Supplementary Information

A dicationic distibine stabilized by intramolecular π-π interaction and second-sphere coordination

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This document includes:

1. Materials and Methods

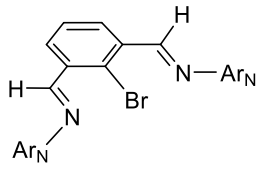
General Remarks

Unless otherwise noted, all syntheses were carried out in a nitrogen-filled glove box or using standard Schlenk techniques under an inert atmosphere of anhydrous nitrogen. Solvents were dried by refluxing under nitrogen over Na (hexane, THF, toluene) or CaH_2 (MeCN) and stored under nitrogen atmosphere over 4 Å molecular sieves. Dry deuterated benzene (C_6D_6), deuterated chloroform ($CDCl_3$), and deuterated acetonitrile (CD_3CN) purchased from J&K Scientific Ltd. were degassed and stored over molecular sieves (4Å) for at least two days prior to use. Commercial reagents were used without further purification unless indicated otherwise. NMR spectra were obtained on Bruker Avance II 400 at room temperature. Variable temperature NMR spectra were obtained on Bruker Avance II 600 MHz NMR spectrometer. ^{1}H and $^{13}C\{^{1}H\}$ NMR chemical shifts (δ/ppm) are referenced to the residual solvent resonance of the deuterated solvent. ^{19}F chemical shifts (δ/ppm) are referenced to $CFCl_3$. ^{31}P NMR spectra were referenced externally to 85% aqueous H_3PO_4 (δ = 0 ppm). Mass spectroscopy (MS) studies were performed on an LCMS-IT-TOF (ESI). EPR was recorded on a Bruker EMXplus spectrometer.

2. Syntheses and Spectroscopic Data

2.1 Syntheses

Synthesis of **L**Br (**L** = 2-Br-1,3-(Ar_NN=CH)$_2$-C_6H_3, Ar_N = o-$Me_2NC_6H_4$)



A catalytic amount of TsOH, 4 Å molecular sieves, and a THF solution (30 mL) of 2-bromobenzene-1,3-dialdehyde (572.0 mg, 2.69 mmol) were combined in a Schlenk flask in a glove box. Subsequently, 2-Amino-*N,N*-dimethylaniline (0.71 mL, 5.42 mmol) was added dropwise to the mixture. The color of the solution changed from brown to yellow. The flask was sealed and placed into an oil bath heated at 55 °C, and the solution was stirred at 55 °C overnight. All volatiles were removed, and the residue was extracted with *n*-hexane (30 mL). After filtration, the resulting solution was concentrated and stored at 4 °C overnight. The precipitated solid was isolated by filtration and dried under vacuum to give **L**Br as a yellow powder (613.8 mg, yield 51%). **^{1}H NMR** (400 MHz, $CDCl_3$, 25 °C): δ (ppm) 8.99 (s, 2H, NC*H*), 8.41 (d, $^3J_{H\text{-}H}$ = 7.6 Hz, 2H, BrAr-*H*), 7.51 (t, $^3J_{H\text{-}H}$ = 7.6 Hz, 1H, BrAr-*H*), 7.26-7.17 (m, 2H, NAr-*H*), 7.05-6.96 (m, 6H, NAr-*H*), 2.90 (s, 12H, NCH_3). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$, 25 °C): δ (ppm) 157.47 (s), 147.10 (s), 144.37 (s), 135.93 (s), 131.87 (s), 128.83 (s),127.82 (s), 127.33 (s), 121.91 (s), 119.82 (s), 117.79 (s) 44.09 (s). **HRMS** (ESI) [M+H] $C_{24}H_{26}N_4Br^+$ calc. 449.1336 m/z; found 449.1335 m/z.

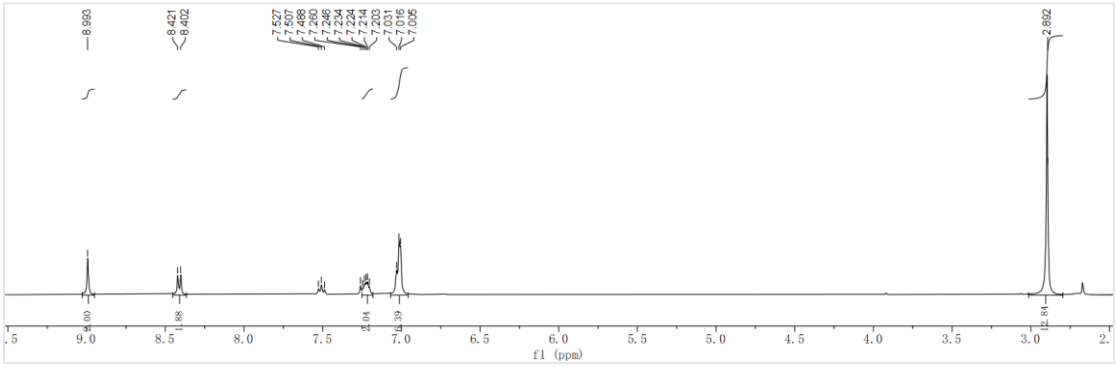


Fig. S1 ^{1}H NMR spectrum of **L**Br (400 MHz, $CDCl_3$).

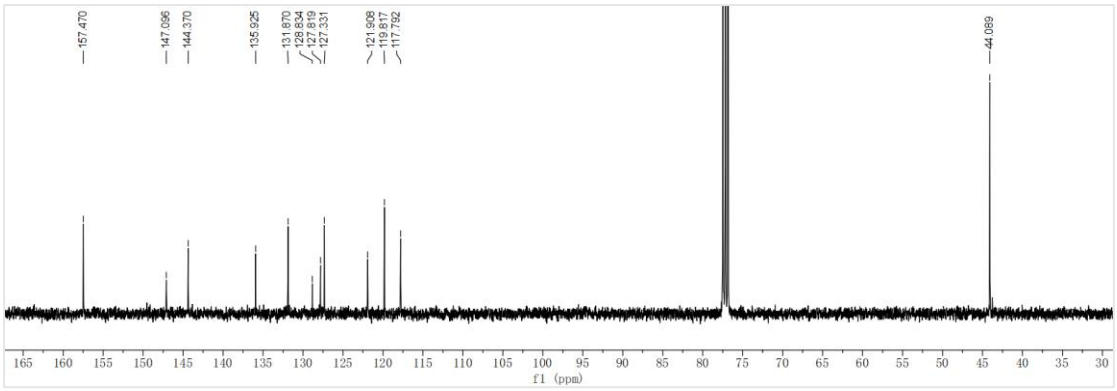
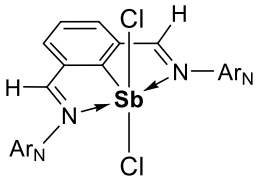


Fig. S2 $^{13}C\{^{1}H\}$ NMR spectrum of **L**Br (100 MHz, $CDCl_3$).

Synthesis of **L**$SbCl_2$



A solution of *n*BuLi (1.60 M in *n*-hexane, 0.50 mL, 0.80 mmol) was added dropwise to a THF solution of **L**Br (326.4 mg, 0.73 mmol) at -110 °C. The color of the solution gradually changed from yellow to purple. The mixture was stirred at -110 °C for 2 hours. Then, a THF solution (10 mL) of $SbCl_3$ (191.1 mg, 0.84 mmol) was added dropwise at -110°C. As a result, the color of the solution turned from yellow to brown. The reaction mixture was then allowed to warm up to room temperature. After stirring at room temperature for an additional 4 hours, the volatiles in the reaction solution were removed under vacuum. Subsequently, the residue was extracted by 20 mL of DCM, which was filtered. The resulting filtrate was concentrated to a final volume of approximately 10 mL. Upon stirring, 20 mL of toluene was added, leading to the precipitation of a brown solid. After filtration, the precipitate was washed with toluene and *n*-hexane and dried under vacuum to give **L**$SbCl_2$ as a brown powder (228.6 mg, yield 56%). **^{1}H NMR** (400 MHz, $CDCl_3$, 25 ºC): δ (ppm) 9.18 (s, 2H, NC*H*), 7.95 (d, $^{3}J_{H\text{-}H}$ = 7.6 Hz, 2H, SbAr-*H*), 7.64 (t, $^{3}J_{H\text{-}H}$ = 7.6 Hz, 1H, SbAr-*H*), 7.43-7.31(m, 6H, NAr-*H*), 7.18 (t, $^{3}J_{H\text{-}H}$ = 7.6 Hz, 2H, NAr-*H*), 2.77 (s, 12H, NCH_3). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$, 25 ºC): δ (ppm) 162.52 (s), 148.98 (s), 139.36 (s), 138.32 (s), 134.58 (s), 129.62 (s), 124.99 (s), 121.83 (s), 121.37 (s), 45.90 (s),44.71 (s). **HRMS** (ESI) [M+H] $C_{24}H_{26}N_4Cl_2Sb^+$ calc. 561.0568 m/z; found 561.0467 m/z.

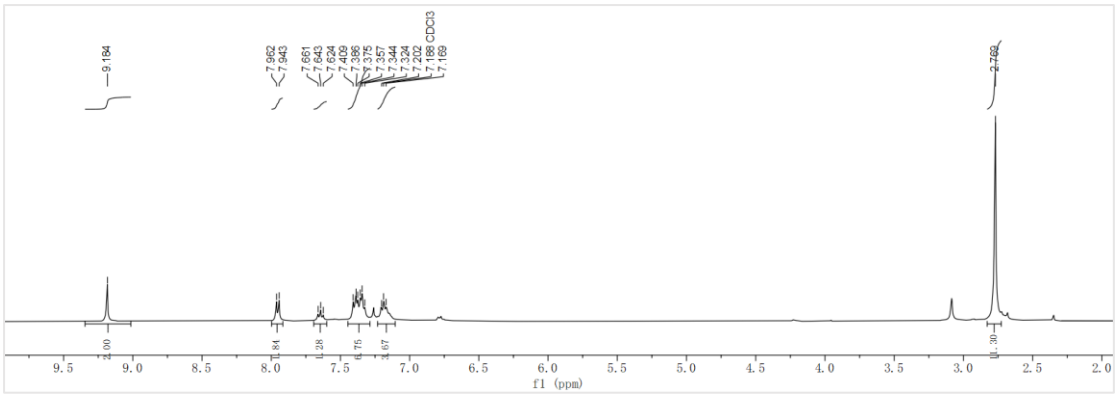


Fig. S3 ^{1}H NMR spectrum of **L**$SbCl_2$ (400 MHz, $CDCl_3$).

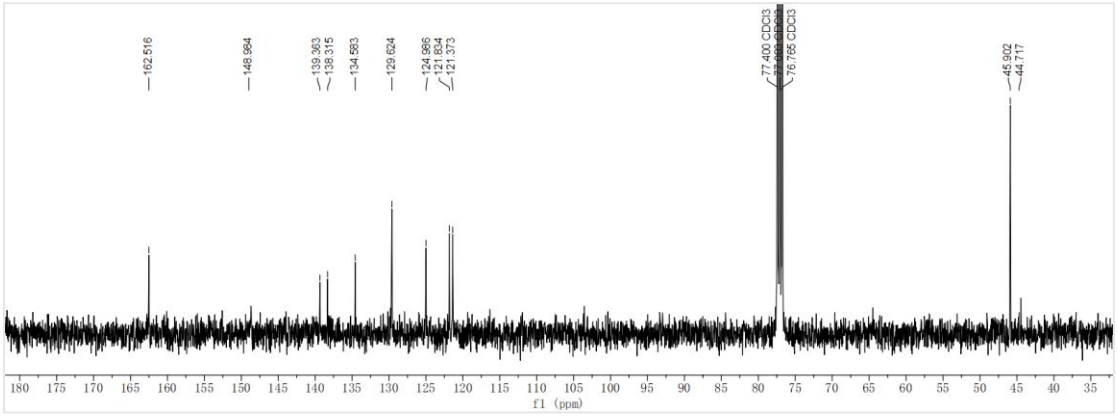
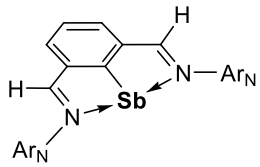


Fig. S4 $^{13}C\{^{1}H\}$ NMR spectrum of **L**$SbCl_2$ (100 MHz, $CDCl_3$).

Synthesis of **1**



L$SbCl_2$ (243.3 mg, 0.43 mmol) was dissolved in 8 mL of THF. Then, a THF solution (10 mL) of cobaltocene (161.7 mg, 0.86 mmol) was added dropwise. The color of the solution gradually turned from brown to green. After stirring at room temperature for an additional 4 hours, the volatiles in the reaction solution were removed under vacuum. The residue was extracted with 30 mL of *n*-hexane. After filtration, all volatiles in the filtrate were removed under vacuum to give **1** as a dark-green powder (126.4 mg, yield 59%). Green crystals of **1** were obtained by storing a saturated *n*-hexane solution at -35 °C. **^{1}H NMR** (400 MHz, C_6D_6, 25 °C): δ (ppm) 9.07 (s, 2H, NC*H*), 7.76 (d, $^{3}J_{H\text{-}H}$ = 7.5 Hz, 2H, SbAr-*H*), 7.19-7.17 (m, 1H, SbAr-*H*), 7.11 (d, $^{3}J_{H\text{-}H}$ = 7.8 Hz, 2H, NAr-*H*), 7.04 (t, $^{3}J_{H\text{-}H}$ = 7.7 Hz, 2H, NAr-*H*), 6.92-6.84 (m, 4H, NAr-*H*), 2.41 (s, 12H, NCH_3). **$^{13}C\{^{1}H\}$ NMR**

(100 MHz, C_6D_6, 25 ºC): δ (ppm) 175.67 (s), 156.40 (s), 147.05 (s), 142.88 (s), 137.64 (s), 133.24 (s), 126.85 (s), 124.75 (s), 122.71(s), 120.68 (s), 119.26 (s), 43.55 (s). **HRMS** (ESI) [M+H] $C_{24}H_{26}N_4Sb^+$ calc. 491.1191 m/z; found 491.1189 m/z.

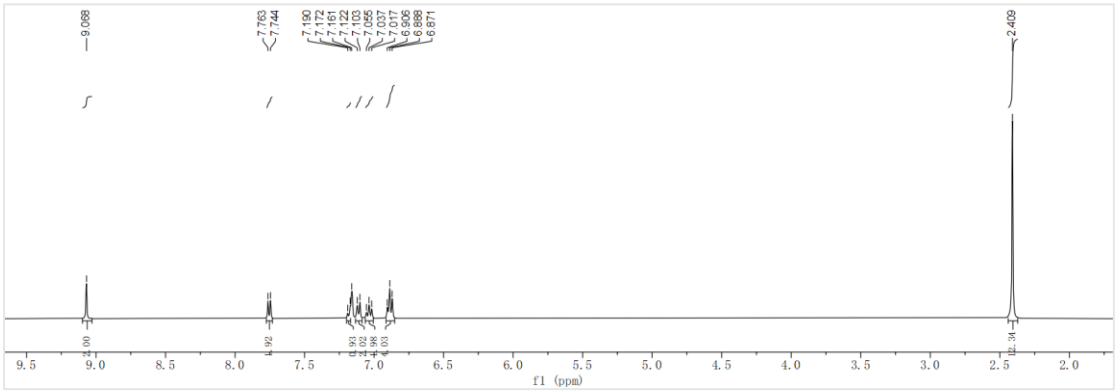


Fig. S5 ^{1}H NMR spectrum of **1** (400 MHz, C_6D_6).

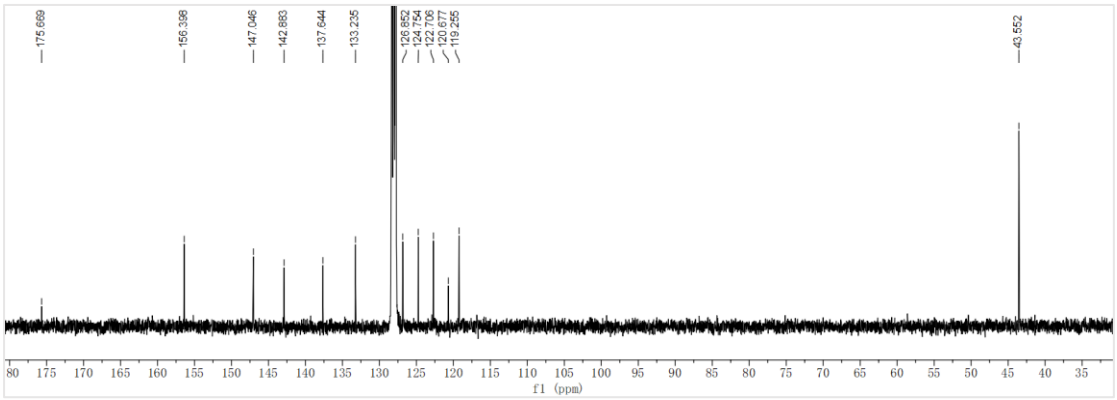
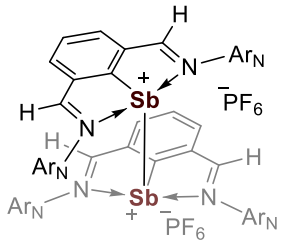


Fig. S6 $^{13}C\{^1H\}$ NMR spectrum of **1** (100 MHz, C_6D_6).

Synthesis of **2**



1 (98.7mg, 0.20 mmol) was dissolved in 5 mL of MeCN, then a MeCN (3 mL) solution of $Cu(MeCN)_4PF_6$ (74.9 mg, 0.20 mmol) was added dropwise at room temperature. The color of the solution gradually changed from green to red, accompanied by the precipitation of a red solid. After 2 hours, all volatiles were removed under vacuum. The residue was extracted with 10 mL of THF. The resulting solution was filtered and concentrated to a final volume of approximately 2 mL. Upon stirring, 8 mL of toluene was added, leading to the precipitation of a red solid. After filtration, the precipitate was washed with toluene (5 mL × 3) and dried under

vacuum to give **2** as a red powder (94.6 mg, yield 74%). Red crystals of **2**·1.5Toluene were obtained by storing a saturated solution in MeCN and toluene at -35 °C. **^{1}H NMR** (400 MHz, CD_3CN, 25 °C): δ (ppm) 8.88 (s, 2H, NC*H*), 8.00 (d, $^{3}J_{H\text{-}H}$ = 7.6 Hz, 2H, SbAr-*H*), 7.71 (t, $^{3}J_{H\text{-}H}$ = 7.6 Hz, 1H, SbAr-*H*), 7.42 (t, $^{3}J_{H\text{-}H}$ = 7.7 Hz, 2H, NAr-*H*), 7.21 (t, $^{3}J_{H\text{-}H}$ = 7.7 Hz, 2H, NAr-*H*), 7.16 (d, *J* = 8.5 Hz, 2H, NAr-*H*), 6.65 (d, $^{3}J_{H\text{-}H}$ = 8.5 Hz, 2H, NAr-*H*), 2.33 (s, 16H, NCH_3). **^{13}C{^{1}H} NMR** (100 MHz, CD_3CN, 25°C): δ (ppm) 165.90 (s), δ146.23 (s), δ139.59 (s), δ136.12 (s), δ131.26 (s), δ130.24 (s), δ128.94 (s), δ125.24 (s), δ124.91 (s), δ121.74(s), δ120.86 (s), δ44.01 (s). **^{31}P{^{1}H} NMR** (162 MHz, CD_3CN, 25 °C): δ (ppm) 144.58 (hept, $^{1}J_{P\text{-}F}$ =705.6Hz). **^{19}F{^{1}H} NMR** (376 MHz, CD_3CN, 25 °C): δ (ppm) -72.96 (d, $^{1}J_{F\text{-}P}$ =705.6Hz). **HRMS** (ESI) [M] $C_{48}H_{50}N_8Sb^{2+}$ calc. 490.1114 m/z; found 490.1064 m/z.

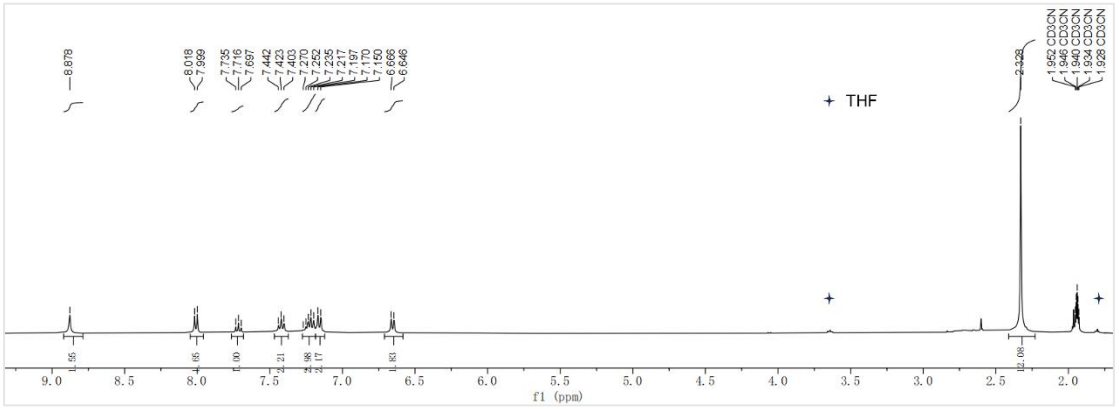


Fig. S7 ^{1}H NMR spectrum of **2** (400 MHz, CD_3CN).

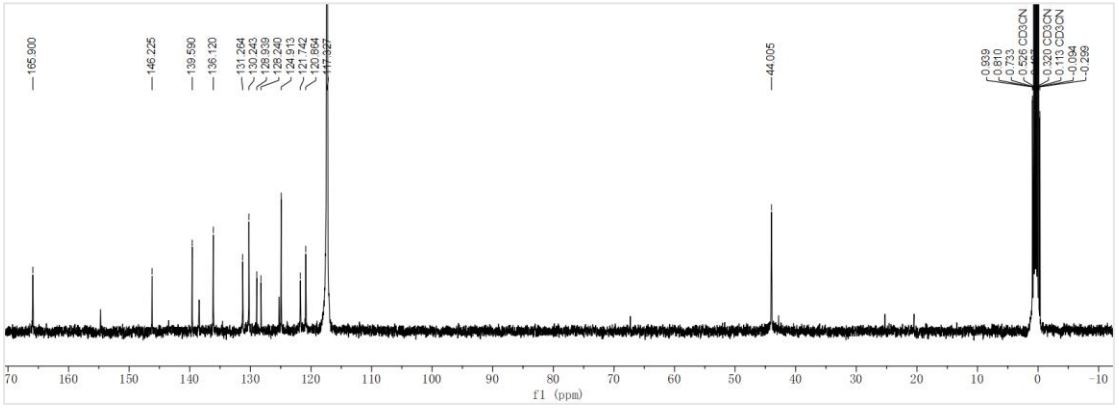


Fig. S8 ^{13}C{^{1}H} NMR spectrum of **2** (100 MHz, CD_3CN).

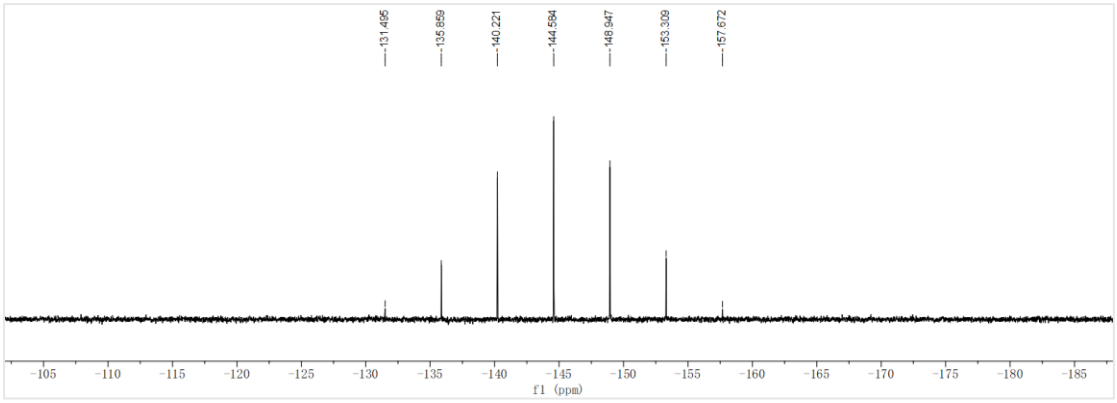


Fig. S9 $^{31}P\{^{1}H\}$ NMR spectrum of **2** (162 MHz, CD_3CN).

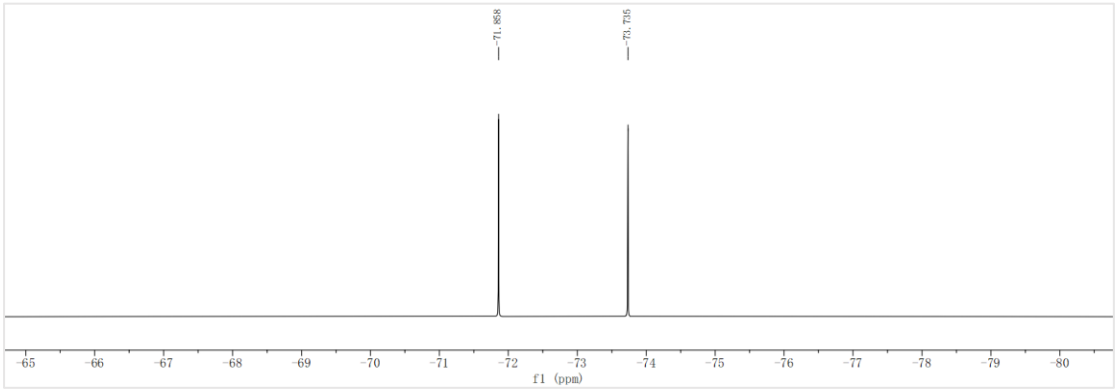


Fig. S10 $^{19}F\{^{1}H\}$ NMR spectrum of **2** (376 MHz, CD_3CN).

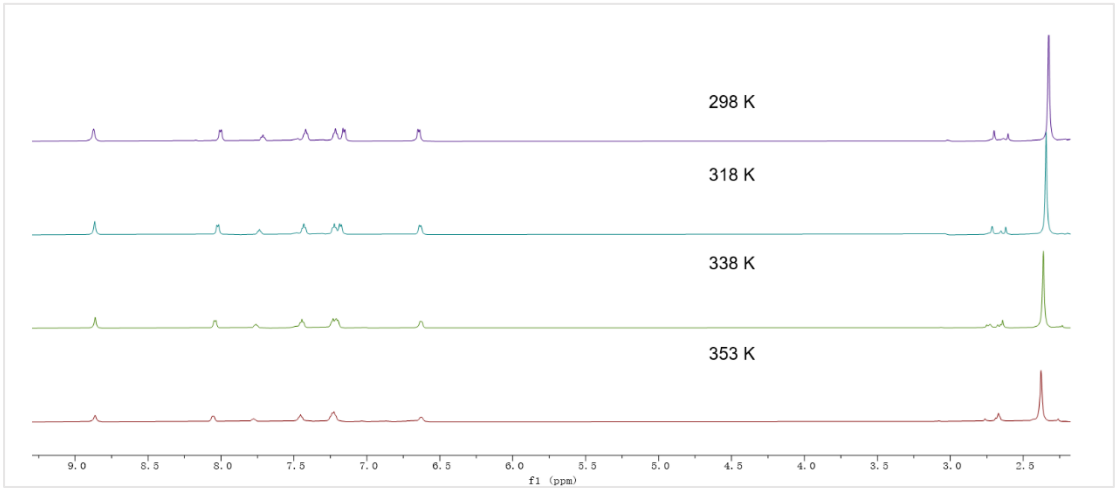
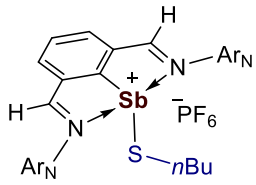


Fig. S11 Variable temperature ^{1}H NMR spectrum of **2** (600 MHz, CD_3CN).

Synthesis of **3**



*n*BuSS*n*Bu (2.9 mg, 0.016 mmol) and a MeCN solution (8 mL) of **2** (20.1 mg, 0.016 mmol) were combined in a Schlenk tube in a glove box. The tube was then sealed and placed into an oil bath heated at 60 °C. The mixture was stirred at 60 °C for 2 hours. The color of the solution gradually turned from red to yellow. Subsequently, the reaction mixture was filtered and the volatiles in the filtrate were removed under vacuum. The residue was washed with *n*-hexane and dried to give a yellow powder (19.9 mg, containing **3**: 19.1 mg, yield: 82%, and 4.2% of *n*BuSS*n*Bu). **^{1}H NMR** (400 MHz, CD_3CN, 25 ºC): **3**: δ (ppm) 9.31 (s, 2H, NC*H*), 8.19 (d, $^{3}J_{H\text{-}H}$ = 7.5 Hz, 2H, SbAr-*H*), 7.93 (t, $^{3}J_{H\text{-}H}$ = 7.5 Hz, 1H, SbAr-*H*), 7.46-7.36 (m, 6H, NAr-*H*), 7.25-7.21(m, 2H, NAr-*H*), 2.72 (s, 12H, NCH_3), 2.37 (t, $^{3}J_{H\text{-}H}$ = 7.2 Hz, 2H, SCH_2). 1.05-0.95 (m, 2H, SCH$_2$CH_2), 1.05-0.95 (m, 2H, SCH$_2$CH$_2$CH_2), 0.56 (t, $^{3}J_{H\text{-}H}$ = 7.2 Hz, 3H, CH_3); *n*BuSS*n*Bu: δ (ppm) 2.71 (t, $^{3}J_{H\text{-}H}$ = 7.3 Hz, 2H, SCH_2), 1.68-1.59 (m, 2H, SCH$_2$CH_2), 1.45-1.34 (m, 2H, SCH$_2$CH$_2$CH_2), 0.95-0.89 (m, 3H, CH_3). **^{13}C{^{1}H} NMR** (100 MHz, CD_3CN), 25 ºC): **3**: δ (ppm) 165.10 (s), 147.90 (s), 141.58 (s), 139.42 (s), 136.12 (s), 131.03 (s), 125.61 (s), 122.77 (s), 121.52 (s), 85.87 (s), 68.30 (s), 45.11 (s), 36.28 (s), 30.30 (s), 26.26 (s), 13.60 (s); *n*BuSS*n*Bu: δ (ppm) 39.21 (s), 31.98 (s), 22.26 (s), 13.95 (s). **^{31}P{^{1}H} NMR** (162 MHz, CD_3CN, 25 ºC): δ (ppm) 144.58 (hept, $^{1}J_{P\text{-}F}$ = 705.6Hz). **^{19}F{^{1}H} NMR** (376 MHz, CD_3CN, 25 ºC): δ (ppm) -72.80 (d, $^{1}J_{F\text{-}P}$ = 705.6Hz). **HRMS** (ESI) [M] $C_{28}H_{34}N_4SSb^+$ calc. 579.1537 m/z; found 579.1504 m/z.

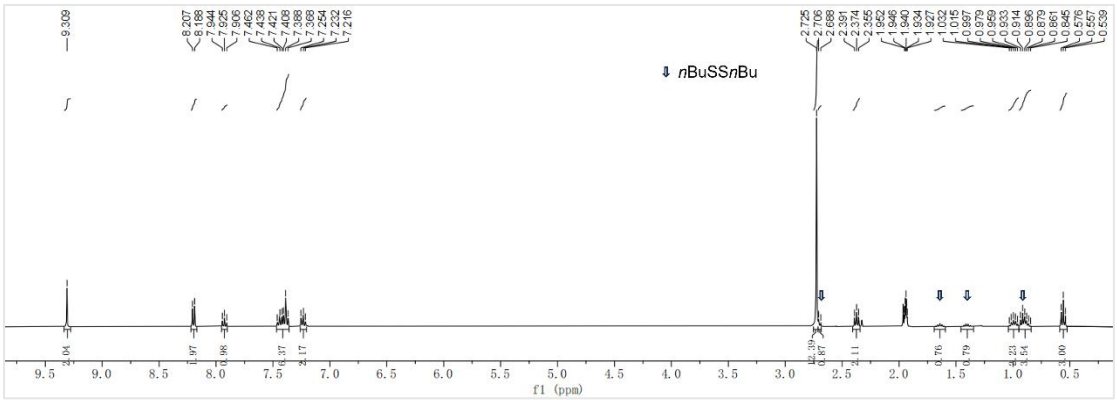


Fig. S12 ^{1}H NMR spectrum of **3** (400 MHz, CD_3CN).

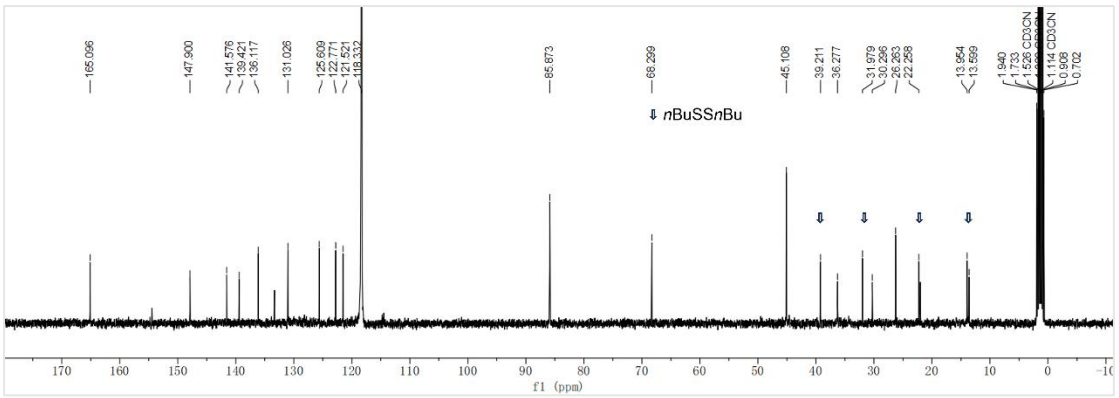


Fig. S13 $^{13}C\{^{1}H\}$ NMR spectrum of **3** (100 MHz, CD_3CN).

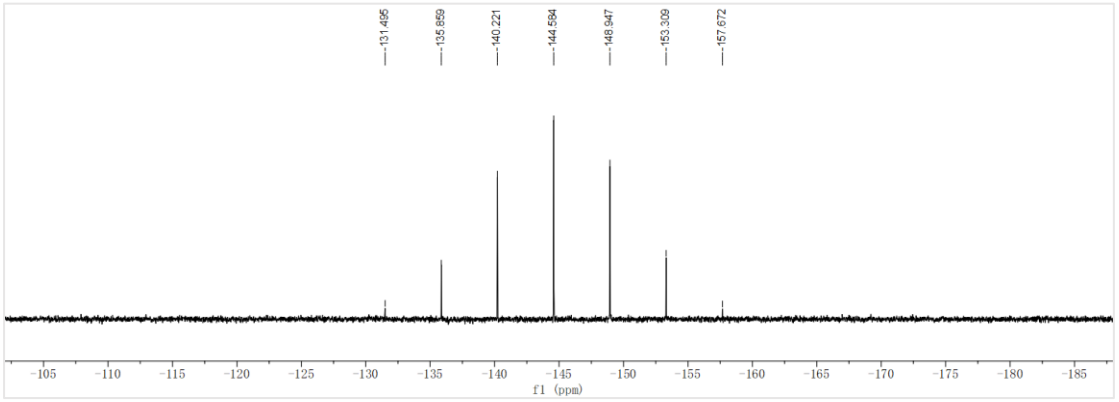


Fig. S14 $^{31}P\{^{1}H\}$ NMR spectrum of **3** (162 MHz, CD_3CN).

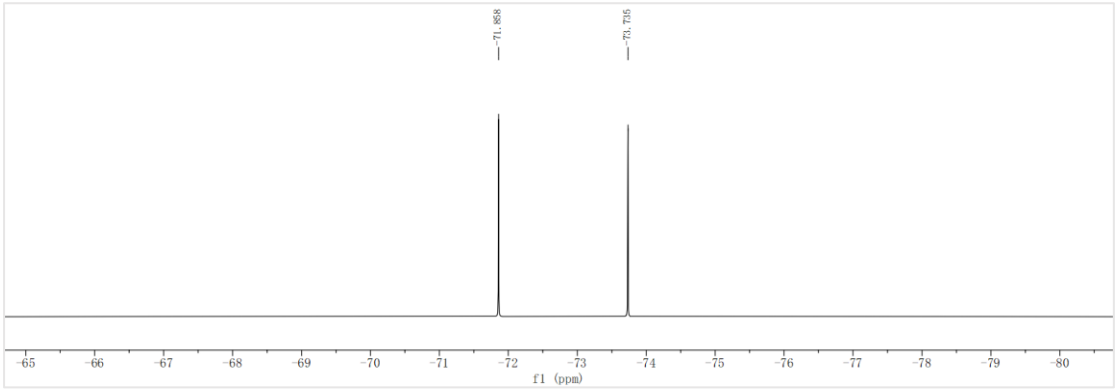
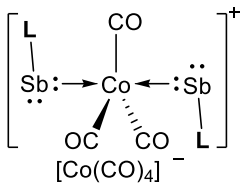


Fig. S15 $^{19}F\{^{1}H\}$ NMR spectrum of **3** (376 MHz, CD_3CN).

Synthesis of **4**



A MeCN solution (3 mL) of $Co_2(CO)_8$ (9.0 mg, 0.026 mmol) was added dropwise to a MeCN solution (8 mL) of **2** (33.8 mg, 0.027 mmol). The resulting reaction mixture was then transferred into a Schlenk tube. The tube was then sealed and placed into an oil bath heated at 60 °C. The mixture was stirred at 60 °C for 2 hours. The color of the solution

gradually changed from red to dark-red. The reaction mixture was subsequently filtered, and the filtrate was concentrated to a final volume of approximately 3 mL. Then, 4 mL of toluene was added. Storing the solution at -35 °C afforded dark-red crystals, which were isolated by decanting the supernatant and dried under vacuum to give **4** as a dark-red crystalline solid (21.7 mg, yield 63%). **^{1}H NMR** (400 MHz, CD_3CN, 25 °C): δ (ppm) 9.05 (s, 2H, NC*H*), 8.00 (d, $^{3}J_{H\text{-}H}$ = 7.5 Hz, 2H, SbAr-*H*), 7.68 (t, $^{3}J_{H\text{-}H}$ = 7.5 Hz, 1H, SbAr-*H*), 7.34 (t, $^{3}J_{H\text{-}H}$ = 7.7 Hz, 2H, NAr-*H*), 7.17 (d, $^{3}J_{H\text{-}H}$ = 8.1 Hz, 2H, NAr-*H*), 7.06 (t, $^{3}J_{H\text{-}H}$ = 8.3 Hz, 2H, NAr-*H*), 6.80 (d, $^{3}J_{H\text{-}H}$ = 7.9 Hz, 2H, NAr-*H*), 2.47 (s, 12H, NCH_3). **^{13}C{^{1}H} NMR** (100 MHz, CD_3CN, 25 °C): δ (ppm) 171.94(s), 162.37 (s), 147.07(s), 140.31 (s), 140.07 (s), 133.84 (s), 128.62 (s),128.52 (s), 123.93 (s), 121.19 (s), 120.30 (s), 44.21 (s). **HRMS** (ESI) [M−Co(CO)$_4^-$] $C_{51}H_{50}N_8O_3CoSb_2^+$ calc. 1125.1413 m/z; found 1125.1379 m/z.

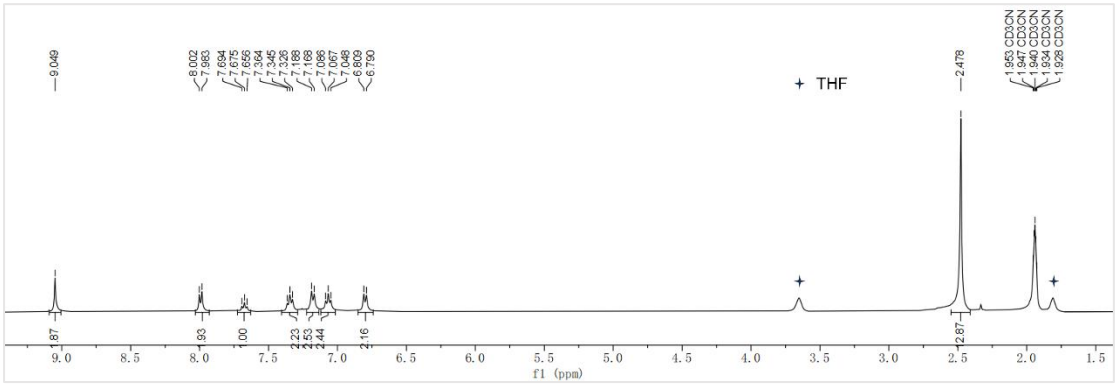


Fig. S16 ^{1}H NMR spectrum of **4** (400 MHz, CD_3CN).

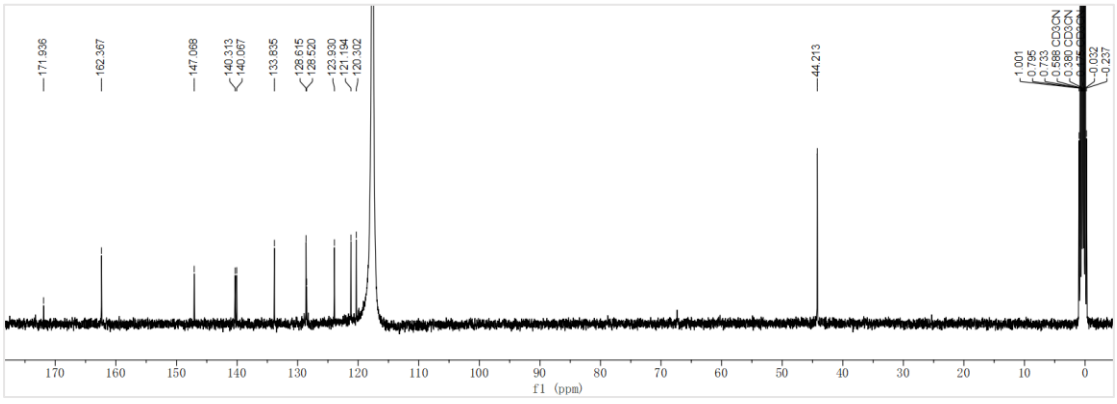


Fig. S17 ^{13}C{^{1}H} NMR spectrum of **4** (100 MHz, CD_3CN).

2.2 Reaction of 2 and cobaltocene

2 (10.2 mg, 0.008 mmol) and cobaltocene (3.0 mg, 0.016 mmol) were combined in 0.6 mL CD_3CN. The color of the solution changed from red to green within one minute. The resulting reaction mixture was then transferred into a J. Young NMR tube and performed NMR spectroscopy immediately. The NMR spectra of the reaction solution confirmed the exclusive formation of **1**. **^{1}H NMR** (400 MHz, CD_3CN, 25 °C): δ (ppm) 9.37 (s, 2H, NC*H*), 8.09 (d, $^3J_{H\text{-}H}$ = 7.3 Hz, 2H, SbAr-*H*), 7.70 (t, $^3J_{H\text{-}H}$ = 7.3 Hz, 1H, SbAr-*H*), 7.25-7.15 (m, 6H, NAr-*H*), 7.09-7.03 (m, 2H, NAr-*H*), 2.58 (s, 12H, NCH_3).

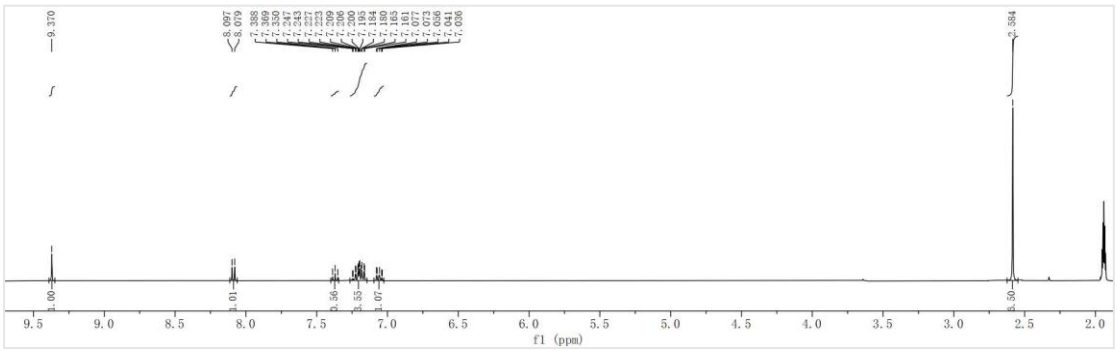


Fig. S18 ^{1}H NMR spectrum of the reaction of the 2 and cobaltocene at room temperature (400 MHz, CD_3CN).

2.3 The reaction of 2 and $Co_2(CO)_8$ at room tempreture

$Co_2(CO)_8$ (1.4 mg, 0.0041 mmol), **2** (5.0 mg, 0.0039 mmol) were combined in 0.6 mL CD_3CN. The resulting reaction mixture was then transferred into a J. Young NMR tube. The tube was then capped and placed into an oil bath heated at 25 °C. The progress of the reaction was monitored by NMR spectroscopy analysis. The NMR spectra of the reaction solution confirmed an intermediate **B** which turned into **4** gradually. **^{1}H NMR** (400 MHz, CD_3CN, 25 °C): δ (ppm) 9.39 (s, 2H, NC*H*), 8.27 (d, $^3J_{H\text{-}H}$ = 7.35 Hz, 2H, SbAr-*H*), 7.98 (t, $^3J_{H\text{-}H}$ = 7.35 Hz, 1H, SbAr-*H*), 7.47-7.30 (m, 6H, NAr-*H*), 7.27-7.19 (m, 2H, NAr-*H*), 2.72 (s, 12H, NCH_3). **HRMS** (ESI) [M] $C_{28}H_{25}N_4O_4CoSb^+$ calc. 661.0241 m/z; found 661.0254 m/z.

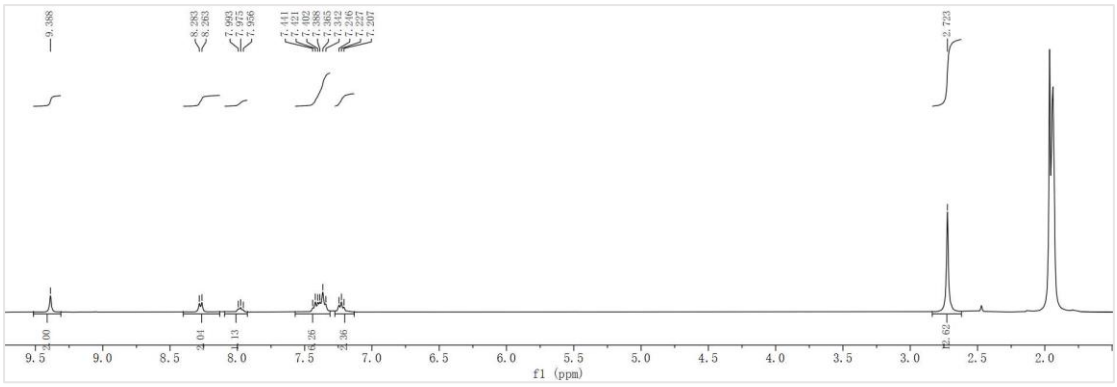


Fig. S19 ^{1}H NMR spectrum of the reaction of the **2** with $Co_2(CO)_8$ at 25ºC for 10 minutes (400 MHz, CD_3CN).

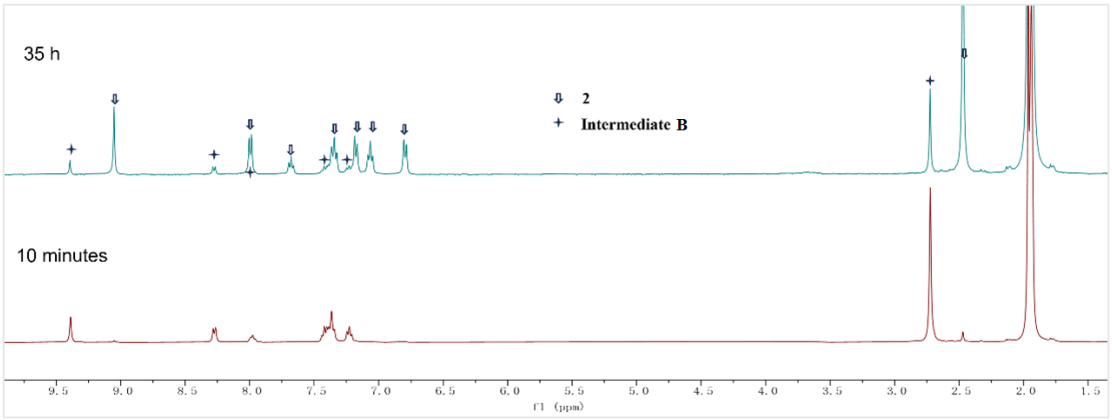


Fig. S20 ^{1}H NMR spectrum of the reaction of the **2** with $Co_2(CO)_8$ at 25ºC for 35 h and 10 minutes (400 MHz, CD_3CN).

2.4 EPR spectroscopy

Procedure for sample preparation

In the glovebox, **2** was dissolved in MeCN (0.2–0.3 M). The resulting solution was transferred into an EPR sample tube. The tube was sealed, taken out of the glovebox, and introduced in the EPR instrument at the room temperature. No EPR signal was detected in this experiment.

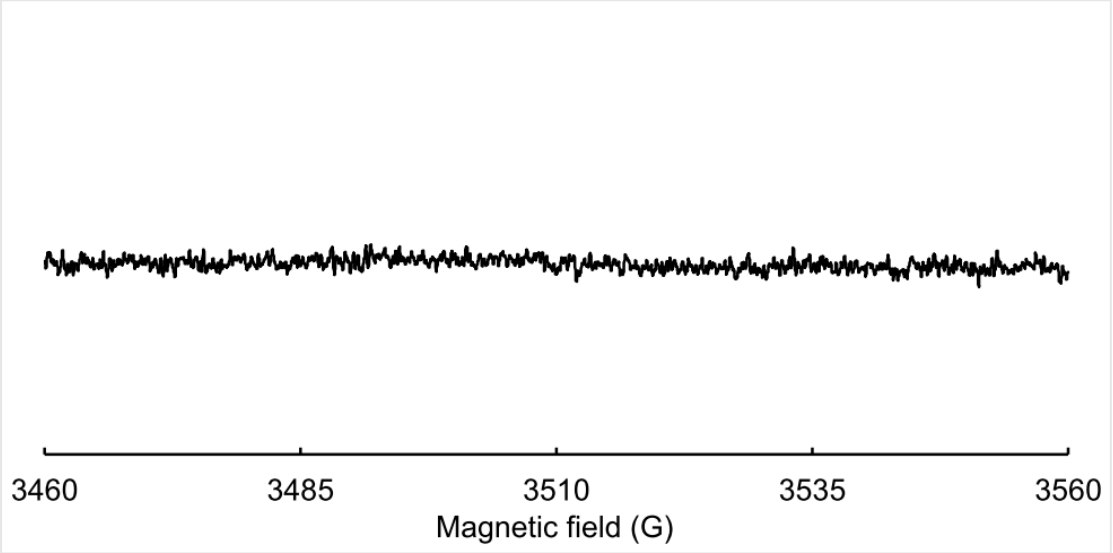


Fig. S21 EPR spectrum of **2** in MeCN at 25 °C

2.5 Electrochemical data

The experiments were carried out at room temperature in THF solution containing [*n*Bu$_4$N][PF$_6$] (0.1 M) at a scan rate of 0.01 V s^{-1}. The setup consisted of a glassy carbon as working electrode (surface area = 0.06 cm^2), a platinum wire as the counter electrode, and a silver nitrate/silver wire immersed (0.1 M $AgNO_3$ in dry THF) as the reference electrode. The CV data have been referenced to the external standard Fc/Fc$^+$ (ferrocene/ferrocenium) couple which was measured under same condition before and after the measurement of samples.

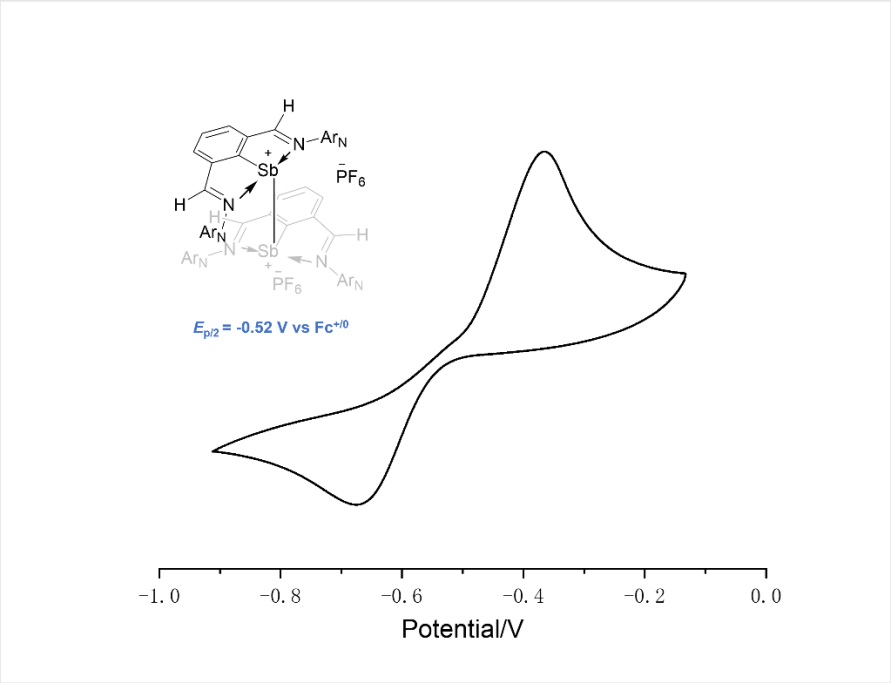


Fig. S22 Cyclic voltammogram of a 1 mM solution of **2** in THF using 0.1 M [*n*Bu$_4$N][PF$_6$] as the supporting electrolyte at ambient temperature; scan rate: 0.01 V s^{-1}. Potential in V vs Fc$^{0/+}$.

3. Summary of Crystallographic Data

The crystallographic measurements were performed at 150~160 K using a Bruker D8 Quest diffractometer (Mo−Kα radiation, λ 0.71069 Å). In each case, a specimen of suitable size and quality was selected and mounted onto a nylon loop. Semiempirical absorption corrections were applied. The structures were solved by direct methods, which successfully located most of the non-hydrogen atoms. Subsequent refinement using the SHELXTL/PC package (version 6.1) allowed location of the remaining non-hydrogen atoms which were refined anisotropically. Hydrogen atoms were added at calculated positions using a riding model. Calculations were carried out using the SHELXL-2014 and Olex2 program.[S1] The data has been deposited with the Cambridge Structural Database. CCDC 2429478 (**1**), 2429479 (**2**·1.5Toluene), and 2429480 (**4**·MeCN) contain the supplementary crystallographic data for this paper.

Table S1 Crystallographic data and refinement parameters for **1**, **2** and **4**.

	1	**2**·1.5Toluene	**4**·MeCN
formula	$C_{24}H_{25}N_4Sb$	$C_{34.50}H_{37}F_6N_4PSb$	$C_{57}H_{53}Co_2N_9O_7Sb_2$
formula Mass	491.23	774.4	1337.44
color	dark green	red	red
cryst system	monoclinic	monoclinic	triclinic
space group	$P2_1/c$	$C2/c$	$P\bar{1}$
a, Å	12.2927(12)	19.8847(5)	12.196(2)
b, Å	7.5486(7)	14.7666(4)	15.812(3)
c, Å	23.983(2)	23.3770(6)	16.798(3)
α, deg	90	90	73.724(4)
β, deg	103.267(3)	96.4900(10)	70.084(4)
γ, deg	90	90	76.072(4)
V, Å^3	2166.1(4)	6820.2(3)	2885.4(9)
Z	4	8	2
D_{calcd}, (mg/m^3)	1.506	1.508	1.539
F(000)	992	3136	1340
T(K)	158	153	153
θ range, deg	2.140 to 26.751	1.878 to 26.372	2.63 to 26.74
no. of independent reflns	4617	6990	11820
No. of params	266	505	703
final R_1, wR (I > 2σ(I))	0.0340,0.0486	0.0238, 0.0252	0.0252,0.0315
goodness of fit on F^2	1.026	1.125	1.052

4. Computational Details

DFT calculations were carried out with the Gaussian 16 package.[S2] Geometry optimizations were performed with the M06-2X functional.[S3] The Def2-SVP basis set was used for all the atoms. The SMD method was used with MeCN as the solvent, while Bondi radii[S4] were chosen as the atomic radii to define the molecular cavity. Frequency calculations at the same level of theory were performed to identify the number of imaginary frequencies (zero for local minimum). The Gibbs energy corrections from frequency calculations were added to the single-point energies to obtain the Gibbs free energies in solution. NBO analysis was performed using the NBO 7.0 program[S5] at the SMD/M06-2X/def2-TZVP level of theory. QTAIM and IGMH analysis were carried out using the Multiwfn program.[S6] Molecular structures, MOs, NBOs, QTAIM plot, and IGMH plot were visualized by the VMD program.[S7]

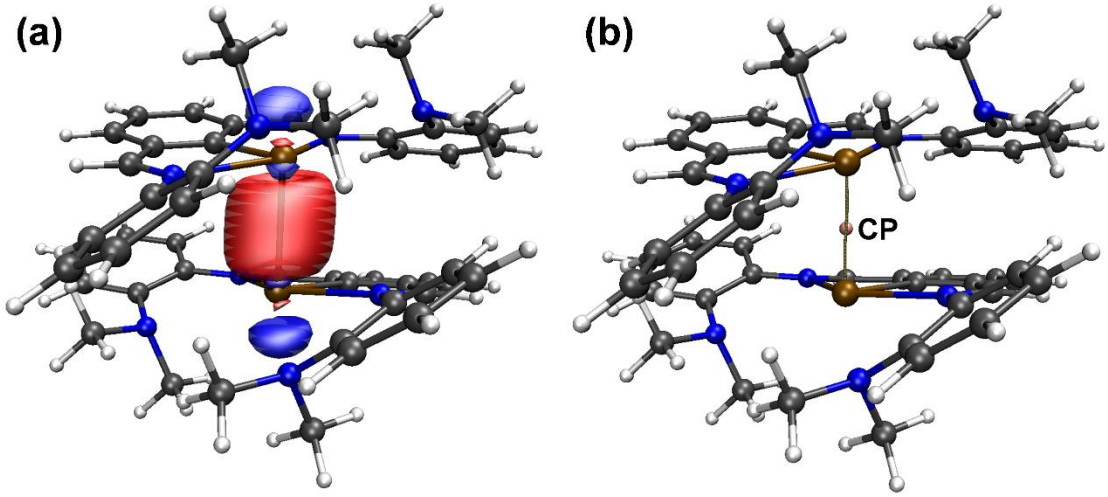


Fig. 23 DFT-optimized structure of **2**. PF_6^- anions omitted for clarity (a) NBO plot of the Sb−Sb bond. (b) Molecular graphs based on a QTAIM analysis. Selected bond paths colored in tan, BCPs colored in pink. Irrelevant BCPs, RCPs and cage critical points (CCPs) omitted for clarity.

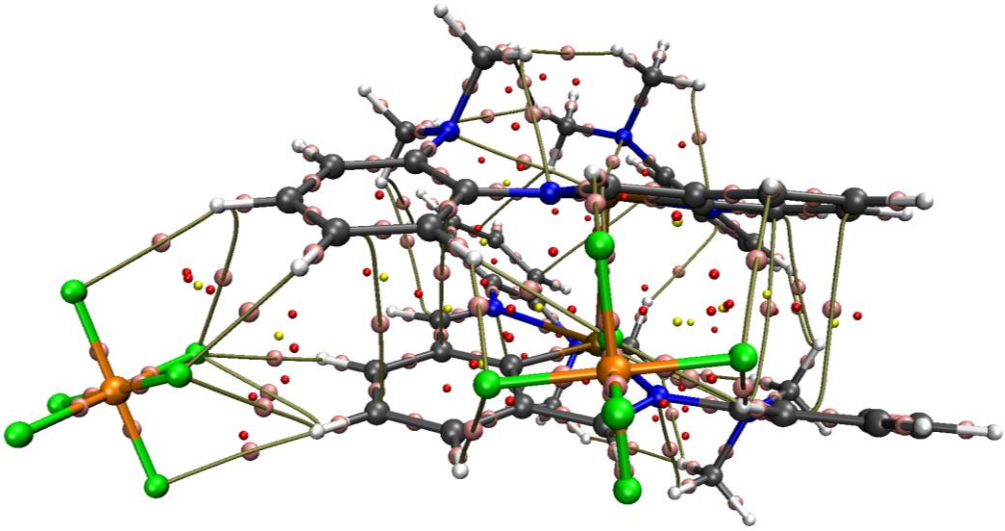


Fig. S24 Molecular graphs of **2** based on a QTAIM analysis. Bond paths colored in tan, BCPs colored in pink, RCPs colored in red, and cage critical points (CCPs) colored in yellow.

Cartesian Coordinates:

1:

Sb	-0.21042233	-0.30263481	-0.11404467
N	-3.11297847	-1.78892073	-0.81718653
N	2.08121677	0.06275114	-0.46336841
N	-2.43070557	0.76749137	0.07329255
N	4.37342787	0.38889682	1.25885429
C	-3.92285912	-1.15874347	0.14159932
C	-3.61157128	0.16283083	0.55311753
C	-3.13930935	-1.21191346	-2.15390554
H	-4.06064633	-1.50053185	-2.69702780
H	-2.27215388	-1.57262527	-2.72669709
H	-3.08849379	-0.11747471	-2.11159521
C	-5.02218081	-1.79700630	0.73381101
H	-5.27312772	-2.81468677	0.43478582
C	0.01652534	1.73100523	-0.50003965
C	2.38466864	1.29259636	-0.74842959
H	3.41891688	1.59655430	-0.94737061
C	-0.90875838	3.96939296	-0.79681465
H	-1.77049700	4.64176038	-0.78979237
C	-1.08878213	2.61415934	-0.50446540

C	0.36876739	4.46508399	-1.09146766
H	0.50169317	5.52321329	-1.31917124
C	1.30347384	2.24568331	-0.78914928
C	-3.13991223	-3.23567845	-0.85364018
H	-3.04419528	-3.64460335	0.16121236
H	-2.28552658	-3.58682750	-1.45101041
H	-4.06246198	-3.64247943	-1.31272111
C	3.07463436	-0.93935370	-0.34768527
C	-2.37422457	2.03590377	-0.16493433
H	-3.26634900	2.67566026	-0.10837632
C	1.46932918	3.60921137	-1.08630891
H	2.46763904	3.99433961	-1.30902172
C	4.98431034	-2.97823375	-0.24638005
H	5.74352878	-3.76135234	-0.20487148
C	3.36117035	0.63766074	2.27613036
H	2.35159496	0.44781336	1.89019399
H	3.41568763	1.68820364	2.59711068
H	3.51605843	-0.00455334	3.16519177
C	-4.41452801	0.80398930	1.50328424
H	-4.13722581	1.80525096	1.83803582
C	4.20893545	-0.78168950	0.49565718
C	3.84890465	-3.13993586	-1.03443052
H	3.70164507	-4.04602396	-1.62365322
C	-5.80754933	-1.14958606	1.68826098
H	-6.65526419	-1.67427782	2.13252724
C	5.15398156	-1.81916902	0.51262015
H	6.03669774	-1.72441452	1.14451903
C	2.89986222	-2.11863975	-1.07543531
H	2.01341603	-2.20597911	-1.70728061
C	-5.51334620	0.15788464	2.06788663
H	-6.11779976	0.66884831	2.81864504
C	5.70697443	0.66995695	1.74618363
H	5.73370026	1.70344221	2.11976847
H	6.43957107	0.57677961	0.93296913
H	6.01730889	0.00435237	2.57597656

A (G = -2326.937138 Hartree)**:**

Sb	1.33031500	0.28747100	-0.15255400

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N	-0.92171100	1.04284300	0.35384100
N	4.39787200	0.45614400	0.59784200
N	0.73694400	3.23443100	0.52178100
C	-1.07784700	-1.20217700	1.06028600
C	0.85202800	-2.62888700	0.76001300
C	2.24166900	-2.72735700	0.31231700
H	2.77169600	-3.68888000	0.36145600
C	-1.65439800	0.12891300	0.88079300
H	-2.69250300	0.31510600	1.17987700
C	0.25220500	-1.36731500	0.66264300
C	-1.44534000	2.30535500	0.00457700
C	-0.57629900	3.41915900	0.03977900
C	0.12457900	-3.71789000	1.25903000
H	0.59722100	-4.69998400	1.32924300
C	4.12667200	-1.62921200	-0.61464000
C	-2.75800200	2.44266400	-0.46100600
H	-3.40127100	1.56276500	-0.52007800
C	4.91886700	-0.50026800	-0.29517600
C	-1.81227600	-2.28891500	1.55443100
H	-2.85759100	-2.14982000	1.83654700
C	4.60955700	-2.61928200	-1.47446400
H	3.96699800	-3.46514800	-1.72617400
C	-1.05287600	4.65105800	-0.42663200
H	-0.39566400	5.52064100	-0.41669100
C	5.87268900	-2.49324600	-2.04926200
H	6.23888400	-3.26190900	-2.73098800
C	6.64597400	-1.36709600	-1.77031300
H	7.62961100	-1.25168400	-2.22879600
C	-2.36106500	4.78078600	-0.89274300
H	-2.70994400	5.75099100	-1.25054600
C	-1.20355500	-3.54177000	1.65518300
H	-1.77175000	-4.39080000	2.03686700
C	4.23073300	0.00922500	1.97855800
H	3.79050200	-0.99390000	2.01992300
H	3.55870700	0.70371800	2.50524700
H	5.20002100	-0.01221500	2.51161500

C	6.17638300	-0.38145800	-0.90144200
H	6.80105800	0.48433700	-0.68276200
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H	0.66093800	3.95904800	2.52273600
H	1.85370000	2.66178000	2.20205000
H	0.11754600	2.26834100	2.29974300
C	-3.21841900	3.68084100	-0.90228300
H	-4.23943000	3.77561400	-1.27464500
C	1.73323500	4.17429800	0.04246100
H	1.64819800	4.29250700	-1.04596300
H	2.73146500	3.77570800	0.27220100
H	1.64763700	5.17022500	0.51696600
C	4.98139200	1.78243100	0.53895100
H	6.00999000	1.81641900	0.94580200
H	4.36289100	2.46101200	1.14360200
H	4.99709400	2.14768500	-0.49692100
P	-5.02343600	-1.20065100	-0.44771100
F	-5.43460900	0.32533200	-0.82707400
F	-6.54349800	-1.49969200	0.01916100
F	-5.37553300	-1.67885800	-1.95244900
F	-4.59393700	-2.71395400	-0.05553300
F	-3.49050700	-0.88810100	-0.90527500
F	-4.65807700	-0.71264700	1.06714000

2 (G = -4653.902335 Hartree)**:**

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N	-0.38688900	2.05982300	-1.56010900
N	-3.22095900	-2.46952200	-2.41414600
N	-3.00102400	2.22276700	-2.53889800
C	1.56341600	0.70433200	-1.60547900
C	1.34964500	-1.67939800	-1.26830500
C	0.45061000	-2.82100500	-1.10897000
H	0.87511600	-3.83397700	-1.07126700
C	0.88498700	1.99201900	-1.73746100
H	1.47988900	2.87597300	-1.99816100
C	0.76358500	-0.41623400	-1.37499100
C	-1.04085900	3.31751200	-1.59827700

C	-2.38036300	3.38983500	-2.04577400
C	2.74290400	-1.81771500	-1.35931100
H	3.20375800	-2.80239500	-1.26221400
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C	-0.39590300	4.47495800	-1.14739000
H	0.62201000	4.40717500	-0.76776500
C	-2.99452900	-3.56793300	-1.56376800
C	2.95555900	0.56925200	-1.70729900
H	3.57283100	1.45572500	-1.87017800
C	-1.44830300	-4.81366900	-0.15138000
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C	-3.03939500	4.62544300	-1.99087700
H	-4.07298000	4.69613900	-2.32936800
C	-2.39926100	-5.81658200	0.02272100
H	-2.16056100	-6.68786300	0.63395900
C	-3.65831100	-5.68288800	-0.56139500
H	-4.41695100	-6.45367200	-0.41500100
C	-2.38758100	5.77103400	-1.53418700
H	-2.92425800	6.72094000	-1.50596000
C	3.54016500	-0.69265400	-1.57697000
H	4.62303300	-0.80805000	-1.63487600
C	-2.47437900	-2.50869600	-3.66732100
H	-1.41566900	-2.74028600	-3.49017300
H	-2.53634700	-1.52520000	-4.15691300
H	-2.88742600	-3.26906300	-4.35711300
C	-3.95234600	-4.56856600	-1.34640700
H	-4.93050000	-4.48499100	-1.82086100
C	-2.51584300	1.80149900	-3.84959100
H	-2.84262700	2.50217100	-4.64158100
H	-2.91564600	0.80290800	-4.08105200
H	-1.41858200	1.74758500	-3.86608400
C	-1.05852300	5.69956200	-1.12481700
H	-0.53757700	6.58455700	-0.75575900
C	-4.44996500	2.20365100	-2.48561700
H	-4.79315900	2.56852500	-1.50801500
H	-4.79659500	1.16836000	-2.62005600
H	-4.91719300	2.82400700	-3.27455200

C	-4.60142900	-2.08380400	-2.62360800
H	-5.14103900	-2.76684400	-3.30790800
H	-4.62192100	-1.07744300	-3.06962900
H	-5.13155000	-2.05404600	-1.66334200
Sb	-1.52413300	-0.24257800	1.50393800
N	-3.86606100	0.52004100	1.06645800
N	0.77952900	0.53647500	1.91181500
N	-3.97861300	-1.96420000	2.24924400
N	0.69879500	-2.15374000	2.69774000
C	-0.42413100	2.58191300	2.00590600
C	-2.78414000	2.58688000	1.47963900
C	-3.97635100	1.79499400	1.17560100
H	-4.94794700	2.30274800	1.09619000
C	0.79439500	1.79424300	2.17836300
H	1.69861500	2.29762700	2.54160600
C	-1.58079800	1.89450400	1.63437800
C	1.98192000	-0.21360100	1.97870700
C	1.93374500	-1.58513800	2.31838900
C	-2.82267900	3.97662600	1.67164000
H	-3.76486900	4.51494800	1.54507900
C	-4.98245900	-0.30424300	0.79045800
C	3.20692300	0.37777800	1.64894200
H	3.23272200	1.42405200	1.35075700
C	-4.99985700	-1.60419100	1.35045600
C	-0.45904400	3.96873600	2.20509000
H	0.45558900	4.49908700	2.47970300
C	-6.03641800	0.11644700	-0.02907700
H	-6.01536800	1.11701400	-0.45938000
C	3.12204100	-2.32792500	2.26890700
H	3.09962300	-3.38892300	2.51740800
C	-7.08863800	-0.74529400	-0.33034200
H	-7.89783900	-0.40517000	-0.97784100
C	-7.08205900	-2.04566800	0.17325600
H	-7.89145200	-2.73468500	-0.07403600
C	4.33396800	-1.73185800	1.91893200
H	5.24186000	-2.33422900	1.86247900
C	-1.66045500	4.65940200	2.03401100

H	-1.69044700	5.73973000	2.18021500
C	-4.04758400	-1.29893800	3.54605600
H	-4.19237400	-0.21667500	3.42800400
H	-3.10459700	-1.46475300	4.08853800
H	-4.87822400	-1.69812700	4.15855000
C	-6.04689100	-2.47049200	1.00544000
H	-6.06275500	-3.48085400	1.41544800
C	0.22658800	-1.72475400	4.01082000
H	0.84793700	-2.15487800	4.81949900
H	-0.81121000	-2.06225300	4.15167300
H	0.25073300	-0.63020500	4.10148200
C	4.37956000	-0.37060300	1.62743300
H	5.31661300	0.10097400	1.33109100
C	0.59040600	-3.59243700	2.55058000
H	0.98877600	-3.90064900	1.57470900
H	-0.47066300	-3.87724100	2.60830600
H	1.13428400	-4.14616900	3.34002700
C	-3.70163100	-3.37941000	2.38568100
H	-4.46165200	-3.91122500	2.99004400
H	-2.72868200	-3.50089900	2.88687400
H	-3.64774000	-3.84713300	1.39464200
P	3.35357900	4.23724900	0.40370100
F	4.44160400	3.05192900	0.18247100
F	4.53797700	5.32760200	0.49823200
F	3.25419000	4.44806900	-1.20406000
F	2.24259100	5.40262000	0.62363400
F	2.15054800	3.12996600	0.30860100
F	3.41596700	3.99473400	2.00926500
P	6.99905900	-2.65888300	-0.84235200
F	8.55296800	-2.22056700	-0.96803600
F	7.25834800	-3.16748600	0.67938200
F	5.43624400	-3.09667000	-0.71495000
F	7.36217900	-4.13412100	-1.40440200
F	6.62756600	-1.17911900	-0.27883300
F	6.72128100	-2.14234600	-2.35700000

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