C23	1.357(4)
Co1–O1	1.887(2)	N2–C37	1.396(4)
Co1–S2	2.2069 (12)	N1–C1	1.354(4)
S2–C42	1.743(4)	N1–C15	1.426(4)
S1–C21A	1.756(13)	C24–C25	1.357(4)
S1–C21B	1.743(8)	C22A–C21A	1.354(18)
S1–C20	1.770(4)	C37–C38	1.393(6)
C27–C26	1.370(5)	C27–C28	1.424(5)
C24–C23	1.420(4)	C2–C3	1.429(4)
C25– C26	1.423(5)	C1–C6	1.408(4)
C28–C23	1.425(5)	C4–C5	1.433(5)
C2–C1	1.430(5)	C22B–C21B	1.358(15)
C3–C4	1.369(5)	C5–C6	1.357(5)
N1–Co1–O2	129.75(12)	O2–Co1–N2	83.68(10)
N1–Co1–N2	101.94(11)	N1–Co1–O1	83.43(11)
O2–Co1–O1	92.65(10)	N2–Co1– O1	174.63(11)
N1–Co1–S2	98.76(9)	O2–Co1–S2	131.47(9)
N2–Co1–S2	84.99 (9)	O1–Co1–S2	94.58(9)
C42–S2–Co1	95.12(13)	C2–O1–Co1	113.5(2)
C23–N2–Co1	114.1(2)	C37–N2–Co1	117.6(2)
C28–O2–Co1	113.8(2)		

Table S2: Crystallographic parameters and refinement data for complex **1**.

Empirical formula	$C_{42}H_{50}CoN_2O_2S_2$, $CHCl_3$
Formula weight	857.26
CCDC Number	1468751
Crystal habit, colour	Block, violet
Crystal size, mm^3	0.24×0.18×0.14
Temperature, T	293(2)
Wavelength, λ (Å)	0.71073
Crystal system	monoclinic
Space group	P 21/c
Unit cell dimensions	a = 19.3263(9) Å b = 9.6193(4) Å c = 25.4228(11) Å α = 90.00°, γ = 108.384(5)°, β = 90.00°
Volume, V ($Å^3$)	4485.0(4)
Z	4
Calculated density, $Mg \cdot m^{-3}$	1.270
Absorption coefficient, μ (mm^{-1})	0.690
F(000)	1796
θ range for data collection	2.99° to 25.00°
Limiting indices	$-22 \le h \le 12$, $-11 \le k \le 10$, $-26 \le l \le 30$
Reflection collected/unique	19539/7888 [R(int)=0.0280]
Completeness to θ	99.7% (θ = 25.00°)
Max. and min. transmission	0.908/0.862
Refinement method	'SHELXL-2014/7'
Data/restraints/parameters	7908/211/578
Goodness–of–fit on F^2	1.035
Final R indices [I>2sigma(I)]	R1 = 0.0577, wR2 = 0.1491
R indices (all data)	R1 = 0.0829, wR2 = 0.1653
Largest diff. peak and hole	0.543 and –0.477 $e \cdot Å^{-3}$

Table S3: Coordinates for the geometrical optimized structure of complex **1**.

Co	0.17393000	0.33871300	-0.96389800
N	1.26403800	-0.63367500	0.16642300
N	-1.40124600	-0.69707700	-1.03425200
O	1.63362000	1.54269600	-1.02114800
O	-1.01194500	1.74574200	-0.63230900
C	2.72029700	1.06213200	-0.48741000

C	4.00089600	1.71021900	-0.51582300
C	5.04057500	1.04997000	0.14613500
C	4.90791800	-0.19580000	0.83956100
C	3.65676300	-0.81374400	0.86457100
C	2.56401400	-0.20248500	0.20179600
H	6.02929500	1.52270100	0.13397000
H	3.49838400	-1.76401100	1.39303800
C	-4.49759700	1.66771200	0.39548900
C	-3.21885600	2.21380900	0.25165100
C	-2.22403900	1.35160100	-0.31940400
C	-2.52610900	-0.03073900	-0.60927100
C	-3.85927000	-0.50517900	-0.49404100
C	-4.85254600	0.33558400	0.01242100
H	-5.28947200	2.30949300	0.80477800
H	-4.10375400	-1.52404400	-0.80714600
C	6.10463400	-0.87170200	1.54455400
C	6.37315200	-2.24419200	0.87989600
H	7.22926700	-2.75300200	1.37060900
H	5.49506200	-2.91672400	0.95355400
H	6.61618300	-2.12461900	-0.19562200
C	7.39438600	-0.03357200	1.45436400
H	7.27965600	0.96029400	1.93288500
H	8.21798700	-0.55972200	1.97809800
H	7.71837200	0.12324100	0.40559600
C	5.76996500	-1.08220200	3.04077800
H	6.61820300	-1.57317400	3.56195800

H	5.57105000	-0.11446200	3.54437400
H	4.87656000	-1.72311200	3.17928600
C	4.18326900	3.05342800	-1.24237300
C	3.82093700	2.88168200	-2.73883300
H	2.77258500	2.55193200	-2.86455100
H	3.94619900	3.84670500	-3.27286200
H	4.48320200	2.13521800	-3.22348300
C	5.63401300	3.56273100	-1.15376900
H	5.95284800	3.73923800	-0.10590400
H	6.35332000	2.85923500	-1.62132400
H	5.71905100	4.52829000	-1.69196700
C	3.25523500	4.11481500	-0.59948000
H	2.19309200	3.81192800	-0.66460800
H	3.51089800	4.26833300	0.46913000
H	3.37265900	5.08762700	-1.12114100
C	-2.87426500	3.66241800	0.64103400
C	-4.07680500	4.39005300	1.27074800
H	-3.77832000	5.42004600	1.55241500
H	-4.93004200	4.47566700	0.56700600
H	-4.43491200	3.88536200	2.19166800
C	-2.44050900	4.44789100	-0.62233900
H	-1.55381900	3.98627600	-1.09579500
H	-3.26005600	4.47746800	-1.36952300
H	-2.18803300	5.49443100	-0.35086800
C	-1.71835400	3.65520500	1.67232100
H	-2.01375200	3.11534100	2.59590400

H	-0.81471900	3.16930100	1.25894700
H	-1.45493900	4.69571900	1.95557800
C	-6.31597400	-0.12420100	0.17470200
C	-6.52275800	-1.58104300	-0.27968100
H	-6.26975200	-1.72130800	-1.35006100
H	-5.91274100	-2.29015800	0.31633000
H	-7.58579900	-1.86859700	-0.14935200
C	-7.23436400	0.78386400	-0.67912600
H	-8.29476200	0.47415400	-0.56994300
H	-7.16355200	1.84766900	-0.37681800
H	-6.96645900	0.72082400	-1.75336600
C	-6.72818000	-0.02014200	1.66342000
H	-6.64235700	1.01568400	2.04830300
H	-7.78370600	-0.33756100	1.79577100
H	-6.09444400	-0.67184000	2.29946600
S	-0.53456300	-0.27174200	2.42635900
S	0.72695500	-0.61091200	-2.85335600
C	-0.46414200	-3.10063800	2.36330800
C	-0.03001200	-1.87083200	1.83225600
C	0.88828700	-1.87059600	0.74442200
C	1.36187200	-3.09172800	0.22623300
C	0.92911900	-4.30972100	0.76902900
C	0.01553800	-4.30900200	1.83483500
H	-1.19500000	-3.11257800	3.18448100
H	2.05382700	-3.06412600	-0.62800000
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C	-0.26615500	-2.02981300	-2.62567000
C	-0.09522200	-3.21967400	-3.36956700
C	-0.93773600	-4.30991700	-3.14426500
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H	-3.55602800	0.26158600	2.83225100
H	-1.31632100	-1.17463900	4.63728000

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