Supporting Information

Stabilization of a Cobalt-Cobalt Bond by Two Cyclic Alkyl Amino Carbenes

Kartik Chandra Mondal, Prinson P. Samuel, Herbert W. Roesky,* Elena Carl, Regine Herbst-Irmer, Dietmar Stalke,* Brigitte Schwederski, Wolfgang Kaim, Liviu Ungur, Liviu F. Chibotaru, Markus Hermann and Gernot Frenking*

[1] Institut für Anorganische Chemie, Georg-August-Universität

Tammannstrasse 4

37077-Göttingen, Germany

Fax: (+49)551-39-3373

Email:hroesky@gwdg.de; dstalke@chemie.uni-goettingen

[2] Division of Quantum and Physical Chemistry and INPAC-Institute of Nanoscale Physics and Chemistry,

Katholieke Universiteit Leuven Celestijnenlaan 200F,

3001 Heverlee, Belgium. E-mail: liviu.chibotaru@chem.kuleuven.be

[3] Fachbereich Chemie, Philipps-Universität Marburg,

Hans-Meerwein-Str.

35032 Marburg

Fax: (+49)6421-28-25566

Email: frenking@chemie-uni-marburg.de

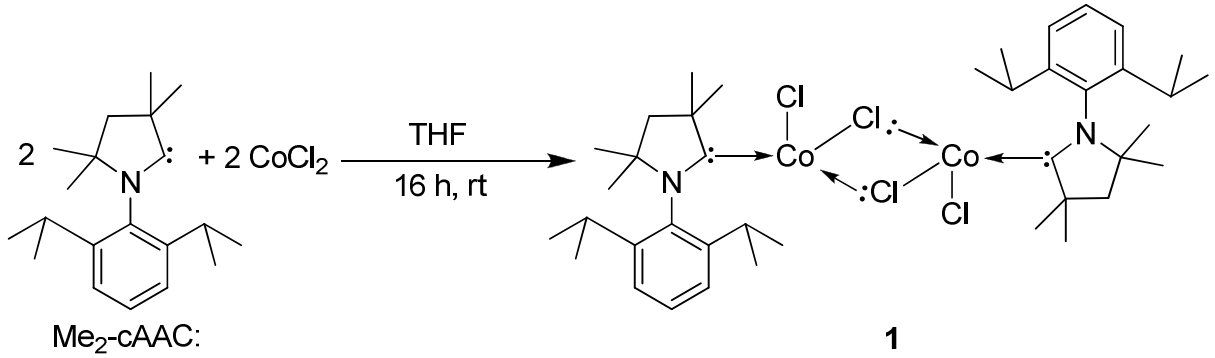
Acknowledgements: H. W. R. thanks the Deutsche Forschungsgemeinschaft (DFG RO 224/60-I) for financial support. We thank to Sven Neudeck from the group of Prof. F. Meyer for UV-measurements.

Content:

(S1) Synthesis

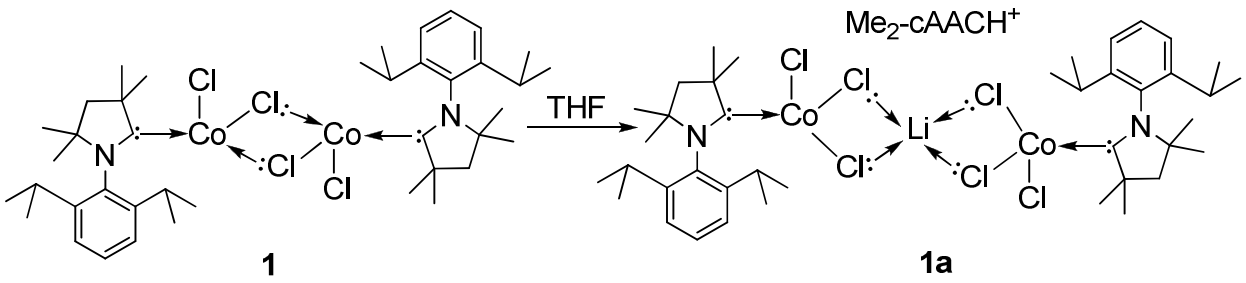
All reactions and handling of reagents were performed under an atmosphere of dry nitrogen or argon using standard Schlenk techniques or a glove box where the O_2 and H_2O levels were usually kept below 1 ppm. Ligand Me_2-cAAC: was prepared according to literature methods.[S1a] Solvents were purified with the M-Braun solvent drying system. Solution NMR spectra were recorded on Bruker Avance 200, Bruker Avance 300, and Bruker Avance 500 MHz NMR spectrometers. Deuterated NMR solvent C_6D_6 was dried by stirring for 2 days over Na/K alloy followed by distillation in vacuum and degassed. EI-MS spectra were obtained with a Finnigan MAT 8230 or a Varian MAT CH5 instrument (70 eV) by EI-MS methods. Elemental analyses were performed by the Analytisches Labor des Instituts für Anorganische Chemie der Universität Göttingen. Melting points were measured in sealed glass tubes on a Büchi B-540 melting point apparatus.

(Me_2-cAAC:Co^{II}(μ-Cl)Cl)$_2$ (**1**): A 1:1 molar mixture of cyclic alkyl(amin) carbene (Me_2-cAAC:) (2850 mg; 10 mmol) and $CoCl_2$ (1300 mg; 10 mmol) was taken into a 100 mL round bottom flask and THF (80 mL) was added at room temperature. The resulting suspension was stirred for 30 minutes to obtain a clear blue solution which was further overnight (16 hours) to produce crystalline blue powder of **1**. The volume of the solution was reduced to 20 mL under vacuum and separated by filtration. The yield is 80%. C, H and N analysis (%) found (calcd) for $C_{40}H_{62}N_2Co_2Cl_4$; C 57.76 (57.84), H 7.55 (7.52), N 3.41 (3.37). Decomposes above 293 °C and turns blue-grey solid, UV-visible bands 653, 576, 367 and 320 nm.



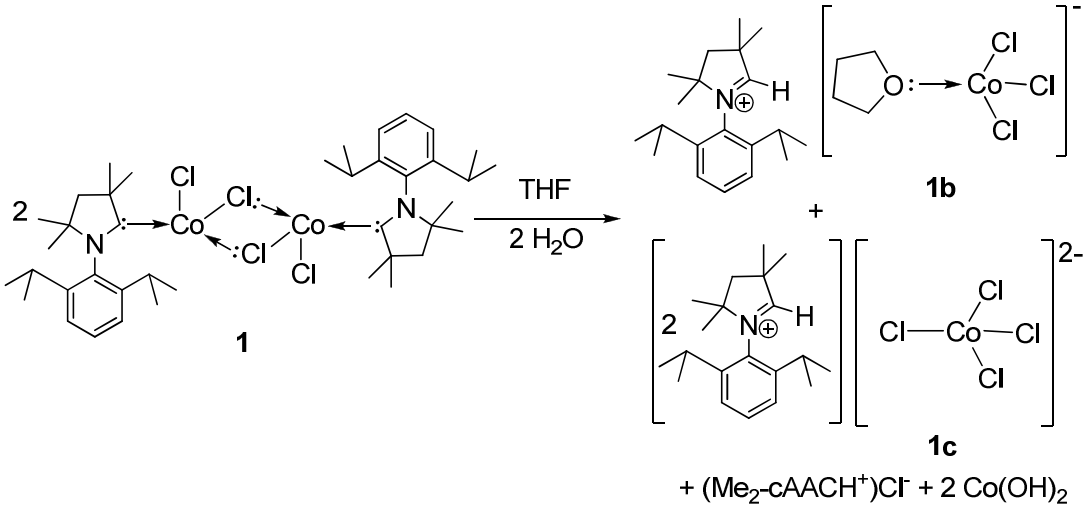
Scheme S1. Synthesis of compound **1**. Me_2-cAAC: = :C(CH_2)(CMe_2)$_2$N-2,6-*i*$Pr_2C_6H_3$.

(Me_2-cAACH)[(Me_2-cAAC:)Co(μ-Cl)$_2$Cl(Li)$_{0.5}$]$_2$ (**1a**): Compound (Me_2-cAAC:Co^{II}(μ-Cl)Cl)$_2$ (**1**) is insoluble in toluene and benzene. It is moderately soluble in THF and hence it was attempted to crystallize it from THF. The THF solution of **1** initially produces a dark blue solution which slowly turns to a green-blue color indicating the decomposition. Compound (Me_2-cAACH)[(Me_2-cAAC:)Co(μ-Cl)$_2$Cl(Li)$_{0.5}$]$_2$ (**1a**) was isolated as green blue needles from a solution of THF and *n*-hexane (7:1) in the presence of two equivalents of lithium triflate. Decomposes above 181 °C.



Scheme S2. Decomposition of compound **1** to **1a** under an inert atmosphere in THF solution.

Stability of compound **1** in air: Cobalt(II)dichloride-carbene compounds are often used as a catalyst for organic transformation and hence the stability of **1** was examined by exposing the THF solution of **1** suggesting it should be handled in an inert atmosphere. The blue color THF solution of **1** immediately undergoes hydrolysis and insoluble precipitate of cobalt(II)hydroxide is deposited. The same volume of *n*-hexane was then immediately added to the resulting solution and closed with a stopper and stored at room temperature. After one week two types of crystals were formed. The dark blue hexagonal crystals were characterized as (Me_2-cAACH$^+$)[(THF)$CoCl_3^-$] (**1b**) and light blue rods as (Me_2-cAACH$^+$)$_2$[$CoCl_4$]$^{2-}$ (**1c**). Compounds **1b** and **1c** decompose above 275 °C (turns green-blue liquid) and 247 °C respectively.



Scheme S3. Hydrolysis of THF solution of compound **1** to **1b** and **1c** on exposure to air.

Synthesis of compound (Me_2-cAAC:)$_2Co_2$ (**2**): The 1:4 molar mixture of (Me_2-cAAC:Co^{II}(μ-Cl)Cl)$_2$ (**1**) (1 mmol) and KC_8 (4 mmol) and THF (80 mL) were separately cooled to -78 °C and then THF was added through a cannula. Then the reaction solution was slowly warmed to room temperature and stirred for 12 hours. During this period the color of the solution changed from dark blue to black brown. The black residue was separated by filtration and dried under vacuum and extracted with toluene (70 mL). The volume of toluene solution was decreased to 5 mL. Dark black needles of **2·toluene** were formed after two weeks when stored at -32 °C in a refrigerator. Compound **2·toluene** was separated by filtration and dried under vacuum. C, H and N analysis (%) found (calcd) for $C_{40}H_{62}N_2Co_2$; C 69.68 (69.75), H 9.11 (9.07), N 4.02 (4.06). m.p. 249-250 °C. UV-visible bands 680, 526 and 366 nm; ^{1}H NMR (298 K, C_6D_6, 300.13 MHz, δ ppm): 5.87 (s, 2H, *m*-H_{ar}), 4.45 (s, H, *p*-H_{ar}), 2.92 (m, 2H, $CHMe_2$), 2.14 (s, 6H, $NCMe_2$), 1.78 (s, 2H, CH_2), 1.23 (s, 12H, $CHMe_2$), 1.18 (s, 6H, CMe_2); ^{13}C NMR (δ ppm): 109.5, 101.4, 87.9 (aromatic phenyl ring), 77.9, 68.4, 57.9, 54.9 (five-membered carbene ring), 30.5, 30.2, 28.9, 28.4, 27.6.

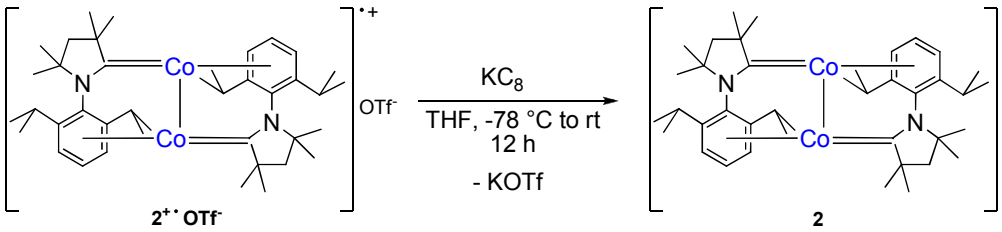
An alternative synthetic route for the compound (Me_2-cAAC:)$_2Co_2$ (**2**): A 2:1 molar mixture of Me_2-cAAC: (4 mmol; 1140 mg) and $CoCl_2$ (2 mmol; 260 mg) placed in a 100 mL round bottom flask and THF (60 mL) was added at room temperature. The resulting suspension was stirred for a day to produce a dark green solution. KC_8 (4 mmol; 540 mg) was separately taken in another 100 mL round bottom flask. Both the flasks were cooled to -78 °C and then green solution was passed to the other flask contain KC_8 and stirred for five minutes. The reaction mixture was slowly wormed to room temperature over thirty minutes and stirred at room temperature for another thirty minutes to obtain a dark brown solution. The insoluble graphite was separated out by filtration. The dark brown filtrate was dried under vacuum and extracted with toluene (30 mL). The volume of

the solution reduced to 3 mL and stored at -32 °C to form large needles of compound **2** in 30 % yield which was characterized by NMR and mass spectrometry. The toluene insoluble part contains insoluble by product (KCl) and thus discarded.

Synthesis of compound $[(Me_2\text{-cAAC:})_2Co_2]^{+}\,OTf^{-}$ (**2^{+}OTf^{-}**): A 1:3:2 molar mixture of compound $(Me_2\text{-cAAC:}Co^{II}(\mu\text{-Cl})Cl)_2$ (**1**) (1 mmol; 830 mg), KC_8 (3 mmol; 405 mg) and LiOTf (2 mmol; 312 mg) was placed in a 100 mL round bottom flask and THF (80 mL) at -78 °C. The reaction mixture was stirred at this temperature for thirty minutes and temperature was slowly raised to room temperature over twenty minutes and further stirred for twelve hours to obtain a dark brown filtrate. The insoluble graphite was separated out by filtration. The dark brown filtrate was dried under vacuum and washed with toluene (30 mL). The toluene insoluble dark black solid was then dissolved in THF (5 mL) to obtain a dark brown solution to which toluene (5 mL) was added and stored at -32 °C after two weeks dark blocks of **2^{+}OTf^{-}** were formed. **2^{+}OTf^{-}** decomposes above 340 °C. UV-visible bands at 650, 550, 440 and 354 nm. C, H and N analysis (%) found (calcd) for $C_{41}H_{62}N_2O_3SF_3Co_2$; C 58.81 (58.77), H 7.52 (7.45), N 3.31 (3.34).

The reduction of compound **1** with three equivalents of KC_8 produces **2^{+}OTf^{-}** which was further reduced to compound **2** with another equivalent of KC_8. This suggests that compound **2** is formed before it finally reduced to **2^{+}OTf^{-}**.

The synthetic route which involves the reaction of **1**, Me_2-cAAC: and KC_8 given in the main text produces compound **2** in 65% yield (as toluene soluble part) while the toluene insoluble part contains **2^{+}Cl^{-}** which could be isolated as **2^{+}OTf^{-}** in 25 % yield with the addition of lithium triflate and followed by crystallization at -32 °C from a 1:1 mixture solvents (THF and toluene).

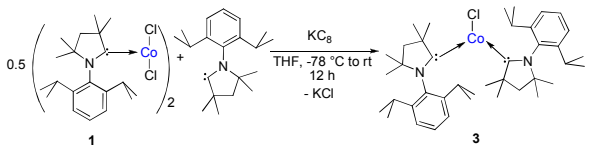


Scheme S4. Conversion of compound **2^{+}OTf^{-}** to **2** under KC_8 reduction.

Regarding characterization of **2$^{\bullet-}$**: We are unable to crystallize and characterize the species containing radical anion **2$^{\bullet-}$**.

Synthesis of compound $(Me_2\text{-cAAC:})_2CoCl$ (**3**): A 1:1 molar mixture of Me_2-cAAC: (2 mmol; 570 mg) and $CoCl_2$ (2 mmol; 260 mg) placed in a 100 mL round bottom flask and THF (50 mL) was added at room temperature. The resulting suspension was stirred for sixteen hours to produce a dark blue solution. A 1:1 molar mixture of Me_2-cAAC: (2 mmol; 570 mg) and KC_8 (2 mmol; 270 mg) was separately taken in another 100 mL round bottom flask. Both the flasks were cooled to -78 °C and then green solution was passed to the other flask contain KC_8 and stirred for thirty minutes. The reaction mixture was slowly wormed to room temperature over twenty minutes and stirred at room temperature for twelve hours to obtain a dark red-brown solution. The insoluble graphite was separated out by filtration. The dark red-brown filtrate was dried under vacuum and extracted with toluene (3×40 mL). The volume of the solution reduced (to 3×5 mL) and stored at 0 °C to form large red rods of compound **3** in 70 % yield. The yield is 80%. C, H and N analysis (%) found (calcd) for $C_{40}H_{62}N_2CoCl$; C 72.75 (72.21), H 9.36 (9.39), N 4.24 (4.21). Decomposes above 187 °C and black solid, UV-visible bands 705, 468, 376 and 335 nm. The ^{1}H NMR spectrum of **3** in C_6D_6 exhibits resonances in the range of +45 to −23 ppm indicating the paramagnetic nature.[S1b]

Compound **3** is air sensitive. Compound **3** looses its color and turns to light blue. The decomposed products were characterized as **1c** and Me_2-cAACH^{+}Cl^{-}.



Scheme S5. Synthesis of compound **3** from **1**.

(S2). UV-visible spectroscopy of **1**, **1a**, **1b**, **1c**, **2**, **2**$^{+}$**OTf**$^{-}$ and **3**

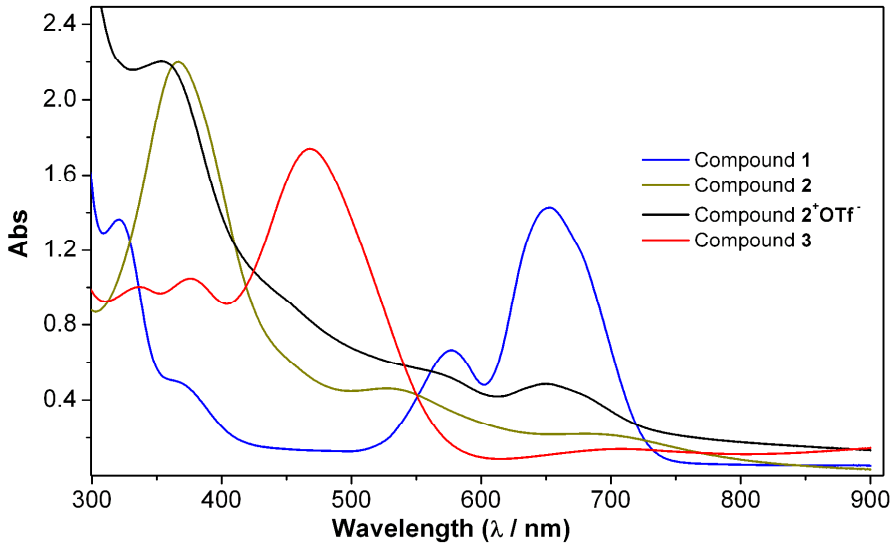


Figure S1. UV-visible spectrum of compound **1**, **2**, **2**$^{+}$**OTf**$^{-}$ and **3** in *n*-hexane (**2**, **3**) or THF (**1**, **2**$^{+}$**OTf**$^{-}$).

(S3). Cyclic voltammogram of compound **2**

Cyclic voltammetry and coulometric experiments were performed with an EG&G 273A potentiostat/galvanostat. Cyclic voltammograms were recorded by using a three electrode arrangement with a glassy carbon working electrode (2 mm diameter), an Ag/0.01 M AgNO3 reference electrode and a Pt wire counter electrode. In case of constant coulometric potentiometry a Pt gauze electrode was used as working electrode. Ferrocene was added as an internal standard after the measurements and all potentials are referenced relative to the $(Cp)_2Fe/(Cp)_2Fe^+$ couple. All experiments were performed under an atmosphere of dry nitrogen or in a glove box in CH_2Cl_2/0.1 M $[n\text{-}Bu_4N]PF_6$. Electronic spectra during coulometric measurements were recorded with a Cary 50 Bio Spectrophotometer supplied with a quarz dip probe (1 mm, Hellma Analytics) and analyzed by Cary Win UV software.

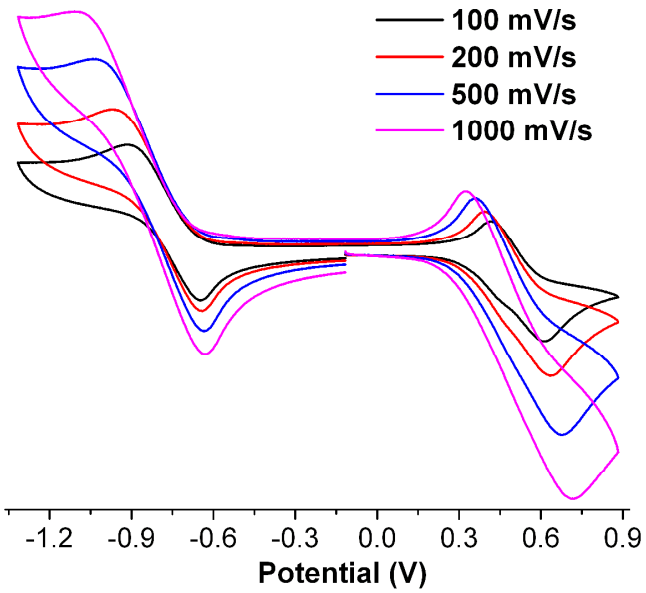


Figure S2. Cyclic voltammogram for CH_2Cl_2 solutions of **2**, containing 0.1 M *n*-Bu_4NPF_6 as electrolyte (potential versus $(Cp_2Fe)/(Cp_2Fe)^+$, at indicated scan rates.

$$[L_2Co_2]^{\cdot -} \underset{+\,e}{\overset{-\,e}{\rightleftharpoons}} [L_2Co_2] \underset{+\,e}{\overset{-\,e}{\rightleftharpoons}} [L_2Co_2]^{\cdot +}$$

Scheme S6. Electro-chemical equilibrium.

(S4). Magnetic susceptibility of compound **2**

Temperature-dependent magnetic susceptibility measurements on compounds **2** (26.1 mg) were carried out with a *Quantum-Design* MPMS-XL-5 SQUID magnetometer equipped with a 5 Tesla magnet in the range from 295 to 2.0 K at a magnetic field of 0.5 T. The powdered sample was placed in a gel bucket and fixed in a non-magnetic sample holder. Each raw data file for the measured magnetic moment was corrected for the diamagnetic contribution of the sample holder and the gel bucket. The molar susceptibility data were corrected for the diamagnetic contribution. The sample was prepared under an atmosphere of dry nitrogen using standard Schlenk techniques or a glove box where the O_2 and H_2O levels were usually kept below 1 ppm. Temperature-independent paramagnetism (*TIP*) and a Curie-behaved paramagnetic impurity (*PI*) with spin $S = 3/2$ were included according to $\chi_{calc} = (1 - PI)\cdot\chi + PI\cdot\chi_{mono} + TIP$.[S2] Paramagnetic contribution is 5.5%.

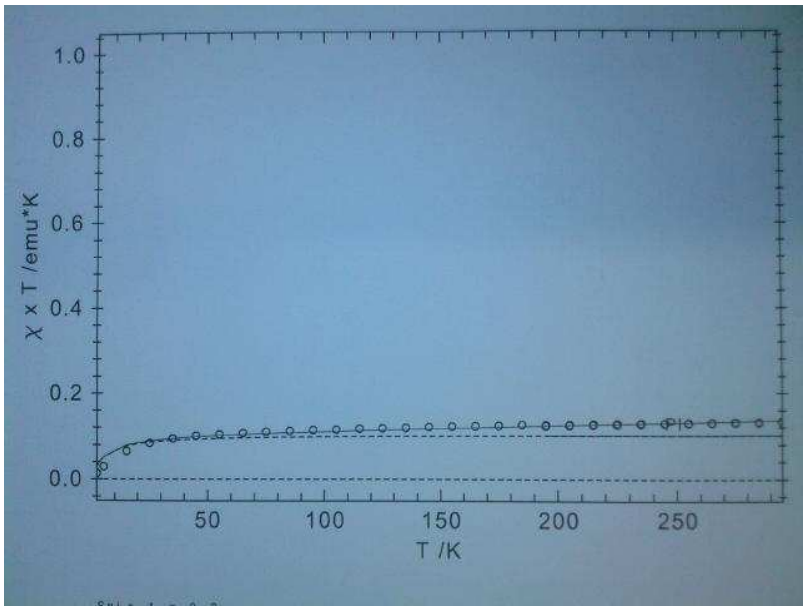


Figure S3. χT vs T plot of compounds **2**. The circles represent the experimental data. The solid and dotted lines represent the fittings. This suggests that compound **2** has a diamagnetic spin ground state.

(S5) EPR of $2^{+}OTf^{-}$

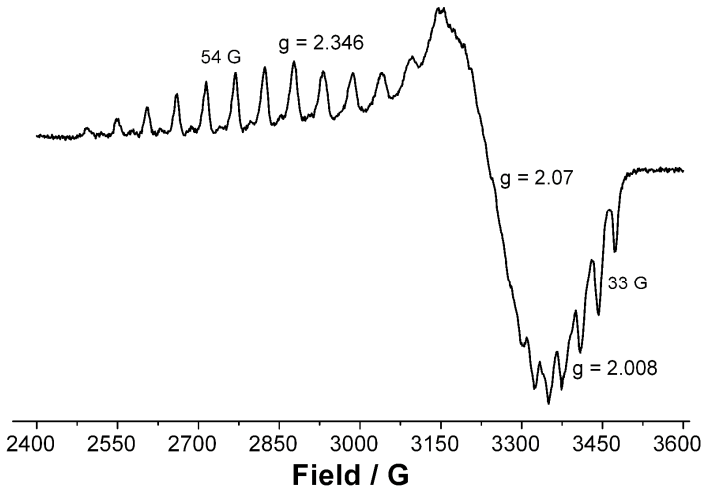


Figure S4. X band EPR spectrum of $\mathbf{2^{+}OTf^{-}}$ at 115 K.

(S6). Crystal data of 1a, 1b, 1c, 2, $2^{+}OTf^{-}$ and 3

Crystal Structure Determination. Suitable single crystals were selected from the mother liquor in the Schlenk flask and covered with perfluorinated polyether oil on a microscope slide, which was cooled with a nitrogen gas flow using the X-Temp2 device.[S3] The diffraction data of **1a** and $\mathbf{2^{+}OTf^{-}}$ were collected at 100 K on a Bruker D8 three circle diffractometer equipped with a SMART APEX II CCD detector and a microfocus source [S4] with INCOATEC Quazar mirror optics (λ = 0.71073 Å) and the data for **1b**, **1c**, **2** and **3** on a Bruker TXS-Mo rotating anode with mirror optics and a Smart Apex II Ultra detector. The data were integrated with SAINT[S5] and a multi-scan absorption correction with SADABS[S6] was applied (TWINABS was utilized for the twinned structure of **3**).[S7] The structures were solved by direct methods (SHELXS-97)[S8a] and refined against all data by full-matrix least-squares methods on F^2 (SHELXL2013)[S8b,c] within the SHELXLE GUI.[S8d] The

hydrogen atoms were refined isotropically on calculated positions using a riding model with their U_{iso} values constrained to 1.5 U_{eq} of their pivot atoms for terminal sp^3 carbon atoms and 1.2 times for all other carbon atoms. All non-hydrogen-atoms were refined with anisotropic displacement parameters. Disordered moieties were refined using distance restraints and anisotropic displacement parameter restraints (SIMU, RIGU and SAME)[S8c] The Supporting Information contains further details.

(Me_2-cAACH)[(Me_2-cAAC:)Co(μ-Cl)$_2$Cl(Li)$_{0.5}$]$_2$ (**1a**)

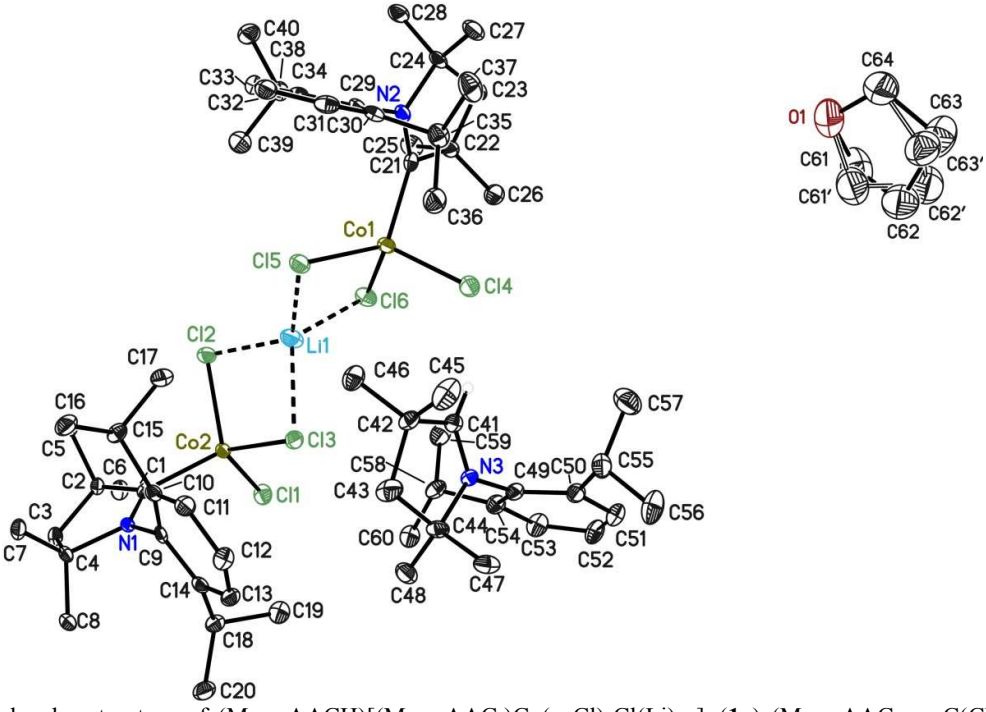


Figure S5. Molecular structure of (Me_2-cAACH)[(Me_2-cAAC:)Co(μ-Cl)$_2$Cl(Li)$_{0.5}$]$_2$ (**1a**) (Me_2-cAAC: = :C(CH_2)(CMe_2)$_2$N-2,6-*i*Pr$_2$C$_6$H$_3$) with one THF solvent molecule in the crystal. Anisotropic displacement parameters are depicted at the 50% probability level. The THF molecule shows a disorder (site occupation factor: 0.682(14)).

Table S1. Crystal data and structure refinement for **1a** :

Compound	(Me_2-cAACH)[(Me_2-cAAC:)Co(μ-Cl)$_2$Cl(Li)$_{0.5}$]$_2$ (THF) (Me_2-cAAC: = :C(CH_2)(CMe_2)$_2$N-2,6-*i*Pr$_2$C$_6$H$_3$) (**1a**)
Empirical formula	C_{64} H_{102} Cl_6 Co_2 Li N_3 O
CCDC no.	969776
Molecular weight	1266.98
Crystal size [mm]	0.1 x 0.05 x 0.04
Crystal system	tetragonal
Space group	*P4;* $^{-}$
a [Å]	25.322(2)
b [Å]	25.322(2)
c [Å]	10.553(2)
α [°]	90
β [°]	90
γ	90
V [Å ^{3}]	6766.6(17)
Z	4
Temperature [K]	101(2)

ρ [gcm^{-3}]	1.244
μ [mm^{-1}]	0.767
F (000)	2696
θ-area [°]	1.137 to 25.365
Reflections collected	101142
Independent reflections	12397 [R(int) = 0.0912]
Number of restraints	176
Parameters	746
$R1$ [$I>2\sigma(I)$]	0.0330
$wR2$ [$I>2\sigma(I)$]	0.0601
$R1$ [all data]	0.0462
$wR2$ [all data]	0.0642
GooF	1.024
Flack(x)[S9]	0.011(7)
Largest diff. peak / hole [e· Å^{-3}]	0.312 and -0.267

Table S2: Bond lengths [Å] and angles [°] for **1a** :

Li(1)-Cl(5)	2.390(7)	Cl(6)-Co(1)-Li(1)	50.00(14)
Li(1)-Cl(6)	2.396(7)	Co(2)-Cl(2)-Li(1)	84.45(17)
Li(1)-Cl(2)	2.401(7)	Co(2)-Cl(3)-Li(1)	84.45(18)
Li(1)-Cl(3)	2.435(7)	Co(1)-Cl(5)-Li(1)	82.99(18)
Li(1)-Co(1)	3.102(7)	Co(1)-Cl(6)-Li(1)	82.75(18)
Li(1)-Co(2)	3.171(7)	C(1)-N(1)-C(9)	124.1(3)
Co(2)-C(1)	2.042(4)	C(1)-N(1)-C(4)	116.1(3)
Co(2)-Cl(1)	2.2568(11)	C(9)-N(1)-C(4)	119.7(3)
Co(2)-Cl(3)	2.2798(11)	C(21)-N(2)-C(29)	123.3(3)
Co(2)-Cl(2)	2.3167(11)	C(21)-N(2)-C(24)	116.1(3)
Co(1)-C(21)	2.038(4)	C(29)-N(2)-C(24)	120.5(3)
Co(1)-Cl(4)	2.2772(12)	C(41)-N(3)-C(49)	125.3(3)
Co(1)-Cl(5)	2.2907(12)	C(41)-N(3)-C(44)	112.8(3)
Co(1)-Cl(6)	2.2964(12)	C(49)-N(3)-C(44)	121.7(3)
N(1)-C(1)	1.298(5)	N(1)-C(1)-C(2)	108.6(3)
N(1)-C(9)	1.463(5)	N(1)-C(1)-Co(2)	130.2(3)
N(1)-C(4)	1.538(5)	C(2)-C(1)-Co(2)	121.1(3)
N(2)-C(21)	1.301(5)	C(1)-C(2)-C(6)	113.0(3)
N(2)-C(29)	1.466(5)	C(1)-C(2)-C(5)	106.4(3)
N(2)-C(24)	1.544(5)	C(6)-C(2)-C(5)	108.9(3)
N(3)-C(41)	1.284(5)	C(1)-C(2)-C(3)	104.3(3)
N(3)-C(49)	1.460(5)	C(6)-C(2)-C(3)	112.1(3)
N(3)-C(44)	1.542(5)	C(5)-C(2)-C(3)	111.9(3)
C(1)-C(2)	1.525(5)	C(4)-C(3)-C(2)	106.4(3)
C(2)-C(6)	1.528(5)	C(8)-C(4)-C(3)	111.8(3)
C(2)-C(5)	1.542(5)	C(8)-C(4)-C(7)	108.5(3)
C(2)-C(3)	1.543(5)	C(3)-C(4)-C(7)	113.9(3)
C(3)-C(4)	1.532(5)	C(8)-C(4)-N(1)	111.7(3)
C(4)-C(8)	1.529(5)	C(3)-C(4)-N(1)	100.5(3)
C(4)-C(7)	1.535(5)	C(7)-C(4)-N(1)	110.3(3)
C(9)-C(10)	1.407(5)	C(10)-C(9)-C(14)	121.5(4)
C(9)-C(14)	1.410(5)	C(10)-C(9)-N(1)	119.1(3)
C(10)-C(11)	1.391(6)	C(14)-C(9)-N(1)	119.4(3)
C(10)-C(15)	1.528(5)	C(11)-C(10)-C(9)	117.6(4)
C(11)-C(12)	1.384(6)	C(11)-C(10)-C(15)	117.7(3)

C(12)-C(13)	1.387(6)	C(9)-C(10)-C(15)	124.7(4)
C(13)-C(14)	1.388(5)	C(12)-C(11)-C(10)	122.2(4)
C(14)-C(18)	1.530(5)	C(11)-C(12)-C(13)	118.9(4)
C(15)-C(17)	1.537(5)	C(12)-C(13)-C(14)	121.9(4)
C(15)-C(16)	1.546(5)	C(13)-C(14)-C(9)	117.9(4)
C(18)-C(20)	1.529(6)	C(13)-C(14)-C(18)	118.2(4)
C(18)-C(19)	1.532(5)	C(9)-C(14)-C(18)	123.8(3)
C(21)-C(22)	1.527(5)	C(10)-C(15)-C(17)	110.0(3)
C(22)-C(26)	1.520(5)	C(10)-C(15)-C(16)	112.2(3)
C(22)-C(23)	1.545(5)	C(17)-C(15)-C(16)	109.5(3)
C(22)-C(25)	1.547(6)	C(20)-C(18)-C(14)	111.9(3)
C(23)-C(24)	1.529(5)	C(20)-C(18)-C(19)	110.1(3)
C(24)-C(28)	1.524(6)	C(14)-C(18)-C(19)	109.3(3)
C(24)-C(27)	1.525(6)	N(2)-C(21)-C(22)	108.6(3)
C(29)-C(30)	1.406(6)	N(2)-C(21)-Co(1)	128.7(3)
C(29)-C(34)	1.410(5)	C(22)-C(21)-Co(1)	122.2(3)
C(30)-C(31)	1.389(5)	C(26)-C(22)-C(21)	112.9(3)
C(30)-C(35)	1.525(6)	C(26)-C(22)-C(23)	112.3(3)
C(31)-C(32)	1.374(6)	C(21)-C(22)-C(23)	103.7(3)
C(32)-C(33)	1.386(6)	C(26)-C(22)-C(25)	108.7(3)
C(33)-C(34)	1.389(5)	C(21)-C(22)-C(25)	106.4(3)
C(34)-C(38)	1.526(5)	C(23)-C(22)-C(25)	112.5(3)
C(35)-C(36)	1.533(6)	C(24)-C(23)-C(22)	107.0(3)
C(35)-C(37)	1.543(6)	C(28)-C(24)-C(27)	108.1(3)
C(38)-C(40)	1.525(6)	C(28)-C(24)-C(23)	114.6(4)
C(38)-C(39)	1.539(6)	C(27)-C(24)-C(23)	112.2(3)
C(41)-C(42)	1.495(5)	C(28)-C(24)-N(2)	111.3(3)
C(42)-C(46)	1.520(6)	C(27)-C(24)-N(2)	110.3(3)
C(42)-C(45)	1.526(6)	C(23)-C(24)-N(2)	100.2(3)
C(42)-C(43)	1.541(6)	C(30)-C(29)-C(34)	121.9(4)
C(43)-C(44)	1.536(5)	C(30)-C(29)-N(2)	120.3(3)
C(44)-C(47)	1.513(6)	C(34)-C(29)-N(2)	117.8(3)
C(44)-C(48)	1.521(6)	C(31)-C(30)-C(29)	117.1(4)
C(49)-C(54)	1.395(6)	C(31)-C(30)-C(35)	118.1(4)
C(49)-C(50)	1.405(6)	C(29)-C(30)-C(35)	124.6(4)
C(50)-C(51)	1.402(6)	C(32)-C(31)-C(30)	122.3(4)
C(50)-C(55)	1.517(6)	C(31)-C(32)-C(33)	119.5(4)
C(51)-C(52)	1.385(6)	C(32)-C(33)-C(34)	121.3(4)
C(52)-C(53)	1.381(6)	C(33)-C(34)-C(29)	117.8(4)
C(53)-C(54)	1.395(5)	C(33)-C(34)-C(38)	117.9(4)
C(54)-C(58)	1.523(6)	C(29)-C(34)-C(38)	124.3(4)
C(55)-C(56)	1.533(6)	C(30)-C(35)-C(36)	110.6(3)
C(55)-C(57)	1.537(6)	C(30)-C(35)-C(37)	111.6(4)
C(58)-C(60)	1.522(6)	C(36)-C(35)-C(37)	108.8(4)
C(58)-C(59)	1.531(6)	C(40)-C(38)-C(34)	112.3(3)
O(1)-C(64)	1.408(6)	C(40)-C(38)-C(39)	109.1(3)
O(1)-C(61)	1.432(10)	C(34)-C(38)-C(39)	110.7(3)
O(1)-C(61')	1.504(17)	N(3)-C(41)-C(42)	114.0(4)
C(61)-C(62)	1.534(12)	C(41)-C(42)-C(46)	112.6(3)
C(62)-C(63)	1.597(13)	C(41)-C(42)-C(45)	107.1(3)
C(63)-C(64)	1.511(10)	C(46)-C(42)-C(45)	109.2(3)
C(64)-C(63')	1.530(17)	C(41)-C(42)-C(43)	101.6(3)

C(61')-C(62')	1.497(19)	C(46)-C(42)-C(43)	112.1(4)
C(62')-C(63')	1.58(2)	C(45)-C(42)-C(43)	114.1(4)
		C(44)-C(43)-C(42)	108.1(3)
Cl(5)-Li(1)-Cl(6)	92.6(2)	C(47)-C(44)-C(48)	110.2(3)
Cl(5)-Li(1)-Cl(2)	123.3(3)	C(47)-C(44)-C(43)	114.9(4)
Cl(6)-Li(1)-Cl(2)	113.6(3)	C(48)-C(44)-C(43)	111.6(4)
Cl(5)-Li(1)-Cl(3)	115.6(3)	C(47)-C(44)-N(3)	109.4(3)
Cl(6)-Li(1)-Cl(3)	123.1(3)	C(48)-C(44)-N(3)	109.7(3)
Cl(2)-Li(1)-Cl(3)	91.5(2)	C(43)-C(44)-N(3)	100.6(3)
Cl(5)-Li(1)-Co(1)	47.13(13)	C(54)-C(49)-C(50)	123.8(4)
Cl(6)-Li(1)-Co(1)	47.25(13)	C(54)-C(49)-N(3)	118.8(3)
Cl(2)-Li(1)-Co(1)	143.8(3)	C(50)-C(49)-N(3)	117.4(3)
Cl(3)-Li(1)-Co(1)	124.7(3)	C(51)-C(50)-C(49)	116.5(4)
Cl(5)-Li(1)-Co(2)	141.7(3)	C(51)-C(50)-C(55)	119.2(4)
Cl(6)-Li(1)-Co(2)	125.8(3)	C(49)-C(50)-C(55)	123.9(4)
Cl(2)-Li(1)-Co(2)	46.65(12)	C(52)-C(51)-C(50)	120.8(4)
Cl(3)-Li(1)-Co(2)	45.69(12)	C(53)-C(52)-C(51)	120.5(4)
Co(1)-Li(1)-Co(2)	166.4(3)	C(52)-C(53)-C(54)	121.4(4)
C(1)-Co(2)-Cl(1)	107.68(10)	C(53)-C(54)-C(49)	116.5(4)
C(1)-Co(2)-Cl(3)	122.26(11)	C(53)-C(54)-C(58)	120.0(4)
Cl(1)-Co(2)-Cl(3)	106.76(4)	C(49)-C(54)-C(58)	123.0(3)
C(1)-Co(2)-Cl(2)	108.66(11)	C(50)-C(55)-C(56)	113.3(4)
Cl(1)-Co(2)-Cl(2)	113.65(4)	C(50)-C(55)-C(57)	109.1(4)
Cl(3)-Co(2)-Cl(2)	97.80(4)	C(56)-C(55)-C(57)	110.5(4)
C(1)-Co(2)-Li(1)	138.18(17)	C(60)-C(58)-C(54)	113.7(3)
Cl(1)-Co(2)-Li(1)	113.75(14)	C(60)-C(58)-C(59)	110.5(3)
Cl(3)-Co(2)-Li(1)	49.85(14)	C(54)-C(58)-C(59)	108.6(3)
Cl(2)-Co(2)-Li(1)	48.90(14)	C(64)-O(1)-C(61)	108.2(5)
C(21)-Co(1)-Cl(4)	103.36(11)	C(64)-O(1)-C(61')	104.2(9)
C(21)-Co(1)-Cl(5)	120.12(11)	O(1)-C(61)-C(62)	99.0(8)
Cl(4)-Co(1)-Cl(5)	114.24(4)	C(61)-C(62)-C(63)	97.8(9)
C(21)-Co(1)-Cl(6)	113.86(12)	C(64)-C(63)-C(62)	99.9(7)
Cl(4)-Co(1)-Cl(6)	107.10(5)	O(1)-C(64)-C(63)	107.7(5)
Cl(5)-Co(1)-Cl(6)	97.88(4)	O(1)-C(64)-C(63')	103.2(9)
C(21)-Co(1)-Li(1)	145.09(18)	C(62')-C(61')-O(1)	106.9(14)
Cl(4)-Co(1)-Li(1)	110.95(14)	C(61')-C(62')-C(63')	89.4(16)
Cl(5)-Co(1)-Li(1)	49.88(14)	C(64)-C(63')-C(62')	98.4(13)
Co(2)-Cl(2)-Li(1)	84.45(17)	Cl(6)-Co(1)-Li(1)	50.00(14)

(Me_2-cAACH$^+$) [(THF)$CoCl_3$]$^-$ (**1b**)

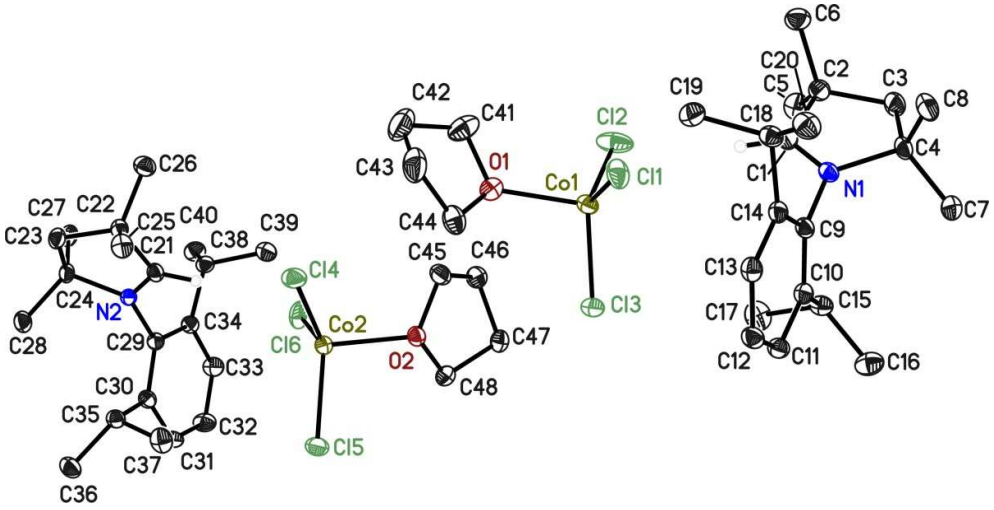


Figure S6. Molecular structure of (Me_2-cAACH$^+$) [(THF)$CoCl_3$]$^-$ (**1b**) (Me_2-cAAC: = :C(CH_2)(CMe_2)$_2$N-2,6-*i*$Pr_2C_6H_3$) with two THF solvent molecules in the crystal. Anisotropic displacement parameters are depicted at the 50% probability level.

Table S3. Crystal data and structure refinement for **1b**.

Compound	(Me_2-cAACH$^+$) [(THF)$CoCl_3$]$^-$ (**1b**) (Me_2-cAAC: = :C(CH_2)(CMe_2)$_2$N-2,6-*i*$Pr_2C_6H_3$)
Empirical formula	C_{24} H_{40} Cl_3 Co N O
CCDC no.	969777
Molecular weight	523.85
Crystal size [mm]	0.1 x 0.1 x 0.1
Crystal system	triclinic
Space group	$P\bar{1}$
a [Å]	12.8180(10)
b [Å]	14.3010(10)
c [Å]	15.8490(10)
α [°]	90.11(2)
β [°]	99.65(2)
γ	108.68(2)
V [Å^3]	2708.5(5)
Z	4
Temperature [K]	101(2)
ρ [gcm^{-3}]	1.285
μ [mm^{-1}]	0.945 mm^{-1}
F (000)	1108
θ-area [°]	1.306 to 25.684
Reflections collected	61259
Independent reflections	10296 [R(int) = 0.0391]
Number of restraints	0
Parameters	557
R1 [I>2σ(I)]	0.0282
wR2 [I>2σ(I)]	0.0668
R1 [all data]	0.0350
wR2 [all data]	0.0713
GooF	1.047
Largest diff. peak / hole [e· Å^{-3}]	0.500 and -0.315

Table S4: Bond lengths [Å] and angles [°] for (**1b**)

Co(1)-O(1)	2.0487(14)	C(45)-O(2)-Co(2)	117.18(10)
Co(1)-Cl(2)	2.2388(7)	C(1)-N(1)-C(9)	121.57(14)
Co(1)-Cl(3)	2.2423(5)	C(1)-N(1)-C(4)	112.75(14)
Co(1)-Cl(1)	2.2592(7)	C(9)-N(1)-C(4)	125.69(14)
Co(2)-O(2)	2.0463(13)	C(21)-N(2)-C(29)	122.11(15)
Co(2)-Cl(5)	2.2450(5)	C(21)-N(2)-C(24)	112.58(14)
Co(2)-Cl(4)	2.2480(7)	C(29)-N(2)-C(24)	125.30(13)
Co(2)-Cl(6)	2.2603(6)	N(1)-C(1)-C(2)	115.15(16)
O(1)-C(41)	1.451(2)	C(1)-C(2)-C(5)	108.06(15)
O(1)-C(44)	1.460(2)	C(1)-C(2)-C(6)	109.56(15)
O(2)-C(48)	1.455(2)	C(5)-C(2)-C(6)	110.01(16)
O(2)-C(45)	1.460(2)	C(1)-C(2)-C(3)	101.33(14)
N(1)-C(1)	1.275(2)	C(5)-C(2)-C(3)	113.01(15)
N(1)-C(9)	1.466(2)	C(6)-C(2)-C(3)	114.34(16)
N(1)-C(4)	1.541(2)	C(4)-C(3)-C(2)	108.10(14)
N(2)-C(21)	1.278(2)	C(7)-C(4)-C(8)	109.17(15)
N(2)-C(29)	1.462(2)	C(7)-C(4)-N(1)	111.31(14)
N(2)-C(24)	1.541(2)	C(8)-C(4)-N(1)	108.61(14)
C(1)-C(2)	1.486(2)	C(7)-C(4)-C(3)	113.63(15)
C(2)-C(5)	1.533(3)	C(8)-C(4)-C(3)	113.61(15)
C(2)-C(6)	1.540(3)	N(1)-C(4)-C(3)	100.16(13)
C(2)-C(3)	1.551(3)	C(14)-C(9)-C(10)	123.74(16)
C(3)-C(4)	1.545(2)	C(14)-C(9)-N(1)	119.10(15)
C(4)-C(7)	1.521(2)	C(10)-C(9)-N(1)	116.92(15)
C(4)-C(8)	1.524(3)	C(11)-C(10)-C(9)	116.77(16)
C(9)-C(14)	1.402(2)	C(11)-C(10)-C(15)	119.77(15)
C(9)-C(10)	1.404(2)	C(9)-C(10)-C(15)	123.24(15)
C(10)-C(11)	1.399(2)	C(12)-C(11)-C(10)	120.97(16)
C(10)-C(15)	1.520(2)	C(11)-C(12)-C(13)	120.60(16)
C(11)-C(12)	1.382(3)	C(12)-C(13)-C(14)	121.29(16)
C(12)-C(13)	1.387(3)	C(13)-C(14)-C(9)	116.53(16)
C(13)-C(14)	1.396(2)	C(13)-C(14)-C(18)	119.69(16)
C(14)-C(18)	1.517(2)	C(9)-C(14)-C(18)	123.62(15)
C(15)-C(16)	1.527(3)	C(10)-C(15)-C(16)	112.59(15)
C(15)-C(17)	1.532(3)	C(10)-C(15)-C(17)	109.72(15)
C(18)-C(20)	1.530(3)	C(16)-C(15)-C(17)	110.81(16)
C(18)-C(19)	1.530(3)	C(14)-C(18)-C(20)	111.84(15)
C(21)-C(22)	1.479(2)	C(14)-C(18)-C(19)	110.49(15)
C(22)-C(25)	1.535(2)	C(20)-C(18)-C(19)	110.18(15)
C(22)-C(26)	1.541(2)	N(2)-C(21)-C(22)	115.07(15)
C(22)-C(23)	1.556(2)	C(21)-C(22)-C(25)	107.85(15)
C(23)-C(24)	1.543(2)	C(21)-C(22)-C(26)	109.96(14)
C(24)-C(27)	1.524(3)	C(25)-C(22)-C(26)	110.25(15)
C(24)-C(28)	1.525(2)	C(21)-C(22)-C(23)	101.53(14)
C(29)-C(34)	1.400(2)	C(25)-C(22)-C(23)	113.24(15)
C(29)-C(30)	1.407(2)	C(26)-C(22)-C(23)	113.52(15)
C(30)-C(31)	1.393(3)	C(24)-C(23)-C(22)	107.62(14)
C(30)-C(35)	1.521(2)	C(27)-C(24)-C(28)	109.35(15)
C(31)-C(32)	1.386(3)	C(27)-C(24)-N(2)	108.46(14)

C(32)-C(33)	1.383(3)	C(28)-C(24)-N(2)	111.32(14)
C(33)-C(34)	1.398(3)	C(27)-C(24)-C(23)	113.79(15)
C(34)-C(38)	1.520(2)	C(28)-C(24)-C(23)	113.36(15)
C(35)-C(36)	1.532(3)	N(2)-C(24)-C(23)	100.19(13)
C(35)-C(37)	1.535(3)	C(34)-C(29)-C(30)	123.35(16)
C(38)-C(40)	1.528(3)	C(34)-C(29)-N(2)	119.24(15)
C(38)-C(39)	1.532(3)	C(30)-C(29)-N(2)	117.27(15)
C(41)-C(42)	1.516(3)	C(31)-C(30)-C(29)	116.93(16)
C(42)-C(43)	1.509(4)	C(31)-C(30)-C(35)	119.82(16)
C(43)-C(44)	1.505(3)	C(29)-C(30)-C(35)	123.05(15)
C(45)-C(46)	1.514(3)	C(32)-C(31)-C(30)	121.15(17)
C(46)-C(47)	1.522(3)	C(33)-C(32)-C(31)	120.35(17)
C(47)-C(48)	1.516(3)	C(32)-C(33)-C(34)	121.30(17)
		C(33)-C(34)-C(29)	116.77(16)
O(1)-Co(1)-Cl(2)	103.14(4)	C(33)-C(34)-C(38)	119.36(16)
O(1)-Co(1)-Cl(3)	102.77(4)	C(29)-C(34)-C(38)	123.72(16)
Cl(2)-Co(1)-Cl(3)	113.52(2)	C(30)-C(35)-C(36)	112.18(15)
O(1)-Co(1)-Cl(1)	98.59(4)	C(30)-C(35)-C(37)	109.70(15)
Cl(2)-Co(1)-Cl(1)	117.61(3)	C(36)-C(35)-C(37)	110.30(15)
Cl(3)-Co(1)-Cl(1)	117.31(3)	C(34)-C(38)-C(40)	111.88(15)
O(2)-Co(2)-Cl(5)	100.01(4)	C(34)-C(38)-C(39)	111.07(15)
O(2)-Co(2)-Cl(4)	105.94(4)	C(40)-C(38)-C(39)	109.70(15)
Cl(5)-Co(2)-Cl(4)	115.46(2)	O(1)-C(41)-C(42)	105.03(18)
O(2)-Co(2)-Cl(6)	98.23(4)	C(43)-C(42)-C(41)	103.04(17)
Cl(5)-Co(2)-Cl(6)	119.17(3)	C(44)-C(43)-C(42)	101.69(18)
Cl(4)-Co(2)-Cl(6)	114.04(2)	O(1)-C(44)-C(43)	104.71(17)
C(41)-O(1)-C(44)	109.41(15)	O(2)-C(45)-C(46)	105.51(15)
C(41)-O(1)-Co(1)	122.21(13)	C(45)-C(46)-C(47)	101.76(15)
C(44)-O(1)-Co(1)	119.01(11)	C(48)-C(47)-C(46)	101.85(14)
C(48)-O(2)-C(45)	109.24(13)	O(2)-C(48)-C(47)	104.66(14)
C(48)-O(2)-Co(2)	117.21(10)	C(45)-O(2)-Co(2)	117.18(10)

$(Me_2\text{-cAACH}^+)_2[CoCl_4]^{2-}$ (**1c**)

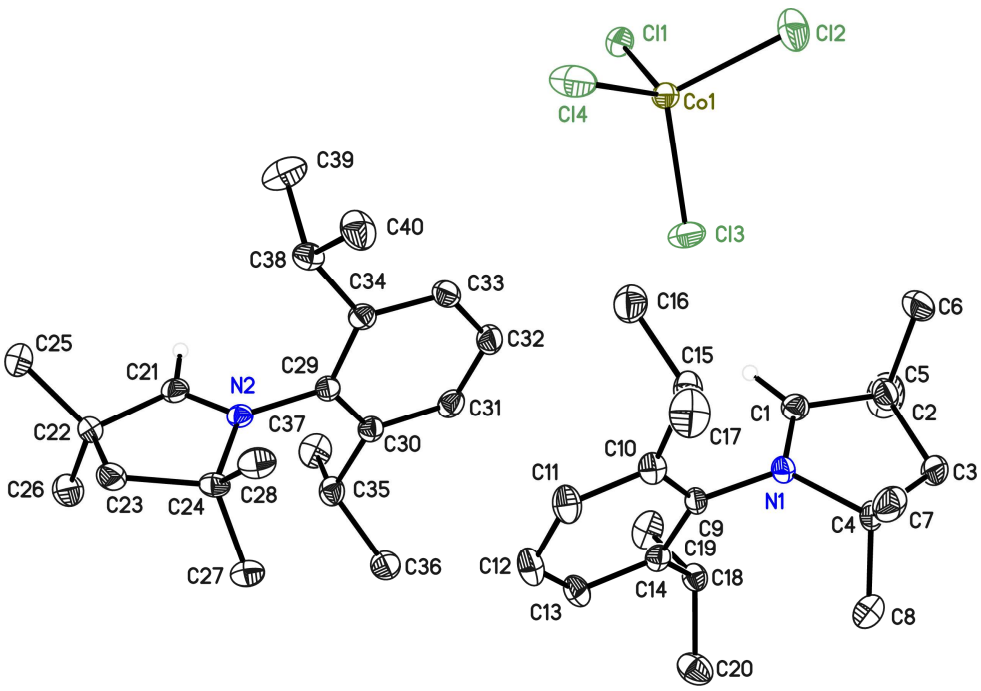


Figure S7. Molecular structure of $(Me_2\text{-}cAACH^+)_2[CoCl_4]^{2-}$ (**1c**) (Me_2-cAAC: = $:C(CH_2)(CMe_2)_2N$-2,6-iPr$_2$C$_6$H$_3$) in the crystal. Anisotropic displacement parameters are depicted at the 50% probability level. The $CoCl_4^-$ anion and the C3, C5 and C6 atoms are disordered (site occupation factor: 0.926(5), 0.709(22) and 0.718(29)). This disorders are not shown for clarity.

Table S5. Crystal data and structure refinement for (**1c**):

Compound	$(Me_2\text{-}cAACH^+)_2[CoCl_4]^{2-}$ (**1c**) (Me_2-cAAC: = $:C(CH_2)(CMe_2)_2N$-2,6-iPr$_2$C$_6$H$_3$)
Empirical formula	C_{40} H_{64} Cl_4 Co N_2
CCDC no.	969779
Molecular weight	773.66
Crystal size [mm]	0.1 x 0.08 x 0.06
Crystal system	orthorhombic
Space group	$P\ 2_1\ 2_1\ 2_1$
a [Å]	10.020(2)
b [Å]	14.726(2)
c [Å]	28.284(2)
α [°]	90.0
β [°]	90.0
γ	90.0
V [Å^3]	4173.4(10)
Z	4
Temperature [K]	101(2)
ρ [gcm^{-3}]	1.231
μ [mm^{-1}]	0.696
F (000)	1652
θ-area [°]	1.440 to 26.031
Reflections collected	78210
Independent reflections	8149 [R(int) = 0.0509]
Number of restraints	244
Parameters	505

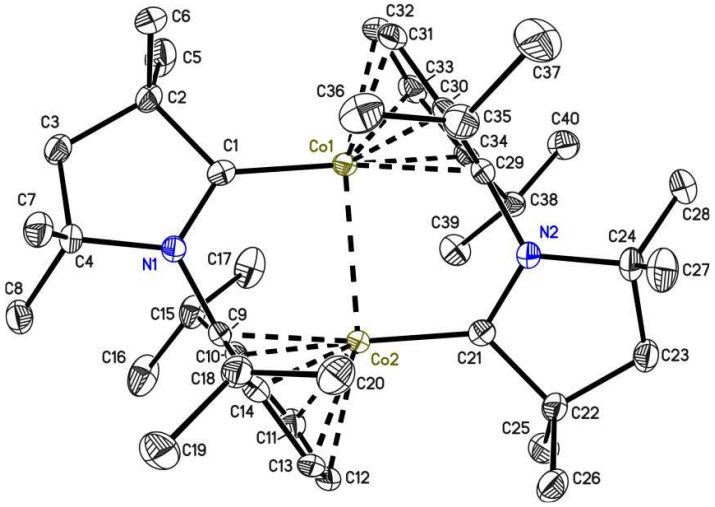
R1 [I>2σ(I)]	0.0270
wR2 [I>2σ(I)]	0.0581
R1 [all data]	0.0324
wR2 [all data]	0.0594
GooF	1.030
Flack(x)[S9]	0.005(5)
Largest diff. peak / hole [e·Å^{-3}]	0.247 and -0.241

Table S6: Bond lengths [Å] and angles [°] for (**1c**):

Co(1)-Cl(4)	2.2566(13)	C(29)-N(2)-C(24)	124.03(18)
Co(1)-Cl(2)	2.2720(14)	C(8)-C(4)-C(7)	109.8(2)
Co(1)-Cl(3)	2.2960(15)	C(8)-C(4)-C(3')	123.2(10)
Co(1)-Cl(1)	2.3030(16)	C(7)-C(4)-C(3')	102.3(10)
Co(1')-Cl(1')	2.265(16)	C(8)-C(4)-N(1)	111.0(2)
Co(1')-Cl(4')	2.278(15)	C(7)-C(4)-N(1)	108.9(2)
Co(1')-Cl(3')	2.293(18)	C(3')-C(4)-N(1)	100.5(6)
Co(1')-Cl(2')	2.325(15)	C(8)-C(4)-C(3)	108.5(4)
N(1)-C(1)	1.274(3)	C(7)-C(4)-C(3)	117.7(5)
N(1)-C(9)	1.461(3)	N(1)-C(4)-C(3)	100.6(3)
N(1)-C(4)	1.543(3)	C(2)-C(3)-C(4)	107.6(4)
N(2)-C(21)	1.281(3)	C(2)-C(3')-C(4)	107.9(10)
N(2)-C(29)	1.458(3)	N(1)-C(1)-C(2)	114.5(2)
N(2)-C(24)	1.541(3)	C(1)-C(2)-C(6')	112.9(9)
C(4)-C(8)	1.505(4)	C(1)-C(2)-C(3)	102.9(3)
C(4)-C(7)	1.516(4)	C(1)-C(2)-C(5)	108.0(3)
C(4)-C(3')	1.538(18)	C(3)-C(2)-C(5)	113.8(6)
C(4)-C(3)	1.551(7)	C(1)-C(2)-C(3')	101.8(7)
C(3)-C(2)	1.531(7)	C(6')-C(2)-C(3')	115.4(13)
C(3')-C(2)	1.538(17)	C(1)-C(2)-C(6)	109.7(4)
C(1)-C(2)	1.482(4)	C(3)-C(2)-C(6)	113.1(6)
C(2)-C(6')	1.517(14)	C(5)-C(2)-C(6)	109.1(4)
C(2)-C(5)	1.534(6)	C(1)-C(2)-C(5')	108.2(6)
C(2)-C(6)	1.540(6)	C(6')-C(2)-C(5')	109.2(9)
C(2)-C(5')	1.582(12)	C(3')-C(2)-C(5')	108.8(14)
C(9)-C(14)	1.395(3)	C(14)-C(9)-C(10)	122.9(2)
C(9)-C(10)	1.402(3)	C(14)-C(9)-N(1)	117.3(2)
C(10)-C(11)	1.391(4)	C(10)-C(9)-N(1)	119.8(2)
C(10)-C(15)	1.521(3)	C(11)-C(10)-C(9)	117.1(2)
C(11)-C(12)	1.385(4)	C(11)-C(10)-C(15)	118.5(2)
C(12)-C(13)	1.378(4)	C(9)-C(10)-C(15)	124.2(2)
C(13)-C(14)	1.395(3)	C(12)-C(11)-C(10)	121.4(2)
C(14)-C(18)	1.522(3)	C(13)-C(12)-C(11)	119.9(2)
C(15)-C(16)	1.524(4)	C(12)-C(13)-C(14)	121.4(2)
C(15)-C(17)	1.535(4)	C(9)-C(14)-C(13)	117.2(2)
C(18)-C(20)	1.520(4)	C(9)-C(14)-C(18)	123.5(2)
C(18)-C(19)	1.528(3)	C(13)-C(14)-C(18)	119.0(2)
C(21)-C(22)	1.487(3)	C(10)-C(15)-C(16)	110.2(2)
C(22)-C(25)	1.534(3)	C(10)-C(15)-C(17)	111.5(2)
C(22)-C(23)	1.540(4)	C(16)-C(15)-C(17)	110.6(2)
C(22)-C(26)	1.544(4)	C(20)-C(18)-C(14)	113.4(2)
C(23)-C(24)	1.535(4)	C(20)-C(18)-C(19)	110.6(2)
C(24)-C(27)	1.522(3)	C(14)-C(18)-C(19)	108.8(2)

C(24)-C(28)	1.523(3)	N(2)-C(21)-C(22)	114.3(2)
C(29)-C(30)	1.402(3)	C(21)-C(22)-C(25)	110.8(2)
C(29)-C(34)	1.404(3)	C(21)-C(22)-C(23)	101.7(2)
C(30)-C(31)	1.388(3)	C(25)-C(22)-C(23)	113.0(2)
C(30)-C(35)	1.527(3)	C(21)-C(22)-C(26)	107.0(2)
C(31)-C(32)	1.376(4)	C(25)-C(22)-C(26)	109.8(2)
C(32)-C(33)	1.383(4)	C(23)-C(22)-C(26)	114.1(2)
C(33)-C(34)	1.390(4)	C(24)-C(23)-C(22)	107.5(2)
C(34)-C(38)	1.519(3)	C(27)-C(24)-C(28)	109.6(2)
C(35)-C(36)	1.534(4)	C(27)-C(24)-C(23)	113.5(2)
C(35)-C(37)	1.535(3)	C(28)-C(24)-C(23)	113.1(2)
C(38)-C(39)	1.526(4)	C(27)-C(24)-N(2)	108.65(18)
C(38)-C(40)	1.530(3)	C(28)-C(24)-N(2)	111.14(19)
		C(23)-C(24)-N(2)	100.51(18)
Cl(4)-Co(1)-Cl(2)	112.32(6)	C(30)-C(29)-C(34)	123.0(2)
Cl(4)-Co(1)-Cl(3)	108.42(9)	C(30)-C(29)-N(2)	119.2(2)
Cl(2)-Co(1)-Cl(3)	109.03(9)	C(34)-C(29)-N(2)	117.8(2)
Cl(4)-Co(1)-Cl(1)	114.39(8)	C(31)-C(30)-C(29)	116.7(2)
Cl(2)-Co(1)-Cl(1)	105.23(9)	C(31)-C(30)-C(35)	119.0(2)
Cl(3)-Co(1)-Cl(1)	107.23(10)	C(29)-C(30)-C(35)	124.1(2)
Cl(1')-Co(1')-Cl(4')	109.1(9)	C(32)-C(31)-C(30)	121.9(2)
Cl(1')-Co(1')-Cl(3')	110.6(12)	C(31)-C(32)-C(33)	119.9(2)
Cl(4')-Co(1')-Cl(3')	107.4(12)	C(32)-C(33)-C(34)	121.4(2)
Cl(1')-Co(1')-Cl(2')	113.0(11)	C(33)-C(34)-C(29)	116.9(2)
Cl(4')-Co(1')-Cl(2')	110.5(8)	C(33)-C(34)-C(38)	119.3(2)
Cl(3')-Co(1')-Cl(2')	106.0(11)	C(29)-C(34)-C(38)	123.5(2)
C(1)-N(1)-C(9)	123.6(2)	C(30)-C(35)-C(36)	111.8(2)
C(1)-N(1)-C(4)	112.7(2)	C(30)-C(35)-C(37)	109.8(2)
C(9)-N(1)-C(4)	123.61(19)	C(36)-C(35)-C(37)	110.6(2)
C(21)-N(2)-C(29)	123.5(2)	C(34)-C(38)-C(39)	109.4(2)
C(21)-N(2)-C(24)	112.4(2)	C(34)-C(38)-C(40)	112.7(2)

$(Me_2\text{-cAAC:})_2Co_2$ (**2**)



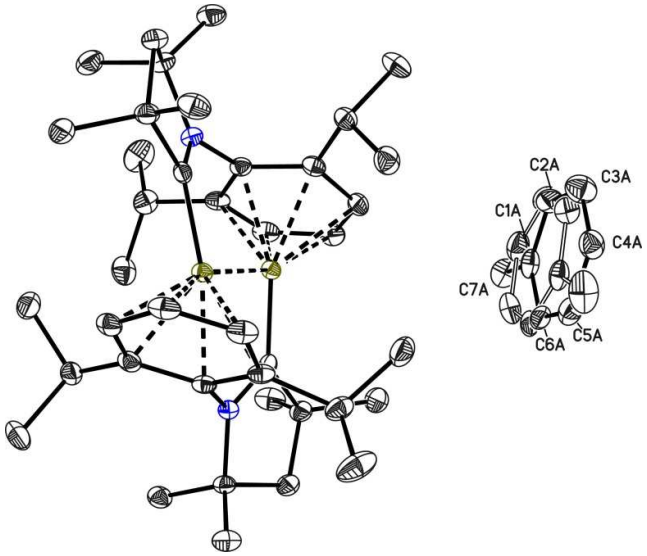


Figure S8. Molecular structure of (Me_2-cAAC:)$_2Co_2$ (**2**) (Me_2-cAAC: = :C(CH_2)(CMe_2)$_2$N-2,6-*i*$Pr_2C_6H_3$) with one toluene solvent molecule in the crystal. Anisotropic displacement parameters are depicted at the 50% probability level. The toluene molecule is disordered. The two positions have a site occupation factor of 0.452(5).

Table S7. Crystal data and structure refinement for **2** :

Compound	(Me_2-cAAC:)$_2Co_2$ (**2**) (Me_2-cAAC: = :C(CH_2)(CMe_2)$_2$N-2,6-*i*$Pr_2C_6H_3$)
Empirical formula	C_{47} H_{70} Co_2 N_2
CCDC no.	969778
Molecular weight	780.91
Crystal size [mm]	0.05 x 0.01 x 0.01
Crystal system	orthorhombic
Space group	*P n a* 2_1
a [Å]	22.773(2)
b [Å]	10.794(2)
c [Å]	16.689(2)
α [°]	90
β [°]	90
γ	90
V [Å ^{3}]	4102.4(10)
Z	4
Temperature [K]	101(2)
ρ [gcm^{-3}]	1.264
μ [mm^{-1}]	0.843
F (000)	1680
θ-area [°]	1.788 to 27.497
Reflections collected	117899
Independent reflections	9411 [R(int) = 0.0614]
Number of restraints	352
Parameters	542
R1 [I>2σ(I)]	0.0249,
wR2 [I>2σ(I)]	0.0551
R1 [all data]	0.0273
wR2 [all data]	0.0560
GooF	1.080
Flack(x)[S9]	0.001(4)
Largest diff. peak / hole [e· Å^{-3}]	0.211 and -0.270

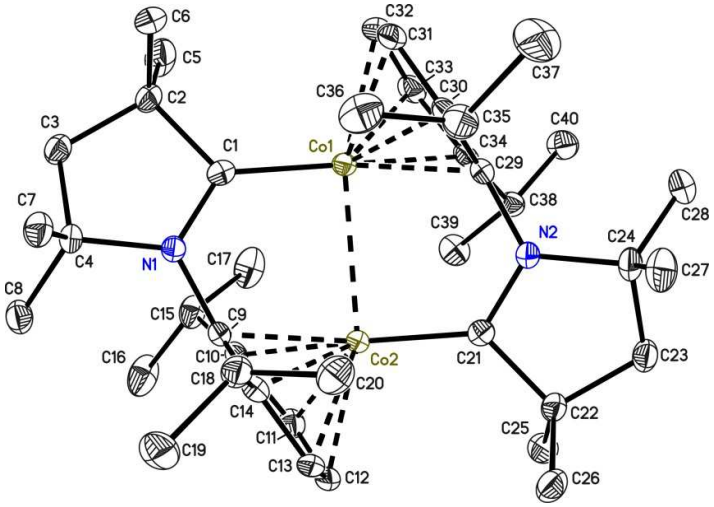
Table S8: Bond lengths [Å] and angles [°] for **2** :

Co(1)-C(1)	1.854(2)	C(14)-Co(2)-Co(1)	104.99(6)
Co(1)-C(29)	2.077(2)	C(13)-Co(2)-Co(1)	143.75(7)
Co(1)-C(30)	2.090(2)	C(12)-Co(2)-Co(1)	160.49(7)
Co(1)-C(31)	2.136(2)	C(11)-Co(2)-Co(1)	124.19(7)
Co(1)-C(32)	2.179(2)	C(10)-Co(2)-Co(1)	92.27(6)
Co(1)-C(33)	2.183(2)	C(1)-N(1)-C(9)	116.97(19)
Co(1)-C(34)	2.184(2)	C(1)-N(1)-C(4)	117.27(18)
Co(1)-Co(2)	2.6550(6)	C(9)-N(1)-C(4)	124.53(18)
Co(2)-C(21)	1.853(2)	C(21)-N(2)-C(29)	116.92(18)
Co(2)-C(9)	2.075(2)	C(21)-N(2)-C(24)	116.94(19)
Co(2)-C(14)	2.091(2)	C(29)-N(2)-C(24)	124.45(19)
Co(2)-C(13)	2.123(2)	N(1)-C(1)-C(2)	104.90(19)
Co(2)-C(12)	2.158(2)	N(1)-C(1)-Co(1)	125.57(17)
Co(2)-C(11)	2.169(2)	C(2)-C(1)-Co(1)	129.38(17)
Co(2)-C(10)	2.187(2)	C(5)-C(2)-C(6)	109.5(2)
N(1)-C(1)	1.369(3)	C(5)-C(2)-C(3)	108.4(2)
N(1)-C(9)	1.435(3)	C(6)-C(2)-C(3)	111.4(2)
N(1)-C(4)	1.502(3)	C(5)-C(2)-C(1)	111.4(2)
N(2)-C(21)	1.367(3)	C(6)-C(2)-C(1)	111.6(2)
N(2)-C(29)	1.434(3)	C(3)-C(2)-C(1)	104.45(18)
N(2)-C(24)	1.501(3)	C(4)-C(3)-C(2)	106.90(19)
C(1)-C(2)	1.554(3)	N(1)-C(4)-C(8)	112.38(19)
C(2)-C(5)	1.530(4)	N(1)-C(4)-C(3)	99.78(18)
C(2)-C(6)	1.544(4)	C(8)-C(4)-C(3)	113.3(2)
C(2)-C(3)	1.545(3)	N(1)-C(4)-C(7)	112.04(19)
C(3)-C(4)	1.524(3)	C(8)-C(4)-C(7)	108.5(2)
C(4)-C(8)	1.519(3)	C(3)-C(4)-C(7)	110.7(2)
C(4)-C(7)	1.534(3)	C(14)-C(9)-N(1)	121.3(2)
C(9)-C(14)	1.427(3)	C(14)-C(9)-C(10)	122.0(2)
C(9)-C(10)	1.440(3)	N(1)-C(9)-C(10)	116.3(2)
C(10)-C(11)	1.407(3)	C(14)-C(9)-Co(2)	70.58(13)
C(10)-C(15)	1.525(3)	N(1)-C(9)-Co(2)	121.90(15)
C(11)-C(12)	1.399(4)	C(10)-C(9)-Co(2)	74.52(13)
C(12)-C(13)	1.396(4)	C(11)-C(10)-C(9)	117.9(2)
C(13)-C(14)	1.416(3)	C(11)-C(10)-C(15)	118.9(2)
C(14)-C(18)	1.523(4)	C(9)-C(10)-C(15)	123.0(2)
C(15)-C(17)	1.521(4)	C(11)-C(10)-Co(2)	70.45(13)
C(15)-C(16)	1.538(3)	C(9)-C(10)-Co(2)	66.11(13)
C(18)-C(20)	1.533(3)	C(15)-C(10)-Co(2)	139.71(17)
C(18)-C(19)	1.536(4)	C(12)-C(11)-C(10)	120.6(2)
C(21)-C(22)	1.546(3)	C(12)-C(11)-Co(2)	70.70(14)
C(22)-C(25)	1.534(4)	C(10)-C(11)-Co(2)	71.86(13)
C(22)-C(26)	1.538(3)	C(13)-C(12)-C(11)	120.7(2)
C(22)-C(23)	1.547(3)	C(13)-C(12)-Co(2)	69.60(13)
C(23)-C(24)	1.529(3)	C(11)-C(12)-Co(2)	71.57(13)
C(24)-C(28)	1.524(4)	C(12)-C(13)-C(14)	121.8(2)
C(24)-C(27)	1.536(4)	C(12)-C(13)-Co(2)	72.33(14)
C(29)-C(30)	1.429(3)	C(14)-C(13)-Co(2)	69.17(13)
C(29)-C(34)	1.441(3)	C(13)-C(14)-C(9)	116.8(2)
C(30)-C(31)	1.416(3)	C(13)-C(14)-C(18)	118.8(2)
C(30)-C(35)	1.514(4)	C(9)-C(14)-C(18)	124.4(2)

C(31)-C(32)	1.393(4)	C(13)-C(14)-Co(2)	71.57(14)
C(32)-C(33)	1.403(4)	C(9)-C(14)-Co(2)	69.37(13)
C(33)-C(34)	1.408(3)	C(18)-C(14)-Co(2)	130.52(17)
C(34)-C(38)	1.520(3)	C(17)-C(15)-C(10)	114.2(2)
C(35)-C(36)	1.532(4)	C(17)-C(15)-C(16)	110.1(2)
C(35)-C(37)	1.538(4)	C(10)-C(15)-C(16)	109.6(2)
C(38)-C(39)	1.526(3)	C(14)-C(18)-C(20)	112.3(2)
C(38)-C(40)	1.539(3)	C(14)-C(18)-C(19)	110.7(2)
C(1A)-C(2A)	1.375(10)	C(20)-C(18)-C(19)	109.6(2)
C(1A)-C(6A)	1.384(12)	N(2)-C(21)-C(22)	105.50(19)
C(1A)-C(7A)	1.498(10)	N(2)-C(21)-Co(2)	124.92(17)
C(2A)-C(3A)	1.408(10)	C(22)-C(21)-Co(2)	129.45(16)
C(3A)-C(4A)	1.370(9)	C(25)-C(22)-C(26)	108.9(2)
C(4A)-C(5A)	1.392(9)	C(25)-C(22)-C(21)	110.7(2)
C(5A)-C(6A)	1.366(11)	C(26)-C(22)-C(21)	112.9(2)
C(1B)-C(6B)	1.377(9)	C(25)-C(22)-C(23)	108.1(2)
C(1B)-C(2B)	1.389(9)	C(26)-C(22)-C(23)	111.7(2)
C(1B)-C(7B)	1.497(8)	C(21)-C(22)-C(23)	104.46(18)
C(2B)-C(3B)	1.392(8)	C(24)-C(23)-C(22)	106.79(19)
C(3B)-C(4B)	1.370(9)	N(2)-C(24)-C(28)	112.5(2)
C(4B)-C(5B)	1.392(9)	N(2)-C(24)-C(23)	99.91(19)
C(5B)-C(6B)	1.389(10)	C(28)-C(24)-C(23)	113.2(2)
		N(2)-C(24)-C(27)	111.8(2)
C(1)-Co(1)-C(29)	161.80(10)	C(28)-C(24)-C(27)	109.0(2)
C(1)-Co(1)-C(30)	128.59(10)	C(23)-C(24)-C(27)	110.3(2)
C(29)-Co(1)-C(30)	40.12(9)	C(30)-C(29)-N(2)	121.2(2)
C(1)-Co(1)-C(31)	109.16(10)	C(30)-C(29)-C(34)	121.8(2)
C(29)-Co(1)-C(31)	70.12(9)	N(2)-C(29)-C(34)	116.6(2)
C(30)-Co(1)-C(31)	39.13(9)	C(30)-C(29)-Co(1)	70.40(13)
C(1)-Co(1)-C(32)	108.59(10)	N(2)-C(29)-Co(1)	121.92(15)
C(29)-Co(1)-C(32)	82.20(9)	C(34)-C(29)-Co(1)	74.27(14)
C(30)-Co(1)-C(32)	70.27(10)	C(31)-C(30)-C(29)	116.6(2)
C(31)-Co(1)-C(32)	37.64(10)	C(31)-C(30)-C(35)	119.1(2)
C(1)-Co(1)-C(33)	127.38(10)	C(29)-C(30)-C(35)	124.3(2)
C(29)-Co(1)-C(33)	70.06(9)	C(31)-C(30)-Co(1)	72.22(13)
C(30)-Co(1)-C(33)	84.16(10)	C(29)-C(30)-Co(1)	69.47(13)
C(31)-Co(1)-C(33)	68.50(10)	C(35)-C(30)-Co(1)	129.81(18)
C(32)-Co(1)-C(33)	37.54(10)	C(32)-C(31)-C(30)	122.1(2)
C(1)-Co(1)-C(34)	158.05(10)	C(32)-C(31)-Co(1)	72.84(14)
C(29)-Co(1)-C(34)	39.44(9)	C(30)-C(31)-Co(1)	68.65(12)
C(30)-Co(1)-C(34)	71.84(10)	C(31)-C(32)-C(33)	120.8(2)
C(31)-Co(1)-C(34)	81.61(10)	C(31)-C(32)-Co(1)	69.51(13)
C(32)-Co(1)-C(34)	67.88(9)	C(33)-C(32)-Co(1)	71.38(14)
C(33)-Co(1)-C(34)	37.62(9)	C(32)-C(33)-C(34)	120.1(2)
C(1)-Co(1)-Co(2)	89.91(7)	C(32)-C(33)-Co(1)	71.09(15)
C(29)-Co(1)-Co(2)	82.19(6)	C(34)-C(33)-Co(1)	71.23(14)
C(30)-Co(1)-Co(2)	104.89(6)	C(33)-C(34)-C(29)	118.3(2)
C(31)-Co(1)-Co(2)	143.67(7)	C(33)-C(34)-C(38)	119.0(2)
C(32)-Co(1)-Co(2)	159.76(7)	C(29)-C(34)-C(38)	122.5(2)
C(33)-Co(1)-Co(2)	123.84(7)	C(33)-C(34)-Co(1)	71.15(14)
C(34)-Co(1)-Co(2)	91.89(6)	C(29)-C(34)-Co(1)	66.28(13)
C(21)-Co(2)-C(9)	162.58(9)	C(38)-C(34)-Co(1)	139.51(16)

C(21)-Co(2)-C(14)	128.98(10)	C(30)-C(35)-C(36)	112.6(2)
C(9)-Co(2)-C(14)	40.06(9)	C(30)-C(35)-C(37)	109.9(2)
C(21)-Co(2)-C(13)	108.52(10)	C(36)-C(35)-C(37)	109.6(2)
C(9)-Co(2)-C(13)	70.43(9)	C(34)-C(38)-C(39)	114.2(2)
C(14)-Co(2)-C(13)	39.26(9)	C(34)-C(38)-C(40)	109.91(19)
C(21)-Co(2)-C(12)	107.46(9)	C(39)-C(38)-C(40)	109.2(2)
C(9)-Co(2)-C(12)	82.64(9)	C(2A)-C(1A)-C(6A)	117.9(7)
C(14)-Co(2)-C(12)	70.63(9)	C(2A)-C(1A)-C(7A)	120.5(7)
C(13)-Co(2)-C(12)	38.06(10)	C(6A)-C(1A)-C(7A)	121.4(7)
C(21)-Co(2)-C(11)	126.48(9)	C(1A)-C(2A)-C(3A)	120.9(7)
C(9)-Co(2)-C(11)	70.11(9)	C(4A)-C(3A)-C(2A)	119.9(7)
C(14)-Co(2)-C(11)	84.20(10)	C(3A)-C(4A)-C(5A)	119.2(6)
C(13)-Co(2)-C(11)	68.95(10)	C(6A)-C(5A)-C(4A)	120.2(8)
C(12)-Co(2)-C(11)	37.73(10)	C(5A)-C(6A)-C(1A)	121.9(9)
C(21)-Co(2)-C(10)	157.50(9)	C(6B)-C(1B)-C(2B)	118.4(7)
C(9)-Co(2)-C(10)	39.37(9)	C(6B)-C(1B)-C(7B)	121.2(6)
C(14)-Co(2)-C(10)	71.72(9)	C(2B)-C(1B)-C(7B)	120.4(6)
C(13)-Co(2)-C(10)	82.02(9)	C(1B)-C(2B)-C(3B)	120.3(7)
C(12)-Co(2)-C(10)	68.24(9)	C(4B)-C(3B)-C(2B)	121.1(6)
C(11)-Co(2)-C(10)	37.70(8)	C(3B)-C(4B)-C(5B)	119.0(6)
C(21)-Co(2)-Co(1)	90.17(7)	C(6B)-C(5B)-C(4B)	119.7(6)
C(9)-Co(2)-Co(1)	82.51(6)	C(1B)-C(6B)-C(5B)	121.5(8)

$[(Me_2\text{-cAAC:})_2Co_2]^{+}\,OTf^{-}$ (**2^{+}OTf^{-}**)



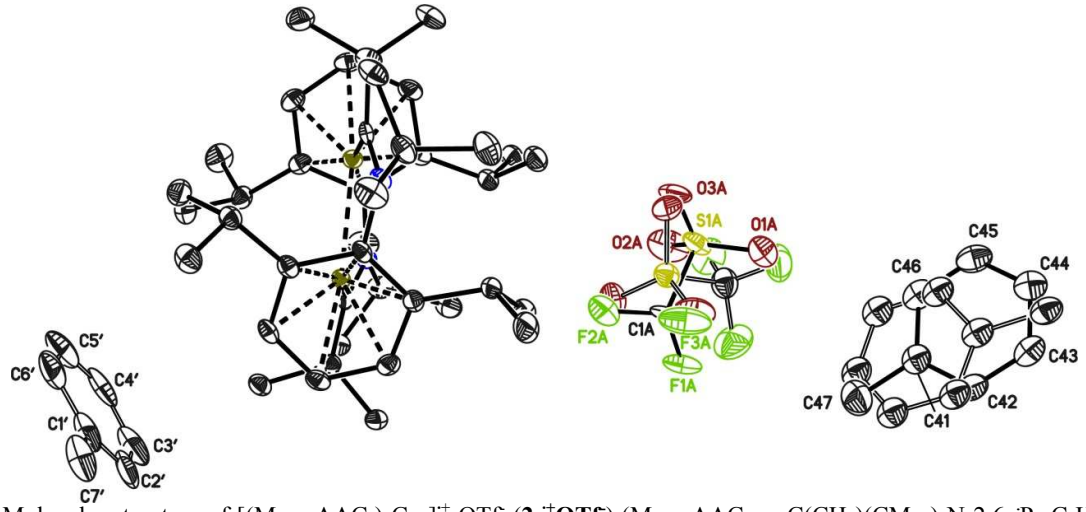


Figure S9. Molecular structure of $[(Me_2\text{-cAAC:})_2Co_2]^{+}$ OTf^- (**2** $^{+}$**OTf**$^-$) (Me_2-cAAC: = $:C(CH_2)(CMe_2)_2N$-2,6-iPr$_2C_6H_3$) with 1.5 toluene solvent molecules in the crystal. Anisotropic displacement parameters are depicted at the 50% probability level. The toluene molecule (C41 to C47) is disordered. The two positions have a side occupation factor of 0.938(3). The toluene molecule C1' to C7' is not disordered but on a special position. The Triflat moiety shows a disorder with a site occupation factor of 0.605(2).

Table S9. Crystal data and structure refinement for (**2** $^{+}$**OTf**$^-$):

Compound	$[(Me_2\text{-cAAC:})_2Co_2]^{+}$ OTf^- (**2** $^{+}$**OTf**$^-$) (Me_2-cAAC: = $:C(CH_2)(CMe_2)_2N$-2,6-iPr$_2C_6H_3$)
Empirical formula	$C_{51.50}H_{74}Co_2F_3N_2O_3S$
CCDC no.	969775
Molecular weight	976.04
Crystal size [mm]	0.09 x 0.07 x 0.03
Crystal system	orthorhombic
Space group	$P\,2_1/n$
a [Å]	21.3850(10)
b [Å]	10.5130(10)
c [Å]	22.5320(10)
α [°]	90
β [°]	107.59(2)°
γ	90
V [Å^3]	4828.8(8)
Z	4
Temperature [K]	101(2)
ρ [gcm^{-3}]	1.343
μ [mm^{-1}]	0.785
F (000)	2072
θ-area [°]	1.151 to 26.423
Reflections collected	90157
Independent reflections	9887 [R(int) = 0.0554]
Number of restraints	1129
Parameters	751
R1 [I>2σ(I)]	0.0441,
wR2 [I>2σ(I)]	0.0867
R1 [all data]	0.0581
wR2 [all data]	0.0911
GooF	1.127
Largest diff. peak / hole [e· Å^{-3}]	0.346 and -0.357

Table S10: Bond lengths [Å] and angles [°] for (**2** $^{+}$**OTf**$^{-}$):

Co(1)-C(1)	1.891(2)	C(1)-N(1)-C(4)	116.5(2)
Co(1)-C(29)	2.053(2)	C(9)-N(1)-C(4)	125.9(2)
Co(1)-C(30)	2.112(2)	C(21)-N(2)-C(29)	116.9(2)
Co(1)-C(34)	2.164(2)	C(21)-N(2)-C(24)	117.0(2)
Co(1)-C(31)	2.182(2)	C(29)-N(2)-C(24)	125.18(19)
Co(1)-C(33)	2.192(2)	N(1)-C(1)-C(2)	106.4(2)
Co(1)-C(32)	2.231(2)	N(1)-C(1)-Co(1)	123.59(18)
Co(1)-Co(2)	2.4610(6)	C(2)-C(1)-Co(1)	129.87(17)
Co(2)-C(21)	1.920(2)	C(5)-C(2)-C(6)	109.3(2)
Co(2)-C(9)	2.061(2)	C(5)-C(2)-C(3)	111.2(2)
Co(2)-C(14)	2.128(2)	C(6)-C(2)-C(3)	109.4(2)
Co(2)-C(10)	2.170(3)	C(5)-C(2)-C(1)	113.5(2)
Co(2)-C(13)	2.206(2)	C(6)-C(2)-C(1)	109.63(19)
Co(2)-C(11)	2.211(3)	C(3)-C(2)-C(1)	103.68(19)
Co(2)-C(12)	2.251(3)	C(4)-C(3)-C(2)	106.6(2)
N(1)-C(1)	1.338(3)	N(1)-C(4)-C(8)	112.0(2)
N(1)-C(9)	1.439(3)	N(1)-C(4)-C(3)	99.07(19)
N(1)-C(4)	1.514(3)	C(8)-C(4)-C(3)	113.6(2)
N(2)-C(21)	1.328(3)	N(1)-C(4)-C(7)	110.3(2)
N(2)-C(29)	1.449(3)	C(8)-C(4)-C(7)	110.2(2)
N(2)-C(24)	1.518(3)	C(3)-C(4)-C(7)	111.3(2)
C(1)-C(2)	1.550(3)	C(14)-C(9)-N(1)	122.1(2)
C(2)-C(5)	1.538(3)	C(14)-C(9)-C(10)	121.7(2)
C(2)-C(6)	1.540(3)	N(1)-C(9)-C(10)	115.8(2)
C(2)-C(3)	1.550(3)	C(14)-C(9)-Co(2)	72.57(14)
C(3)-C(4)	1.528(4)	N(1)-C(9)-Co(2)	118.96(16)
C(4)-C(8)	1.522(4)	C(10)-C(9)-Co(2)	74.22(14)
C(4)-C(7)	1.535(4)	C(11)-C(10)-C(9)	118.4(2)
C(9)-C(14)	1.431(3)	C(11)-C(10)-C(15)	118.6(2)
C(9)-C(10)	1.440(3)	C(9)-C(10)-C(15)	122.7(2)
C(10)-C(11)	1.399(4)	C(11)-C(10)-Co(2)	73.00(15)
C(10)-C(15)	1.531(3)	C(9)-C(10)-Co(2)	66.07(13)
C(11)-C(12)	1.404(4)	C(15)-C(10)-Co(2)	138.44(17)
C(12)-C(13)	1.397(4)	C(10)-C(11)-C(12)	120.7(2)
C(13)-C(14)	1.410(4)	C(10)-C(11)-Co(2)	69.76(14)
C(14)-C(18)	1.516(3)	C(12)-C(11)-Co(2)	73.20(15)
C(15)-C(16)	1.526(4)	C(13)-C(12)-C(11)	119.9(2)
C(15)-C(17)	1.536(4)	C(13)-C(12)-Co(2)	69.99(14)
C(18)-C(20)	1.529(4)	C(11)-C(12)-Co(2)	70.13(14)
C(18)-C(19)	1.538(4)	C(12)-C(13)-C(14)	122.7(2)
C(24)-C(23)	1.523(4)	C(12)-C(13)-Co(2)	73.50(15)
C(24)-C(27)	1.523(4)	C(14)-C(13)-Co(2)	68.04(14)
C(24)-C(28)	1.536(4)	C(13)-C(14)-C(9)	116.4(2)
C(23)-C(22)	1.547(4)	C(13)-C(14)-C(18)	119.3(2)
C(22)-C(25)	1.536(4)	C(9)-C(14)-C(18)	124.2(2)
C(22)-C(26)	1.544(3)	C(13)-C(14)-Co(2)	74.05(15)
C(22)-C(21)	1.545(3)	C(9)-C(14)-Co(2)	67.51(13)
C(29)-C(30)	1.429(3)	C(18)-C(14)-Co(2)	131.83(17)
C(29)-C(34)	1.430(3)	C(16)-C(15)-C(10)	114.0(2)
C(30)-C(31)	1.406(3)	C(16)-C(15)-C(17)	110.2(2)

C(30)-C(35)	1.523(3)	C(10)-C(15)-C(17)	108.7(2)
C(31)-C(32)	1.401(3)	C(14)-C(18)-C(20)	113.3(2)
C(32)-C(33)	1.402(4)	C(14)-C(18)-C(19)	109.4(2)
C(33)-C(34)	1.409(3)	C(20)-C(18)-C(19)	109.6(2)
C(34)-C(38)	1.522(3)	N(2)-C(24)-C(23)	99.0(2)
C(35)-C(36)	1.528(4)	N(2)-C(24)-C(27)	112.0(2)
C(35)-C(37)	1.539(4)	C(23)-C(24)-C(27)	113.9(2)
C(38)-C(39)	1.525(4)	N(2)-C(24)-C(28)	111.1(2)
C(38)-C(40)	1.535(3)	C(23)-C(24)-C(28)	111.3(2)
C(41)-C(42)	1.386(5)	C(27)-C(24)-C(28)	109.3(2)
C(41)-C(46)	1.389(5)	C(24)-C(23)-C(22)	107.3(2)
C(41)-C(47)	1.502(5)	C(25)-C(22)-C(26)	109.0(2)
C(42)-C(43)	1.385(5)	C(25)-C(22)-C(21)	110.5(2)
C(43)-C(44)	1.379(5)	C(26)-C(22)-C(21)	112.1(2)
C(44)-C(45)	1.388(5)	C(25)-C(22)-C(23)	109.1(2)
C(45)-C(46)	1.375(5)	C(26)-C(22)-C(23)	112.5(2)
C(41')-C(46')	1.378(14)	C(21)-C(22)-C(23)	103.5(2)
C(41')-C(42')	1.389(14)	N(2)-C(21)-C(22)	106.7(2)
C(41')-C(47')	1.497(16)	N(2)-C(21)-Co(2)	123.22(18)
C(42')-C(43')	1.385(14)	C(22)-C(21)-Co(2)	129.96(18)
C(43')-C(44')	1.382(14)	C(30)-C(29)-C(34)	122.6(2)
C(44')-C(45')	1.383(14)	C(30)-C(29)-N(2)	121.4(2)
C(45')-C(46')	1.382(14)	C(34)-C(29)-N(2)	115.5(2)
O(1A)-S(1A)	1.440(6)	C(30)-C(29)-Co(1)	72.21(14)
O(2A)-S(1A)	1.426(4)	C(34)-C(29)-Co(1)	74.43(14)
O(3A)-S(1A)	1.426(7)	N(2)-C(29)-Co(1)	119.92(16)
S(1A)-C(1A)	1.828(5)	C(31)-C(30)-C(29)	116.4(2)
C(1A)-F(3A)	1.310(9)	C(31)-C(30)-C(35)	119.4(2)
C(1A)-F(1A)	1.313(6)	C(29)-C(30)-C(35)	124.2(2)
C(1A)-F(2A)	1.326(6)	C(31)-C(30)-Co(1)	73.58(14)
O(1B)-S(1B)	1.452(11)	C(29)-C(30)-Co(1)	67.69(13)
O(2B)-S(1B)	1.448(6)	C(35)-C(30)-Co(1)	130.86(18)
O(3B)-S(1B)	1.449(8)	C(32)-C(31)-C(30)	122.5(2)
S(1B)-C(1B)	1.817(7)	C(32)-C(31)-Co(1)	73.42(14)
C(1B)-F(3B)	1.298(10)	C(30)-C(31)-Co(1)	68.24(14)
C(1B)-F(1B)	1.313(8)	C(31)-C(32)-C(33)	119.6(2)
C(1B)-F(2B)	1.339(8)	C(31)-C(32)-Co(1)	69.59(14)
C(1')-C(2')	1.366(9)	C(33)-C(32)-Co(1)	70.01(14)
C(1')-C(6')	1.387(9)	C(32)-C(33)-C(34)	121.4(2)
C(1')-C(7')	1.499(10)	C(32)-C(33)-Co(1)	73.05(14)
C(2')-C(3')	1.376(8)	C(34)-C(33)-Co(1)	70.06(13)
C(3')-C(4')	1.361(9)	C(33)-C(34)-C(29)	117.3(2)
C(4')-C(5')	1.384(9)	C(33)-C(34)-C(38)	118.8(2)
C(5')-C(6')	1.408(10)	C(29)-C(34)-C(38)	123.8(2)
		C(33)-C(34)-Co(1)	72.20(14)
C(1)-Co(1)-C(29)	166.02(9)	C(29)-C(34)-Co(1)	66.02(13)
C(1)-Co(1)-C(30)	128.97(10)	C(38)-C(34)-Co(1)	136.98(17)
C(29)-Co(1)-C(30)	40.10(10)	C(30)-C(35)-C(36)	112.5(2)
C(1)-Co(1)-C(34)	154.38(9)	C(30)-C(35)-C(37)	109.5(2)
C(29)-Co(1)-C(34)	39.55(9)	C(36)-C(35)-C(37)	109.6(2)
C(30)-Co(1)-C(34)	71.82(9)	C(34)-C(38)-C(39)	114.1(2)
C(1)-Co(1)-C(31)	106.39(10)	C(34)-C(38)-C(40)	108.0(2)

C(29)-Co(1)-C(31)	69.30(9)	C(39)-C(38)-C(40)	110.2(2)
C(30)-Co(1)-C(31)	38.18(9)	C(42)-C(41)-C(46)	118.1(3)
C(34)-Co(1)-C(31)	81.16(9)	C(42)-C(41)-C(47)	121.1(3)
C(1)-Co(1)-C(33)	121.89(10)	C(46)-C(41)-C(47)	120.8(3)
C(29)-Co(1)-C(33)	69.58(9)	C(43)-C(42)-C(41)	120.9(3)
C(30)-Co(1)-C(33)	82.85(9)	C(44)-C(43)-C(42)	120.5(3)
C(34)-Co(1)-C(33)	37.73(9)	C(43)-C(44)-C(45)	118.9(3)
C(31)-Co(1)-C(33)	67.24(9)	C(46)-C(45)-C(44)	120.5(3)
C(1)-Co(1)-C(32)	103.24(10)	C(45)-C(46)-C(41)	121.1(3)
C(29)-Co(1)-C(32)	81.42(9)	C(46')-C(41')-C(42')	119.7(16)
C(30)-Co(1)-C(32)	68.96(9)	C(46')-C(41')-C(47')	121.3(18)
C(34)-Co(1)-C(32)	67.76(9)	C(42')-C(41')-C(47')	119.0(18)
C(31)-Co(1)-C(32)	36.99(9)	C(43')-C(42')-C(41')	120.2(17)
C(33)-Co(1)-C(32)	36.94(9)	C(44')-C(43')-C(42')	119.7(18)
C(1)-Co(1)-Co(2)	91.06(7)	C(43')-C(44')-C(45')	119.9(18)
C(29)-Co(1)-Co(2)	86.03(7)	C(46')-C(45')-C(44')	120.0(18)
C(30)-Co(1)-Co(2)	106.47(7)	C(41')-C(46')-C(45')	120.1(17)
C(34)-Co(1)-Co(2)	96.84(7)	O(3A)-S(1A)-O(2A)	114.0(5)
C(31)-Co(1)-Co(2)	143.61(7)	O(3A)-S(1A)-O(1A)	112.8(5)
C(33)-Co(1)-Co(2)	129.36(7)	O(2A)-S(1A)-O(1A)	118.1(5)
C(32)-Co(1)-Co(2)	164.58(7)	O(3A)-S(1A)-C(1A)	103.7(3)
C(21)-Co(2)-C(9)	165.03(10)	O(2A)-S(1A)-C(1A)	101.8(3)
C(21)-Co(2)-C(14)	128.18(10)	O(1A)-S(1A)-C(1A)	104.0(5)
C(9)-Co(2)-C(14)	39.92(9)	F(3A)-C(1A)-F(1A)	106.9(7)
C(21)-Co(2)-C(10)	155.12(10)	F(3A)-C(1A)-F(2A)	104.9(7)
C(9)-Co(2)-C(10)	39.70(9)	F(1A)-C(1A)-F(2A)	109.8(5)
C(14)-Co(2)-C(10)	71.38(9)	F(3A)-C(1A)-S(1A)	111.9(6)
C(21)-Co(2)-C(13)	106.25(10)	F(1A)-C(1A)-S(1A)	112.8(4)
C(9)-Co(2)-C(13)	68.83(10)	F(2A)-C(1A)-S(1A)	110.3(4)
C(14)-Co(2)-C(13)	37.91(9)	O(2B)-S(1B)-O(3B)	116.9(7)
C(10)-Co(2)-C(13)	80.05(10)	O(2B)-S(1B)-O(1B)	118.0(8)
C(21)-Co(2)-C(11)	122.45(10)	O(3B)-S(1B)-O(1B)	112.9(10)
C(9)-Co(2)-C(11)	69.55(10)	O(2B)-S(1B)-C(1B)	101.7(4)
C(14)-Co(2)-C(11)	82.42(10)	O(3B)-S(1B)-C(1B)	102.4(5)
C(10)-Co(2)-C(11)	37.24(9)	O(1B)-S(1B)-C(1B)	101.2(9)
C(13)-Co(2)-C(11)	66.57(10)	F(3B)-C(1B)-F(1B)	109.3(9)
C(21)-Co(2)-C(12)	103.57(10)	F(3B)-C(1B)-F(2B)	104.7(8)
C(9)-Co(2)-C(12)	81.01(10)	F(1B)-C(1B)-F(2B)	107.2(7)
C(14)-Co(2)-C(12)	68.40(10)	F(3B)-C(1B)-S(1B)	112.6(7)
C(10)-Co(2)-C(12)	66.86(10)	F(1B)-C(1B)-S(1B)	112.4(5)
C(13)-Co(2)-C(12)	36.51(9)	F(2B)-C(1B)-S(1B)	110.2(5)
C(11)-Co(2)-C(12)	36.67(9)	C(2')-C(1')-C(6')	122.0(9)
C(21)-Co(2)-Co(1)	91.25(7)	C(2')-C(1')-C(6')	122.0(9)
C(9)-Co(2)-Co(1)	86.10(7)	C(2')-C(1')-C(7')	119.9(8)
C(14)-Co(2)-Co(1)	106.92(7)	C(6')-C(1')-C(7')	118.1(8)
C(10)-Co(2)-Co(1)	97.24(7)	C(1')-C(2')-C(3')	120.6(8)
C(13)-Co(2)-Co(1)	143.97(7)	C(4')-C(3')-C(2')	119.6(7)
C(11)-Co(2)-Co(1)	129.16(7)	C(3')-C(4')-C(5')	120.1(8)
C(12)-Co(2)-Co(1)	164.09(7)	C(4')-C(5')-C(6')	121.4(9)
C(1)-N(1)-C(9)	116.8(2)	C(1')-C(6')-C(5')	116.3(9)

$(Me_2\text{-cAAC:})_2Co^{I}Cl$ (**3**)

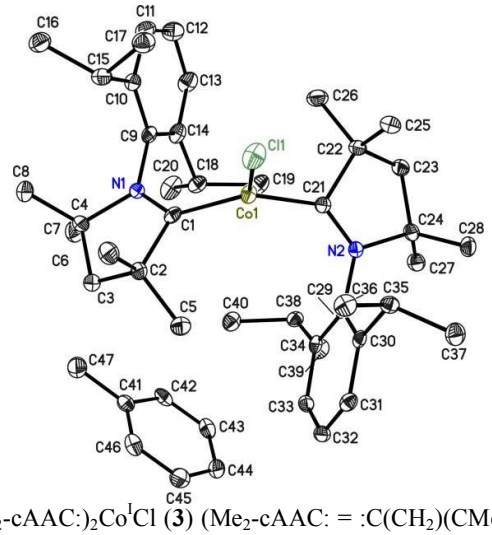


Figure S10. Molecular structure of $(Me_2\text{-cAAC:})_2Co^{I}Cl$ (**3**) (Me_2-cAAC: = :$C(CH_2)(CMe_2)_2$N-2,6-i-$Pr_2C_6H_3$) with one toluene solvent molecules in the crystal. Anisotropic displacement parameters are depicted at the 50% probability level. The data of **3** were collected on a twinned crystal. The twin law is -1 0 0 0 -1 0 0 0.70 0.99. The fractional contribution of the minor component refined to 0.2842.

Table S11. Crystal data and structure refinement for (**3**):

Compound	$(Me_2\text{-cAAC:})_2Co^{I}Cl$ (**3**) (Me_2-cAAC: = :$C(CH_2)(CMe_2)_2$N-2,6-i-$Pr_2C_6H_3$)
Empirical formula	C_{47} H_{70} Cl Co N_2
CCDC no.	969780
Molecular weight	757.43
Crystal size [mm]	0.07 x 0.05 x 0.04
Crystal system	triclinic
Space group	$P1;^{-}$
a [Å]	9.683(2)
b [Å]	11.794(2)
c [Å]	19.932(2)
α [°]	104.34(2)
β [°]	95.28(2)
γ	105.55(2)
V [Å ^{3}]	2093.8(4)
Z	2
Temperature [K]	101(2)
ρ [gcm^{-3}]	1.201
μ [mm^{-1}]	0.507
F (000)	820
θ-area [°]	1.070 to 25.390
Reflections collected	49119
Independent reflections	7693 [R(int) = 0.0368]
Number of restraints	0
Parameters	478
R1 [I>2σ(I)]	0.0392,
wR2 [I>2σ(I)]	0.0688
R1 [all data]	0.0528
wR2 [all data]	0.0736

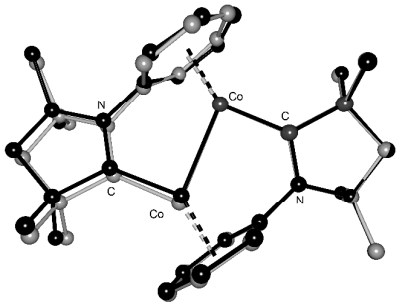
GooF	1.065
Largest diff. peak / hole [e· Å^{-3}]	0.298 and -0.334

Table S12: Bond lengths [Å] and angles [°] for (**3**):

Co(1)-C(1)	1.920(2)	C(5)-C(2)-C(1)	113.43(19)
Co(1)-C(21)	1.932(2)	C(6)-C(2)-C(1)	107.0(2)
Co(1)-Cl(1)	2.2413(9)	C(3)-C(2)-C(1)	104.18(19)
N(1)-C(1)	1.335(3)	C(4)-C(3)-C(2)	106.29(19)
N(1)-C(9)	1.461(3)	C(7)-C(4)-C(8)	106.8(2)
N(1)-C(4)	1.531(3)	C(7)-C(4)-N(1)	112.4(2)
N(2)-C(21)	1.333(3)	C(8)-C(4)-N(1)	112.0(2)
N(2)-C(29)	1.455(3)	C(7)-C(4)-C(3)	112.0(2)
N(2)-C(24)	1.530(3)	C(8)-C(4)-C(3)	113.6(2)
C(1)-C(2)	1.541(3)	N(1)-C(4)-C(3)	100.20(17)
C(2)-C(5)	1.529(3)	C(10)-C(9)-C(14)	120.9(2)
C(2)-C(6)	1.536(4)	C(10)-C(9)-N(1)	119.1(2)
C(2)-C(3)	1.536(3)	C(14)-C(9)-N(1)	119.9(2)
C(3)-C(4)	1.534(3)	C(11)-C(10)-C(9)	118.2(2)
C(4)-C(7)	1.519(4)	C(11)-C(10)-C(15)	117.1(2)
C(4)-C(8)	1.531(3)	C(9)-C(10)-C(15)	124.6(2)
C(9)-C(10)	1.406(3)	C(12)-C(11)-C(10)	121.4(2)
C(9)-C(14)	1.407(3)	C(13)-C(12)-C(11)	119.3(2)
C(10)-C(11)	1.402(4)	C(12)-C(13)-C(14)	122.1(3)
C(10)-C(15)	1.522(3)	C(13)-C(14)-C(9)	118.0(2)
C(11)-C(12)	1.380(4)	C(13)-C(14)-C(18)	118.0(2)
C(12)-C(13)	1.377(4)	C(9)-C(14)-C(18)	123.9(2)
C(13)-C(14)	1.391(4)	C(10)-C(15)-C(17)	110.8(2)
C(14)-C(18)	1.521(4)	C(10)-C(15)-C(16)	111.8(2)
C(15)-C(17)	1.536(3)	C(17)-C(15)-C(16)	109.1(2)
C(15)-C(16)	1.537(3)	C(14)-C(18)-C(19)	111.9(2)
C(18)-C(19)	1.531(3)	C(14)-C(18)-C(20)	111.9(2)
C(18)-C(20)	1.534(4)	C(19)-C(18)-C(20)	109.1(2)
C(21)-C(22)	1.539(3)	N(2)-C(21)-C(22)	106.64(19)
C(22)-C(23)	1.533(3)	N(2)-C(21)-Co(1)	137.39(18)
C(22)-C(26)	1.533(3)	C(22)-C(21)-Co(1)	115.54(16)
C(22)-C(25)	1.540(3)	C(23)-C(22)-C(26)	113.4(2)
C(23)-C(24)	1.531(3)	C(23)-C(22)-C(21)	104.06(19)
C(24)-C(27)	1.518(3)	C(26)-C(22)-C(21)	112.83(19)
C(24)-C(28)	1.536(3)	C(23)-C(22)-C(25)	111.91(19)
C(29)-C(34)	1.412(3)	C(26)-C(22)-C(25)	107.0(2)
C(29)-C(30)	1.416(3)	C(21)-C(22)-C(25)	107.63(19)
C(30)-C(31)	1.391(3)	C(24)-C(23)-C(22)	106.27(19)
C(30)-C(35)	1.522(3)	C(27)-C(24)-N(2)	113.0(2)
C(31)-C(32)	1.377(3)	C(27)-C(24)-C(23)	111.7(2)
C(32)-C(33)	1.382(3)	N(2)-C(24)-C(23)	100.00(18)
C(33)-C(34)	1.395(3)	C(27)-C(24)-C(28)	107.5(2)
C(34)-C(38)	1.516(3)	N(2)-C(24)-C(28)	110.89(19)
C(35)-C(37)	1.532(3)	C(23)-C(24)-C(28)	113.8(2)
C(35)-C(36)	1.534(3)	C(34)-C(29)-C(30)	120.5(2)
C(38)-C(40)	1.531(3)	C(34)-C(29)-N(2)	120.2(2)
C(38)-C(39)	1.535(3)	C(30)-C(29)-N(2)	119.4(2)

C(41)-C(42)	1.388(4)	C(31)-C(30)-C(29)	118.1(2)
C(41)-C(46)	1.402(4)	C(31)-C(30)-C(35)	117.4(2)
C(41)-C(47)	1.508(4)	C(29)-C(30)-C(35)	124.5(2)
C(42)-C(43)	1.380(4)	C(32)-C(31)-C(30)	122.1(2)
C(43)-C(44)	1.385(4)	C(31)-C(32)-C(33)	119.3(2)
C(44)-C(45)	1.382(4)	C(32)-C(33)-C(34)	121.6(2)
C(45)-C(46)	1.390(4)	C(33)-C(34)-C(29)	118.4(2)
		C(33)-C(34)-C(38)	117.4(2)
C(1)-Co(1)-C(21)	122.33(10)	C(29)-C(34)-C(38)	124.1(2)
C(1)-Co(1)-Cl(1)	119.97(7)	C(30)-C(35)-C(37)	111.5(2)
C(21)-Co(1)-Cl(1)	117.66(7)	C(30)-C(35)-C(36)	110.95(19)
C(1)-N(1)-C(9)	121.95(19)	C(37)-C(35)-C(36)	108.6(2)
C(1)-N(1)-C(4)	116.30(19)	C(34)-C(38)-C(40)	110.6(2)
C(9)-N(1)-C(4)	121.55(18)	C(34)-C(38)-C(39)	112.0(2)
C(21)-N(2)-C(29)	122.98(19)	C(40)-C(38)-C(39)	108.9(2)
C(21)-N(2)-C(24)	116.15(19)	C(42)-C(41)-C(46)	117.9(2)
C(29)-N(2)-C(24)	120.52(18)	C(42)-C(41)-C(47)	120.9(2)
N(1)-C(1)-C(2)	106.52(19)	C(46)-C(41)-C(47)	121.3(2)
N(1)-C(1)-Co(1)	136.66(18)	C(43)-C(42)-C(41)	121.4(2)
C(2)-C(1)-Co(1)	116.34(16)	C(42)-C(43)-C(44)	120.4(3)
C(5)-C(2)-C(6)	107.9(2)	C(45)-C(44)-C(43)	119.2(2)
C(5)-C(2)-C(3)	112.4(2)	C(44)-C(45)-C(46)	120.4(2)
C(6)-C(2)-C(3)	111.90(19)	C(45)-C(46)-C(41)	120.6(2)

(S7) A superposition image of **2** and **2**$^{+}$**OTf**$^{-}$



(S8). Theoretical investigation on 2 and 2^{+}**OTf**$^{-}$

Geometry optimisations without symmetry constraints were carried out with the Gaussian 09 optimiser[S10] in conjunction with Turbomole 6.4[S11] energies and gradients at the B3LYP[S12] level of theory using def2-SVP basis sets[S13] and the resolution-of-identity (RI) approximation.[S14] Stationary points were characterized by calculating the Hessian matrix analytically. The AIM analyses were carried out with the program package AIMAll[S15] using a B3LYP/def2-SVP wave function created with Turbomole. The EDA-NOCV calculation was carried out at BP86[S16]/TZVP^{+} [S17] using the program package ADF.[S18]

Figure S11. Shape of the HOMO-1 of 2.

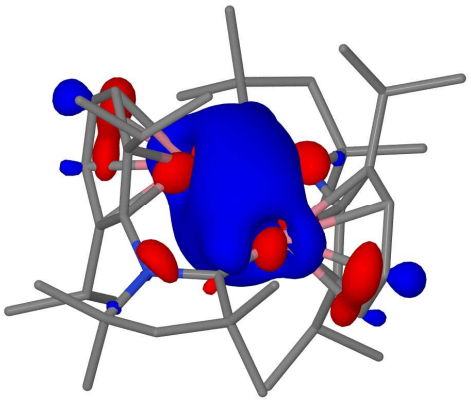


Table S13. EDA-NOVC calculation of 2 using the fragments which are shown in Figure 3. Energy values in kcal/mol.

ΔE_{int}	-195.4
ΔE_{Pauli}	429.1
ΔE_{elstat}	-395.4 (63.6%)
ΔE_{orb}	-229.0 (26.7%)
$\Delta E_{orb}(1)$	-71.5 (31.2%)
$\Delta E_{orb}(2)$	-42.9 (18.7%)
$\Delta E_{orb}(3)$	-39.3 (17.2%)
$\Delta E_{orb}(4)$	-47.7 (20.8%)
ΔE_{rest}	-27.7 (12.1%)

Table S14: Calculated coordinates [Å] and energies [hartree] of 2 and 2^{+}

Compound **2**

Energy =-4433.726183189 hartrees

Co	1.9618573	7.0549720	9.6286094
Co	3.1287601	8.7625131	11.1808897
N	2.5097394	9.5105734	8.2644743
N	3.5021804	6.0789834	12.1030467
C	2.4942311	10.2727370	6.9639302
C	1.2181172	9.6900891	6.3335219
H	1.2721834	9.6667874	5.2341365
H	0.3610522	10.3306613	6.5971866
C	1.0210910	8.2769978	6.9522873

C	1.8245590	8.3310886	8.2915695
C	3.7234150	9.9549298	6.0829684
H	3.8970504	8.8734607	5.9997355
H	4.6381424	10.4218791	6.4671138
H	3.5555313	10.3503494	5.0680941
C	2.4196554	11.7908312	7.1612212
H	2.4219265	12.2872444	6.1776068
H	3.2846458	12.1687643	7.7277343
H	1.5062998	12.0970197	7.6867586
C	1.5197361	7.1776544	5.9894933
H	1.2953899	6.1754047	6.3746667
H	2.6048611	7.2298941	5.8182453
H	1.0176135	7.2769737	5.0120201
C	-0.4819712	8.0575905	7.2205871
H	-1.0496074	8.1392687	6.2766479
H	-0.8771546	8.8107471	7.9189084
H	-0.6818795	7.0701249	7.6547485
C	2.9829493	10.0124886	9.5240723
C	1.9770747	10.5211713	10.4372864
C	2.3579177	10.8166587	11.7596456
H	1.6139646	11.1784891	12.4727955
C	3.7005729	10.6849966	12.1619190
H	3.9847026	10.9135953	13.1905159
C	4.6821710	10.2591249	11.2486640
H	5.7155256	10.1741463	11.5866944
C	4.3653148	9.9114124	9.9118920
C	0.5463415	10.8538718	10.0083493
H	0.4601974	10.6151157	8.9414420
C	-0.5293369	10.0329283	10.7289659
H	-1.5309441	10.2959072	10.3479427
H	-0.5293643	10.2227571	11.8148881
H	-0.3562320	8.9612139	10.5679040
C	0.2711954	12.3635029	10.1683995
H	0.2293011	12.6543411	11.2308417
H	-0.7000346	12.6282001	9.7172718
H	1.0482802	12.9802086	9.6904485
C	5.5040323	9.5348647	8.9734536
H	5.0545503	9.0404132	8.1023849
C	6.2533618	10.7953660	8.4947408
H	7.0106908	10.5407530	7.7341642
H	6.7755287	11.2793890	9.3370271
H	5.5749533	11.5456178	8.0611368
C	6.5019649	8.5438315	9.5946156
H	5.9791238	7.6805963	10.0279056
H	7.1040514	9.0109221	10.3912310
H	7.2071317	8.1826429	8.8285161
C	4.1675259	5.1556850	13.0917621
C	4.1589256	6.0561697	14.3384552
H	5.0141027	5.8542270	15.0018542
H	3.2470173	5.8533147	14.9230288
C	4.1325389	7.5245983	13.8270050
C	3.5571374	7.4141178	12.3782932
C	3.3978472	3.8466793	13.2995592
H	2.3890196	4.0168736	13.6962784
H	3.9394140	3.2154891	14.0222105
H	3.3063071	3.2770345	12.3619824
C	5.6182297	4.8095355	12.6870381
H	5.6553800	4.1062546	11.8465673
H	6.1284020	4.3299371	13.5379769
H	6.1904252	5.7060287	12.4119559
C	5.5429168	8.1513738	13.8733489
H	6.2451048	7.6567685	13.1864220

H	5.9560584	8.0735822	14.8934253
H	5.5176700	9.2153040	13.6079177
C	3.1932097	8.3485660	14.7314416
H	3.1395041	9.3988398	14.4191232
H	3.5523835	8.3184184	15.7754216
H	2.1687610	7.9468049	14.7147728
C	2.6337280	5.6747104	11.0331476
C	3.1425966	5.3073242	9.7379675
C	2.1898814	5.1173950	8.7061347
H	2.5384120	4.8603549	7.7053188
C	0.8096198	5.2763109	8.9260156
H	0.1137817	5.1498328	8.0949081
C	0.3215383	5.5984060	10.2065667
H	-0.7551945	5.6877380	10.3668877
C	1.2083814	5.7684376	11.2862355
C	4.6087590	5.0382603	9.4262591
H	5.1994554	5.4974887	10.2297544
C	5.0747929	5.6666379	8.1027136
H	4.6333140	5.1601702	7.2287877
H	6.1692815	5.5813731	8.0050031
H	4.7979198	6.7283325	8.0536942
C	4.8909484	3.5217895	9.4090308
H	4.3645209	3.0392663	8.5685411
H	4.5538209	3.0232945	10.3304191
H	5.9687755	3.3210841	9.2876691
C	0.6142966	5.9372426	12.6862813
H	1.4510575	5.9905422	13.3931993
C	-0.1968101	7.2250623	12.8707654
H	-1.0761976	7.2534012	12.2064830
H	0.4288857	8.0990969	12.6497513
H	-0.5645379	7.3002739	13.9083502
C	-0.2342079	4.7056583	13.0654358
H	-1.1579939	4.6537739	12.4662836
H	-0.5332863	4.7554493	14.1260546
H	0.3110367	3.7618169	12.9091738

Compound **2**$^{+}$

scf done: -4433.612123874 hartrees

Co	1.957433	6.995651	9.565514
Co	3.009597	8.736236	11.178025
N	2.486035	9.553819	8.270286
N	3.490896	6.033008	12.142716
C	2.465756	10.322463	6.958975
C	1.192468	9.727899	6.333040
H	1.243414	9.713872	5.234437
H	0.328167	10.355173	6.604102
C	1.015753	8.308129	6.939487
C	1.803819	8.369169	8.274244
C	3.700617	10.011590	6.087743
H	3.888881	8.932644	6.007046
H	4.608214	10.494875	6.468120
H	3.529735	10.399701	5.071701
C	2.378302	11.838283	7.160923
H	2.369724	12.331708	6.176927
H	3.245384	12.230056	7.715311
H	1.463739	12.139625	7.687163
C	1.547307	7.215616	5.985212
H	1.362775	6.211161	6.386540

H	2.627115	7.304526	5.799301
H	1.030931	7.284740	5.014017
C	-0.482071	8.047657	7.203366
H	-1.047896	8.123082	6.259559
H	-0.902024	8.782269	7.907367
H	-0.656804	7.047710	7.622258
C	2.960578	10.083831	9.518360
C	1.980892	10.623401	10.427820
C	2.394952	11.004058	11.726736
H	1.652428	11.379251	12.433262
C	3.742174	10.964039	12.101663
H	4.045082	11.293474	13.097577
C	4.700505	10.501915	11.191677
H	5.749708	10.482461	11.488370
C	4.348943	10.037280	9.904469
C	0.531942	10.908671	10.028099
H	0.431746	10.649270	8.967801
C	-0.500799	10.068177	10.789062
H	-1.515967	10.310781	10.436253
H	-0.475106	10.266543	11.873095
H	-0.321546	8.997957	10.625555
C	0.223183	12.413159	10.174928
H	0.176455	12.718552	11.232574
H	-0.757755	12.639442	9.727735
H	0.975740	13.045558	9.679820
C	5.475883	9.588281	8.980904
H	5.011901	9.085445	8.122585
C	6.263302	10.813077	8.469696
H	6.996684	10.508403	7.706293
H	6.818757	11.294260	9.291141
H	5.609405	11.578279	8.025996
C	6.440403	8.587904	9.640273
H	5.904676	7.727985	10.066765
H	7.032263	9.052881	10.444746
H	7.155507	8.210004	8.893434
C	4.137257	5.077517	13.156064
C	4.184163	6.006474	14.382537
H	5.051352	5.792301	15.023606
H	3.283822	5.847598	14.997025
C	4.190054	7.462159	13.838822
C	3.574520	7.323378	12.436964
C	3.305837	3.813249	13.382206
H	2.313484	4.030261	13.795836
H	3.830544	3.168080	14.103403
H	3.180425	3.235885	12.453548
C	5.558226	4.667779	12.723957
H	5.550624	3.953522	11.893575
H	6.049973	4.171434	13.574356
H	6.175253	5.530496	12.438857
C	5.611881	8.063782	13.785669
H	6.289945	7.495084	13.133499
H	6.045803	8.072413	14.798063
H	5.589844	9.099653	13.422730
C	3.301188	8.360989	14.723021
H	3.293623	9.400793	14.369077
H	3.682808	8.355716	15.757172
H	2.259450	8.005279	14.747580
C	2.638869	5.623630	11.036343
C	3.173560	5.221594	9.762875
C	2.242153	4.986117	8.720871
H	2.611251	4.684419	7.740445
C	0.858909	5.145833	8.910702

H	0.174816	4.990221	8.075456
C	0.357778	5.539933	10.162814
H	-0.719254	5.660312	10.293014
C	1.216276	5.735658	11.268226
C	4.648520	4.969069	9.468945
H	5.230734	5.418342	10.284622
C	5.125592	5.616576	8.157514
H	4.694184	5.121240	7.273483
H	6.219984	5.529123	8.071202
H	4.854960	6.680402	8.111137
C	4.934349	3.453020	9.434399
H	4.441584	2.984315	8.567180
H	4.568490	2.933621	10.332823
H	6.015763	3.261869	9.345664
C	0.584179	5.898256	12.654500
H	1.397655	5.946036	13.389305
C	-0.239757	7.179221	12.829586
H	-1.076746	7.231686	12.115372
H	0.383352	8.072460	12.687540
H	-0.670253	7.215541	13.843322
C	-0.271601	4.659329	12.995094
H	-1.184861	4.619945	12.380284
H	-0.588076	4.693743	14.049917
H	0.275263	3.718074	12.834021

(S9). Mass spectrum of 2

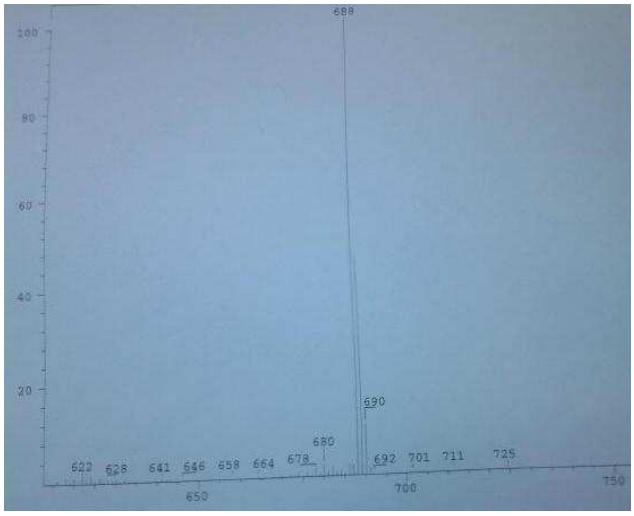


Figure S12. Mass spectrum (Electron Ionization) of compound 2.

(S10). References

(S1) (a) Lavallo, V.; Canac, Y.; Präsang, C.; Donnadieu, B.; Bertrand, G. *Angew. Chem. Int. Ed*. **2005**, *44*, 5705–5709; *Angew. Chem.* **2005**, *117*, 5851-5855. (b) Matsubara, K.; Sueyasu, T.; Esaki, M.; Kumamoto, A.; Nagao, S.; Yamamoto, H.; Koga, Y.; Kawata, S.; Matsumoto, T. *Eur. J. Inorg. Chem*. **2012**, 3079–3086.

(S2) Simulation of the experimental magnetic data was performed with the *julX* program (E. Bill: Max-Planck Institute for Chemical Energy Conversion, Mülheim/Ruhr, Germany).

(S3) (a) D. Stalke, *Chem. Soc. Rev.* **1998**, *27*, 171-178. (b) T. Kottke, D. Stalke, *J. Appl. Crystallogr.* **1993**, *26*, 615-619.

(S4) Schulz, T.; Meindl, K.; Leusser, D.; Stern, D.; Graf, J.; Michaelsen, C.; Ruf, M.; Sheldrick, G. M.; Stalke, D. *J. Appl. Crystallogr*. **2009**, *42*, 885-891.

(S5) SAINT, Bruker AXS Inc., Madison, Wisconsin (USA) 2000.

(S6) Sheldrick, G. M. *SADABS*, Universität Göttingen, Germany, 2000.

(S7) Sheldrick, G. M. *TWINABS 2008/2*, Göttingen, Germany 2008.

(S8) (a) Sheldrick, G. M. *Acta Crystallogr*., Sect. A **1990**, *46*, 467−473. (b) Sheldrick, G. M. *Acta Crystallogr*., Sect. A **2008**, *64*, 112−122. (c) Müller, P.; Herbst-Irmer, R.; Spek, A. L.; Schneider, T. R.; Sawaya, M. R. In *Crystal Structure Refinement−A Crystallographer's Guide to SHELXL, IUCr Texts on Crystallography*; P. Müller, Ed.; Oxford University Press: Oxford, U.K., 2006; Vol. 8. (d) Hübschle, C. B.; Sheldrick, G. M.; Dittrich, B. *J. Appl. Crystallogr*. **2011**, *44*, 1281−1284

(S9) Parsons, S.; Flack, H. D.; Wagner, T. *Acta Cryst.* **2013**, *B69*, 249-259.

(S10) Gaussian 09, Revision C.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A.; Peralta, Jr. J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2010.

(S11) TURBOMOLE V6.4 2012, a development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989-2007, TURBOMOLE GmbH, since 2007; available from www.turbomole.com.

(S12) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648-5652. (b) Lee, C.; Yang, W.; Parr, R.*Phys. Rev. B* **1988**, *37*, 785-791.

(S13) Schaefer, A.; Horn, H.; Ahlrichs, R. *J. Chem. Phys* **1992**, *97*, 2571-2578.

(S14 Eichhorn, K.; Treutler, O.; Ohm, H.; Häser, M.; Ahlrichs, R. *Chem. Phys. Lett.* **1995**, *242*, 652-661.

(S15) AIMAll (Version 12.06.03), Todd A. Keith, TK Gristmill Software, Overland Park KS, USA, 2012 (aim.tkgristmill.com).

(S16) (a) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098-3114. (b) Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822-8831.

(S17) Lenthe, E. v.; Baerends, E. J. *J. Comput. Chem.* **2003**, *24*, 1142-1149.

(S18) ADF2009.01, SCM, Theoretical Chemistry; Vrije Universiteit, Amsterdam, http://www.scm.com.

(S19) (a) Wang, Y.; Xie, Y.; Wei, P.; King, R. B.; Schaefer III, H. F.; Schleyer, P. v. R.; Robinson, G. H. *Science* **2008**, *321*, 1069 –1071. (b) Sidiropoulos, A.; Jones, C.; Stasch, A.; Klein, S.; Frenking, G. *Angew. Chem. Int. Ed.* **2009**, *48*, 9701-9704; *Angew. Chem*. **2009**, *121,* 9881 – 9884. (c) Jones, C.; Sidiropoulos, A.; Holzmann, N.; Frenking, G.; Stasch, A. *J. Chem. Soc. Chem. Commun.* **2012**, *48*, 9855-9857. (d) Wang, Y.; Xie, Y.; Wie, P.; King, R. B.; Schaefer, III, H. F.; Schleyer, P. v. R.; Robinson, G. H. *J. Am. Chem. Soc.* **2008,** *130,*14970-14971. (e) Back, O.; Kuchenbeiser, G.; Donnadieu, B.; Bertrand, G. *Angew. Chem. Int. Ed*. **2009**, *48*, 5530-5533; *Angew.Chem.* **2009**, *121,* 5638 – 5641. (f) Abraham, M. Y.; Wang, Y.; Xie, Y.; Wei, P.; Schaefer, III, H. F.; Schleyer, P. v. R.; Robinson, G. H. *Chem. Eur. J.* **2010**, *16*, 432-435. (g) Brauschweig, H.; Dewhurst, R. D.; Hammond, K.; Mies, J.; Radacki, K.; Vargas, A. *Science* **2012**, *336*, 1420 – 1422.

(S20) For mono-radical-$SiCl_3$, $PN^{\cdot+}$, $P_2^{\cdot+}$, $RP^{\cdot+}$, H-$B^{\cdot+}$, ketene with biradical character, bi-radical $SiCl_2$, bi-radicaloid Si, and $CO^{\cdot+}$ See (a) Mondal, K. C.; Roesky, H. W.; Stückl, A. C.; Ihret, F.; Kaim, W.; Dittrich, B.; Maity, B.; Koley, D.

Angew. Chem. Int. Ed. **2013**, *52*, 11804 – 11807; *Angew.Chem.* **2013**, *125,* 12020 – 12023. (b) Kinjo, R.; Donnadieu, B.; Bertrand, G. *Angew. Chem. Int. Ed.* **2010**, *49*, 5930-5933; *Angew. Chem.* **2010**, *122*, 6066-6069 (c) Back, O.; Donnadieu, B.; Parameswaran, P.; Frenking, G.; Bertrand, G. *Nat. Chem.* **2010**, *2*, 369-373. (d) Back, O.; Celik, M. A.; Frenking, G.; Melaimi, M.; Donnadieu, B.; Bertrand, G. *J. Am. Chem. Soc*. **2010**, *132*, 10262-10263. e) Kinjo, R.; Donnadieu, B.; Celik, M. A.; Frenking, G.; Bertrand, G. *Science* **2011**, *333*, 610-613. (f) Lavallo, V.; Canac, Y.; Donnadieu, B.; Schoeller, W. W.; Bertrand, G. *Angew. Chem. Int. Ed.* **2006**, *45*, 3488-3491; *Angew. Chem.* **2006**, *118*, 3568-3571. (g) Mondal, K. C.; Roesky, H. W.; Schwarzer, M. C.; Frenking, G.; Tkach, I.; Wolf, H.; Kratzert, D.; Herbst-Irmer, R.; Niepötter, B.; Stalke, D. *Angew. Chem. Int. Ed.* **2013**, *52*, 1801-1805; *Angew.Chem.* **2013**, *125,* 1845 – 1850. (h) Mondal, K. C.; Roesky, H. W.; Schwarzer, M. C.; Frenking, G.; Niepötter, B.; Wolf, H.; Herbst-Irmer, R.; Stalke, D. *Angew. Chem. Int. Ed.* **2013**, *52*, 2963-2967; *Angew.Chem.* **2013**, *125,* 3036-3040. (i) Martin, D.; Moore, C. E.; Rheingold, A. L.; Bertrand, G. *Angew. Chem., Int. Ed.* **201**3, *52*, 7014-7017; *Angew. Chem.* **2013**, *125*, 7152-7155.