Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Dinitrogen Activation by a Phosphido-Bridged Binuclear Cobalt Complex

Hai-Jun Li,‡ Rui Feng,‡ Gao-Xiang Wang, Junnian Wei,* Zhenfeng Xi

Email: jnwei@pku.edu.cn

Beijing National Laboratory for Molecular Sciences (BNLMS), Key Laboratory of Bioorganic Chemistry and Molecular Engineering of Ministry of Education, College of Chemistry, Peking University, Beijing 100871, China

Table of Contents

S1. Experimental Materials and Method

General methods

Starting materials were purchased from Sigma-Aldrich, TCI, J&K, and others without further purification. All reactions were carried out under dinitrogen atmosphere. THF was dried by standard methods and freshly distilled over sodium before use. Other solvents were purified by an Mbraun SPS-800 Solvent Purification System. ^{1}H NMR spectra were recorded on Bruker Avance 400 spectrometers, and deuterated solvents were purchased from Cambridge Isotopes, J&K. High resolution mass spectra (HRMS) were obtained using a Bruker Solarix XR Fourier Transform Ion Cyclotron Resonance Mass Spectrometer using ESI source. Elemental analyses were tested on a Vario EL elemental analyzer at the Analytical Center of Peking University. Infrared Spectra of solid samples were recorded on a Bruker AlphaII using a KBr pellet. X-ray single-crystal diffraction analyses were performed on an XtaLAB PRO 007HF(Mo). Silylamine was quantified by gas chromatography using a Shimadzu GC-2014 with a TCD detector using dodecane as internal. All DFT calculations were performed by ORCA 5.0.3.[1,2] Geometric structures were optimized employing the r2SCAN-3c level of theory.[3-5] Calculations for odd-electron complexes were performed in a doublet spin state. The optimized structures match well the crystal structures. The wave function analysis was performed by the Multiwfn software.[6] To pair the α and β orbitals generated by the open shell calculations, biorthogonalization was performed based on the canonical orbitals by the Multiwfn software. The AdNDP analysis was performed to understand the Co-Co interaction.[7]

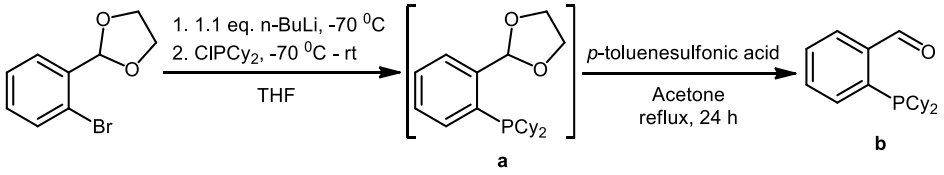


Figure S1. Synthesis of compound **b**

Compound **b** was prepared by the literature method and separated by flash column chromatography on silica gel (DCM : hexanes = 1:4) to afford compound **b** as colorless oil in 52% yield.[8] ^{1}H NMR (400 MHz, $CDCl_3$): 11.04 (d, J = 8.6 Hz, 1H), 8.00 (dd, J = 7.6, 2.4 Hz, 1H), 7.64 – 7.54 (m, 2H), 7.47 (t, J = 7.4 Hz, 1H), 2.02 (t, J = 11.9 Hz, 2H), 1.87 (d, J = 13.0 Hz, 2H), 1.78 (d, J = 13.0 Hz, 2H), 1.66 – 1.60 (m, 5H), 1.37 – 0.85 (m, 11H).

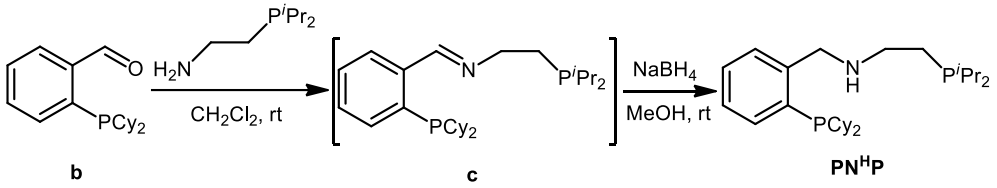


Figure S2. Synthesis of **PN^{H}P**

Compound **PN^{H}P** was prepared by the literature method[9] with around 100% yield. The compound **PN^{H}P** was used for the next step without further purification. ^{1}H NMR (600 MHz, $CDCl_3$): 7.43 – 7.41 (m, 1H), 7.35 – 7.33 (m, 1H), 7.26 (t, *J* = 7.0 Hz, 1H), 7.21 (td, *J* = 7.4, 1.3 Hz, 1H), 4.03 (d, *J* = 1.4 Hz, 2H), 2.73 – 2.69 (m, 2H), 1.91 – 1.86 (m, 4H), 1.76 – 1.72 (m, 2H), 1.71 – 1.66 (m, 2H), 1.63 – 1.62 (m, 4H), 1.57 – 1.53 (m, 2H), 1.49 (d, *J* = 12.8 Hz, 2H), 1.30 – 1.09 (m, 10H), 1.06 – 0.99 (m, 12H); ^{13}C NMR (151 MHz, $CDCl_3$): 146.00 (d, *J* = 24.4 Hz), 132.71 (d, *J* = 19.9 Hz), 131.83 (d, *J* = 2.6 Hz), 128.44 (d, *J* = 6.3 Hz), 127.67, 125.32, 51.74 (d, *J* = 21.6 Hz), 47.15 (d, *J* = 25.6 Hz), 33.00 (d, *J* = 12.3 Hz), 29.59 (d, *J* = 16.9 Hz), 28.17 (d, *J* = 8.6 Hz), 26.18 (d, *J* = 12.6 Hz), 26.05 (d, *J* = 8.2 Hz), 25.37, 22.25 (d, *J* = 11.6 Hz), 21.76 (d, *J* = 17.5 Hz), 19.06 (d, *J* = 15.8 Hz), 17.74 (d, *J* = 9.6 Hz); ^{31}P NMR (243 MHz, $CDCl_3$): -0.68, -16.23. HRMS (ESI), calcd for $C_{27}H_{48}NP_2$ $[M+H]^+$: 448.32565, found: 448.32489.

Synthesis of compound 1. Compound **PN^{H}P** (550 mg, 1.24 mmol) reacted with *n*-BuLi (0.50 mL, 2.4 M in hexane) to generate the lithium salt **PN^{Li}P**. In the dinitrogen-filled glovebox, the THF solution of compound **PN^{Li}P** was added to the THF solution of $CoBr_2$ (260 mg, 1.20 mmol) at room temperature. The solution was stirred overnight, and the color of the solution changed from reddish brown to black green. After completion of the reaction, the solvent was removed under vacuum and washed with cold hexane (2 mL), the residue was dissolved in diethyl ether and filtered through Celite. Part of the solvent was removed under vacuum, and the concentrated solution was recrystallized in diethyl ether under -30 ℃ to give the target compound a green solid in 50% yield (350 mg). Anal. Calcd. for $C_{27}H_{46}BrCoNP_2$ (**1**): C 55.39%, H 7.92%, N 2.39%. Found: C 55.50%, H 7.57%, N 2.28%. Magnetic susceptibility (Evans, C_6D_6, 298K): μ_{eff} = 3.4 μB.

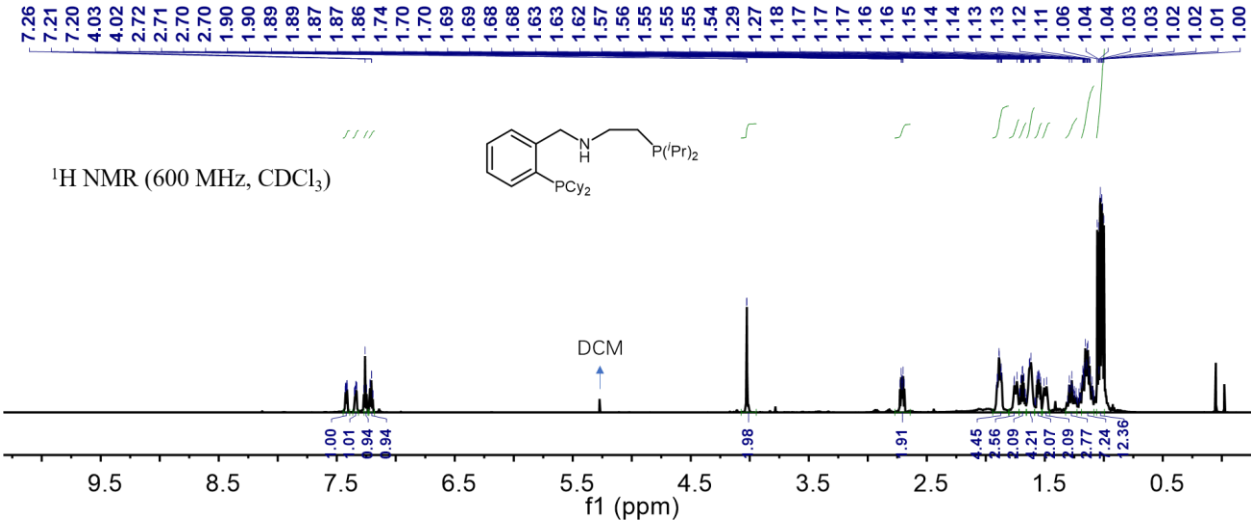
Synthesis of compound 2. KC_8 (122 mg, 0.90 mmol) was added to the THF solution of **1** (200 mg, 0.30 mmol) at room temperature, and the solution was stirred for 15 hours. The color of the

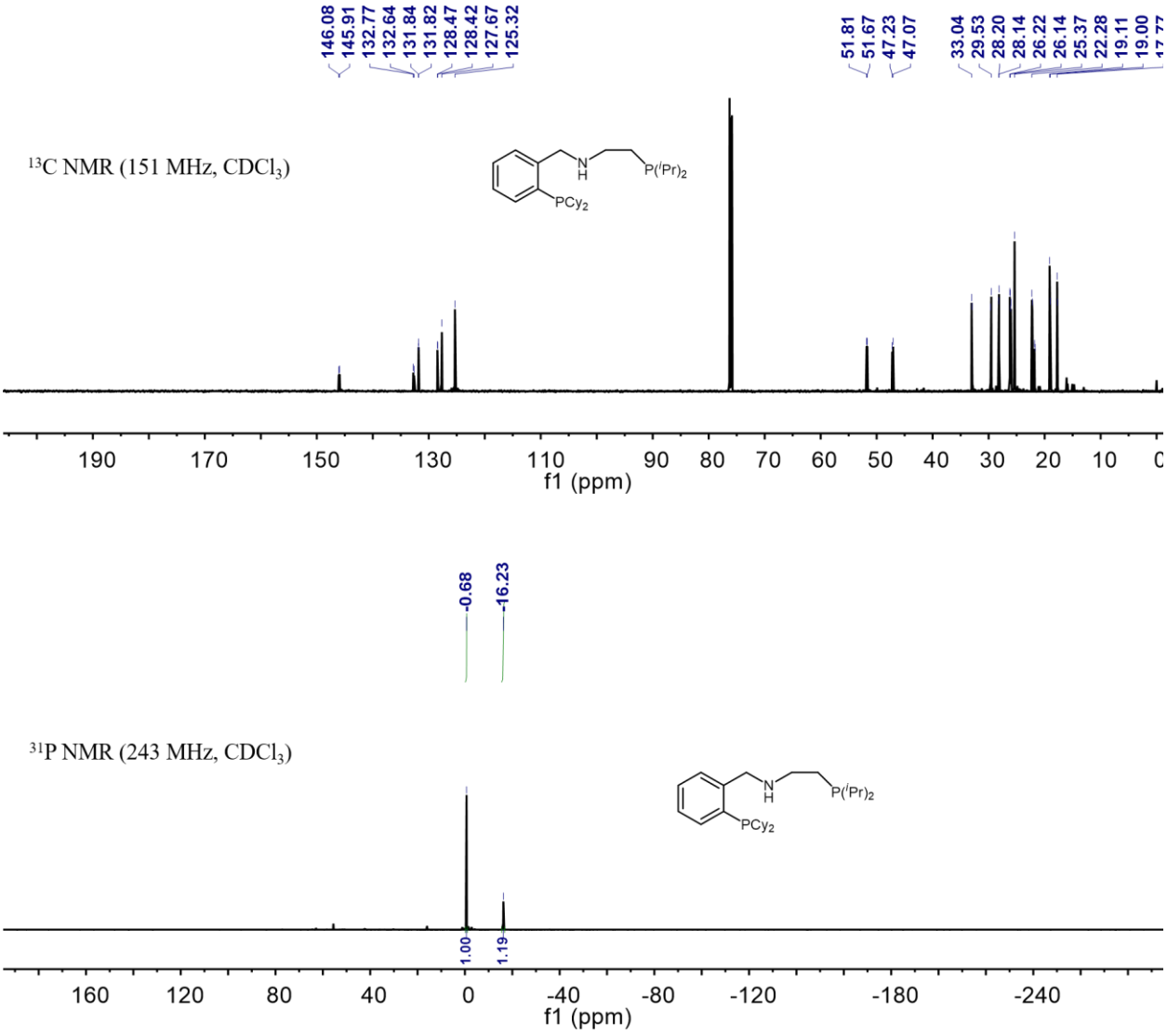
solution was changed from green to brown. The solvent was removed under vacuum, and the residue was extracted with diethyl ether. The solution was filtered through Celite, and the solvent was removed and dried under vacuum. Single crystals of **2** suitable for X-ray crystallography were obtained by recrystallization from Et_2O/hexanes/small amount of THF at -30 ℃ as red solid in 30% yield (30 mg). Anal. Calcd. for $C_{60}H_{114}Co_2KN_4O_3P_4$ [**2**$(THF)_3$]: C 59.05%, H 9.42%, N 4.59%; Found: C 58.37%, H 9.34%, N 3.55%. IR (cm^{-1}) $\upsilon(N_2)$: 1928. Magnetic susceptibility (Evans, C_6D_6, 298K): μ_{eff} = 2.2 μB. The elemental analysis tests were performed four times. However, the results were still unsatisfactory, maybe due to the presence of an indeterminate number of solvent molecules in the crystals.

Synthesis of compound 3. The THF solution of **2** was reacted with one equivalent of 2,2,2-cryptand and stirred for 1 hour. After completion of the reaction, the solvent was removed under vacuum, and the solid was dissolved in a small amount of diethyl ether and recrystallized at -30 ℃ to give red crystals of **3** that are suitable for X-ray crystallography. Anal. Calcd. for $C_{78}H_{156}Co_2KN_6O_9P_4$ [**3**(diethyl ether)$_3$]: C 58.44%, H 9.81%, N 5.24%; Found: C 57.89%, H 9.30%, N 5.27%. IR (cm^{-1}) $\upsilon(N_2)$: 1959.

S2. NMR, IR and UV Spectra

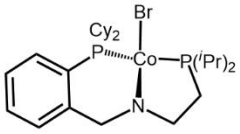
NMR Spectra of Compound PN^HP



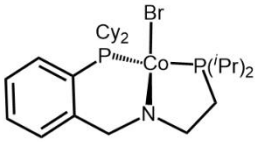


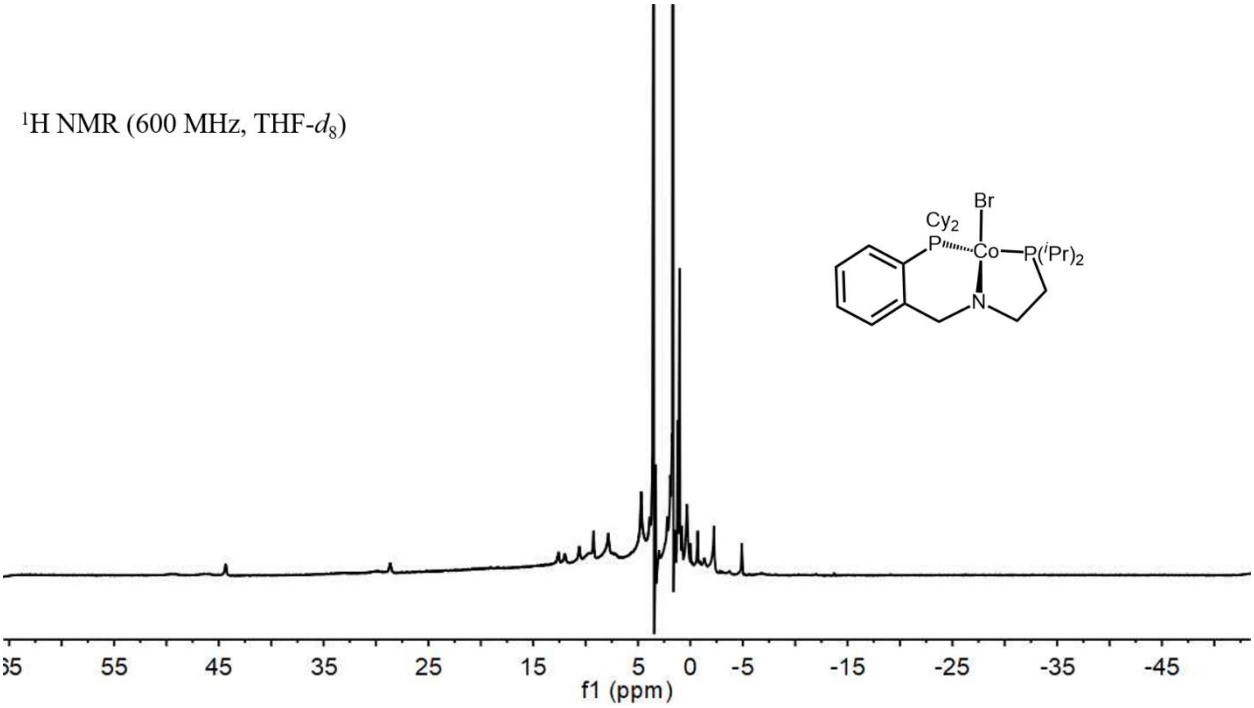
Proton NMR Spectra of Compound 1 in Different Chemical Shift Range:

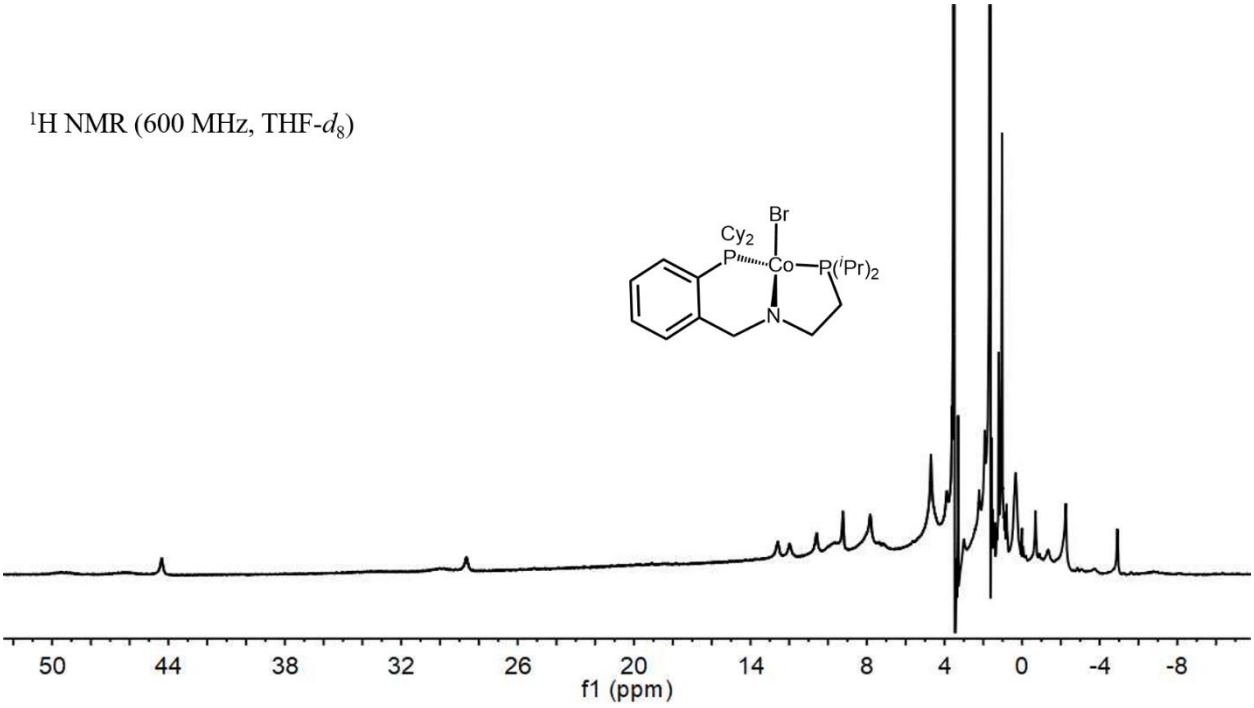
^{1}H NMR (600 MHz, THF-d_8)



^{1}H NMR (600 MHz, THF-d_8)

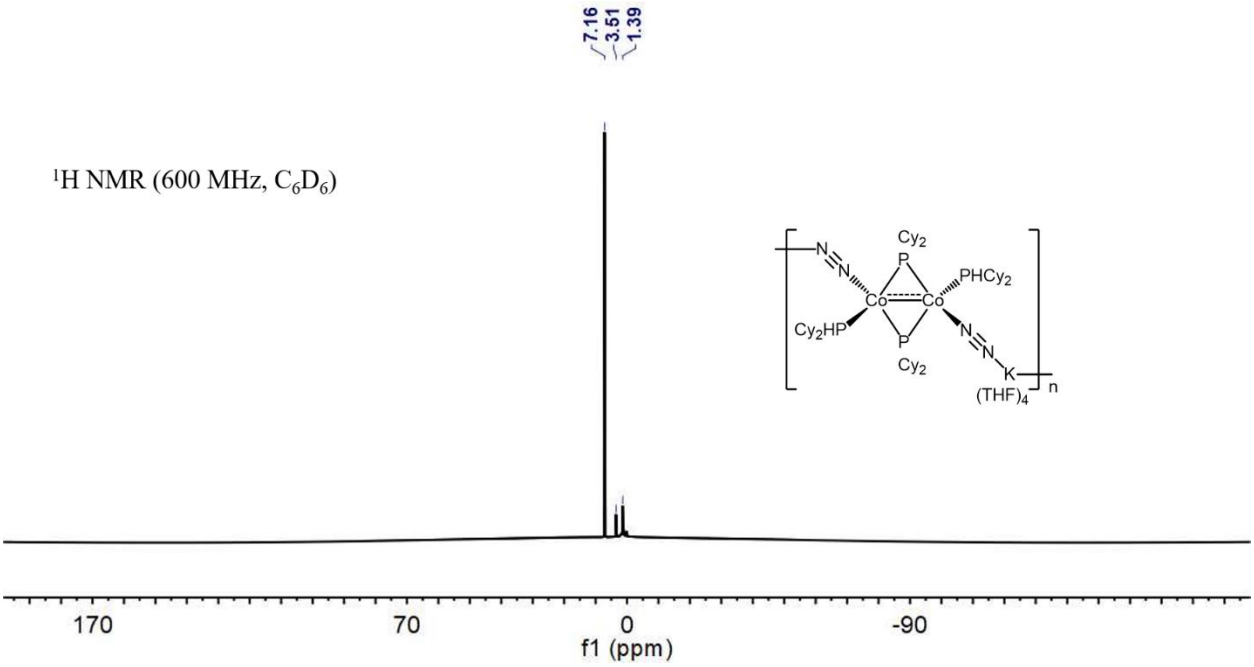




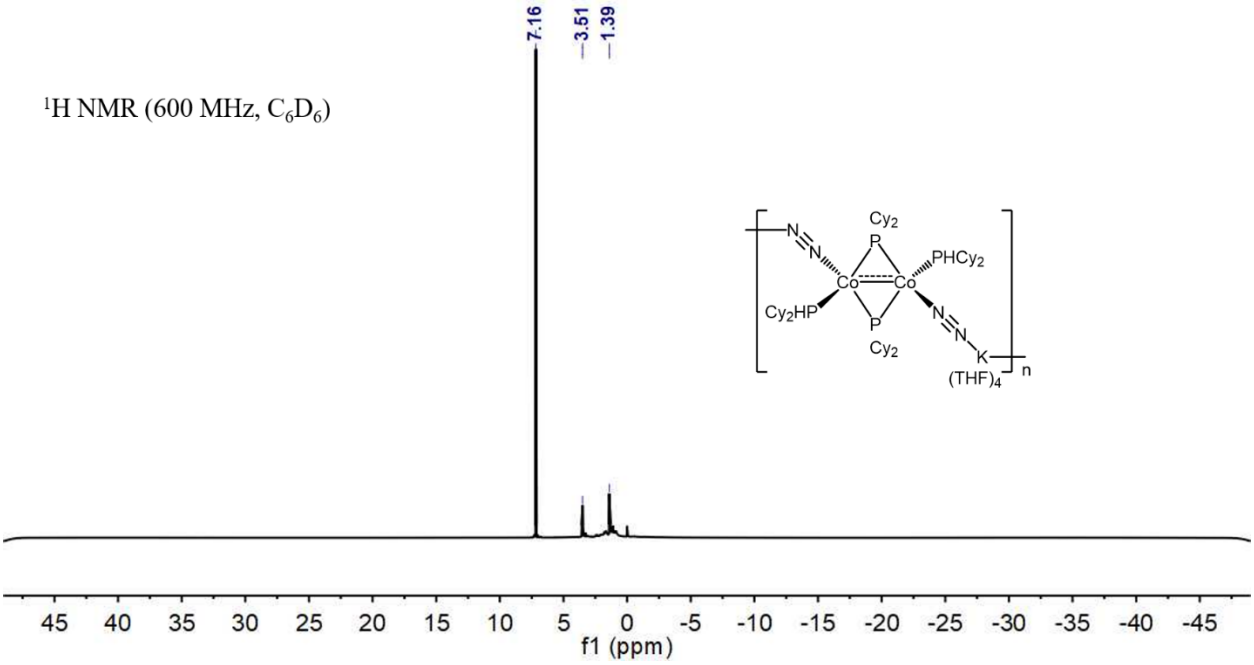


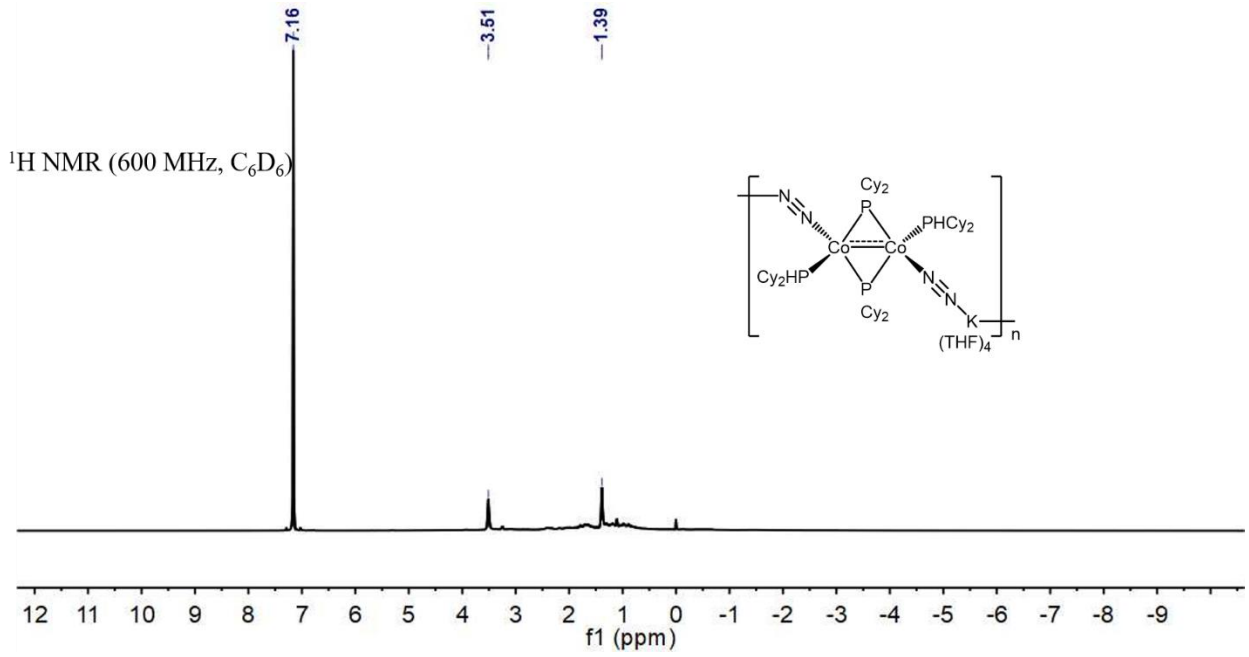
Proton NMR Spectra of Compound 2 in Different Chemical Shift Range:

^{1}H NMR (600 MHz, C_6D_6)



^{1}H NMR (600 MHz, C_6D_6)





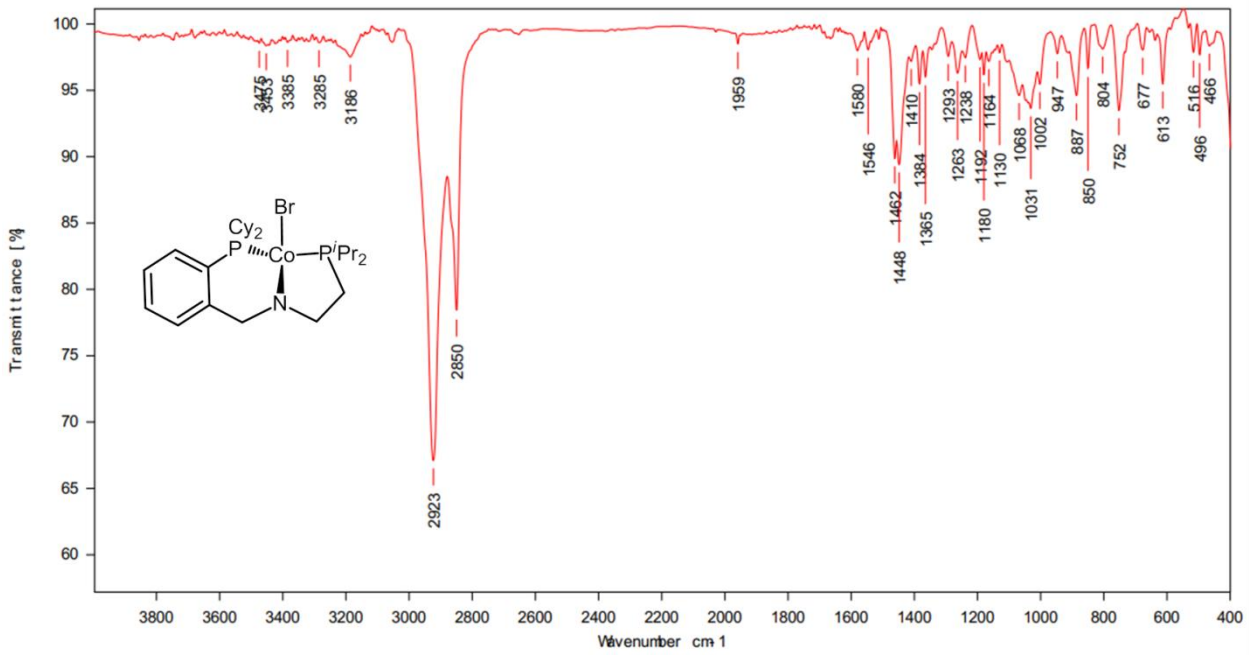


Figure S3. IR spectrum of **1**

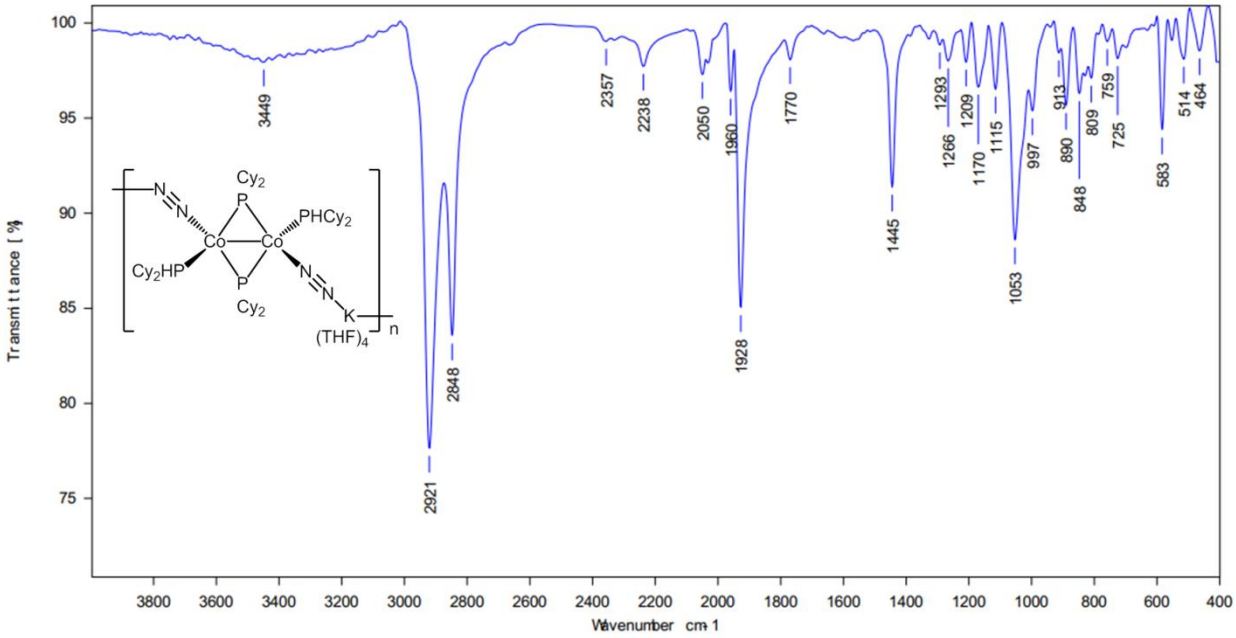


Figure S4. IR spectrum of **2**

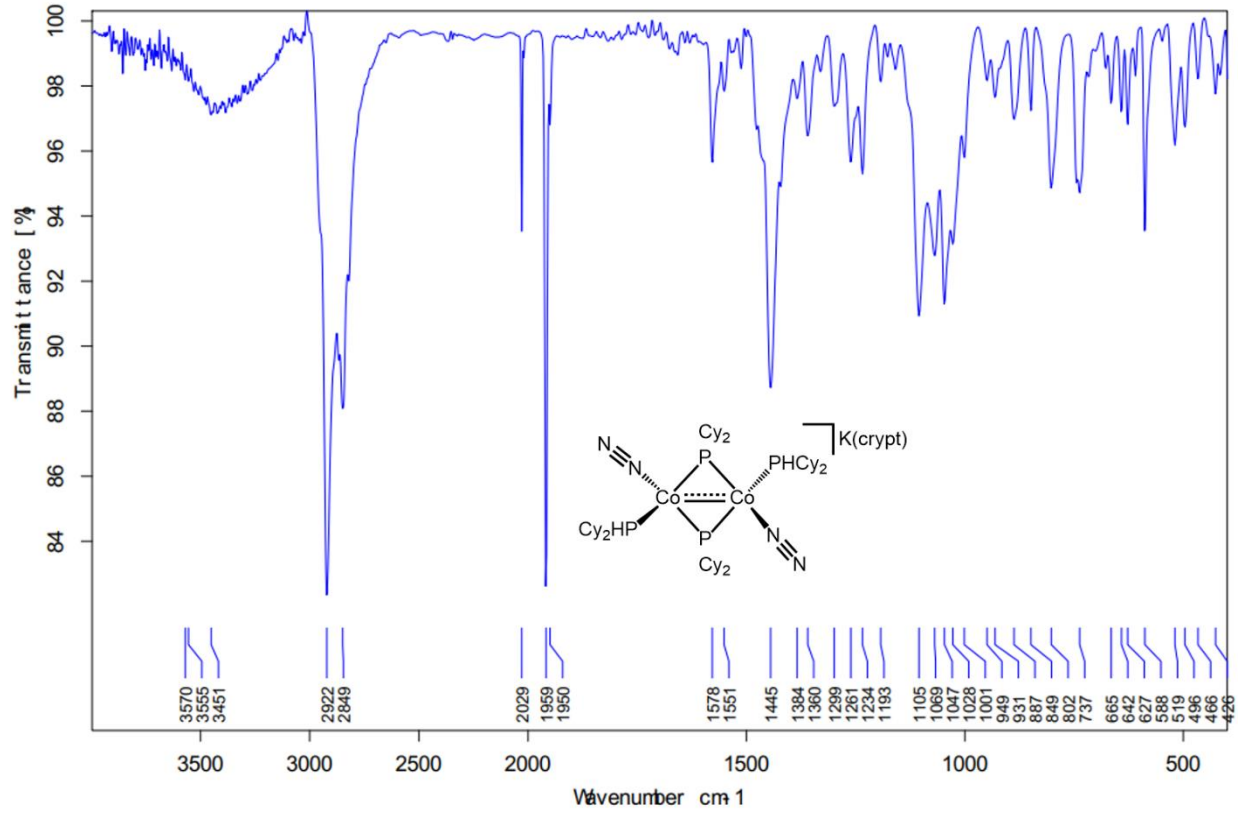


Figure S5. IR spectrum of **3**

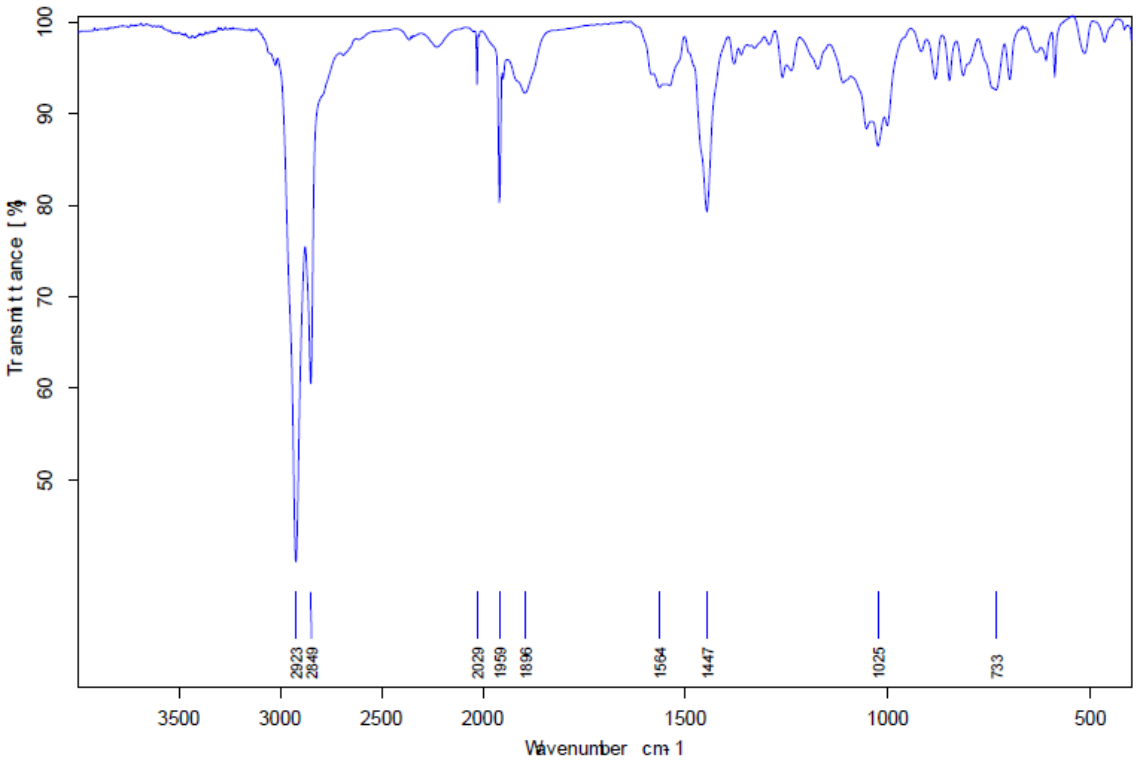


Figure S6. The *in-situ* IR spectrum of ^{15}N-**2**

When a single electron oxidizer, $[Cp_2Fe][BAr_4^F]$ (Ar^F = 3,5-bis(trifluoromethyl)benzene), was added to the THF solution of the dinuclear Co-N_2 anion complex **2** at room temperature and stirred for three hours, a new vibrational peak at 2061 cm^{-1} could be observed in the IR spectrum. It might be assigned to the $\nu_{N\equiv N}$ stretch in the corresponding neutral dicobalt-N_2 complex **4** (Figure S7). As a comparison, the FBO of the N–N bond in the corresponding neutral Co-N_2 complex **4** is 2.63. The calculated $\nu_{N\equiv N}$ stretches 4 is 2153 cm-1, which matches the experimental results.

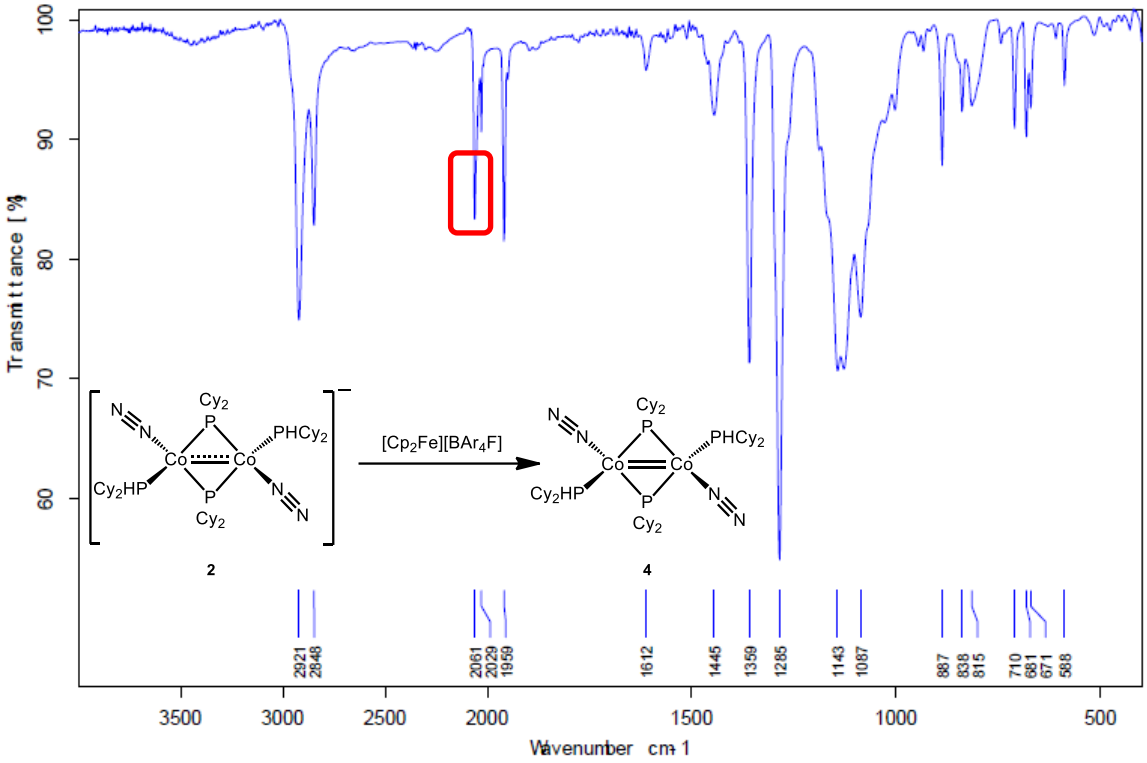


Figure S7. The *in-situ* IR spectrum of **2** + 1 eq. $[Cp_2Fe][BAr_4^F]$ (Ar^F = 3,5-bis(trifluoromethyl)benzene) in THF.

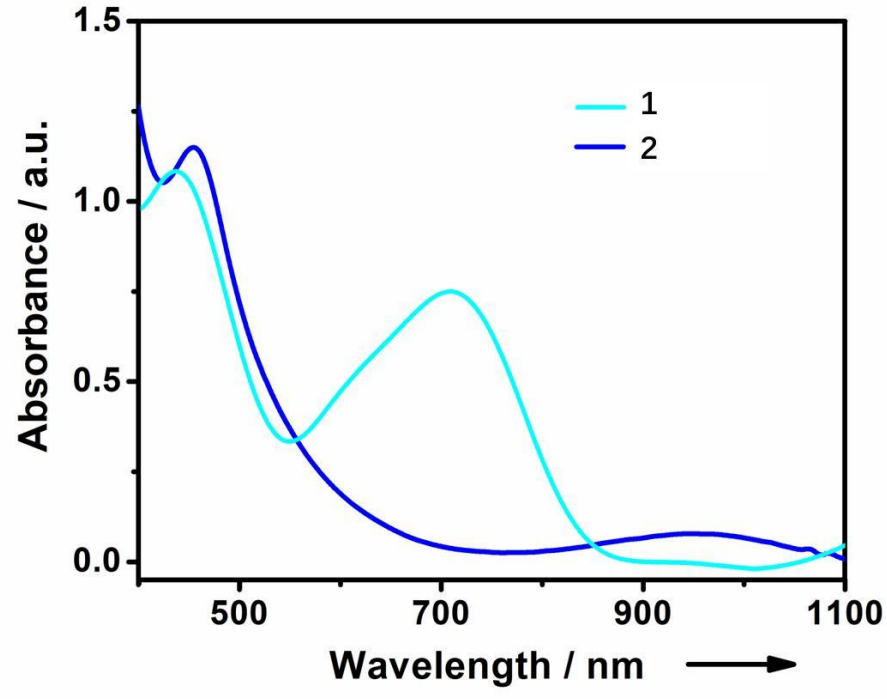


Figure S8. UV spectra of **1** and **2**

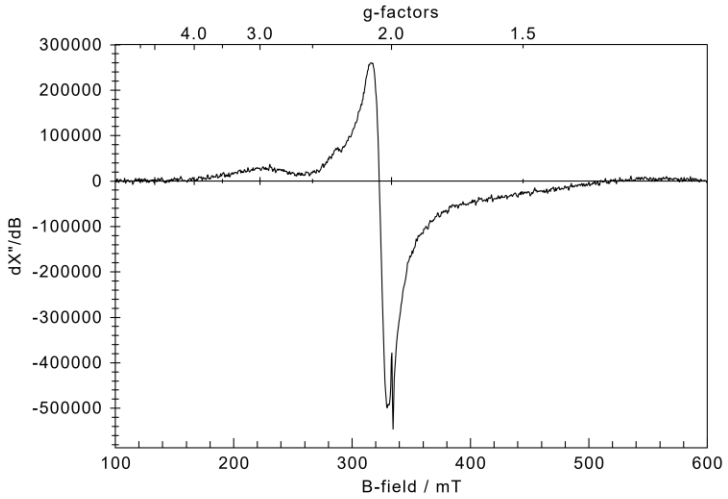


Figure S9. The EPR spectra of **2** in solid state at room temperature.

S3. Catalytic Reduction of Molecular Dinitrogen into Silyamine

General procedure

Under an atmosphere of nitrogen, to a suspension of KC_8 (270 mg, 2 mmol) in THF (10 mL) were added Me_3SiX (X = Cl/I, 2 mmol) and catalyst (0.001 mmol). The mixture was stirred at room temperature for 36 h. To the reaction mixture, dodecane (11 μL, 0.05 mmol) was added as an internal standard for gas-liquid chromatography (GC) analysis. After stirring for 5 minutes, the mixture was centrifuged to remove insoluble materials. The resultant clear supernatant was subjected to GC analyses. Yields were the averaged data of two independent runs.

The reactions with Et_2O as the solvent or the K as the reductant were performed in a similar process. The reaction with 10,000 equiv. of reductants was performed with a catalyst amount of 0.3 μmol.

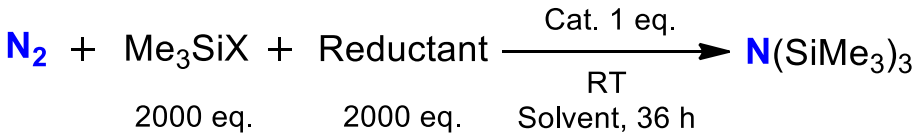


Table S1. Catalytic N_2 silylation with Me_3SiX (X = Cl/I) and KC_8 after 36 h.

Entry	Cat.	Me_3SiX	Reductant	Solvent	Yield based on cat. (eq.)	Yield based on e^- (%)
1	**2**	Me_3SiI	KC_8	THF	28.8	4.3
2	**2**	Me_3SiCl	KC_8	THF	**87.2**	**13.1**

3	**2**	Me_3SiCl	K	THF	84.3	12.6
4	**2**	Me_3SiCl	KC_8	Et_2O	2.6	0.4
5	**1**	Me_3SiCl	KC_8	THF	69.7	10.5

Table S2. Catalytic N_2 silylation with Me_3SiCl and KC_8 with different time points and solvents.

Entry	**Cat.**	**Me_3SiX**	**Reductant**	**Equiv.**	**Solvent**	**Time**	**Yield based on cat. (eq.)**
1	**CoNNK**	Me_3SiCl	KC_8	2000	THF	12 h	51.8
2	**CoNNK**	Me_3SiCl	KC_8	2000	THF	24 h	77.4
3	**CoNNK**	Me_3SiCl	KC_8	2000	THF	36 h	84.2
4	**CoNNK**	Me_3SiCl	KC_8	2000	THF	48 h	84.1
5	**CoNNK**	Me_3SiCl	KC_8	10000	Et_2O	42 h	87.1
6	**CoNNK**	Me_3SiCl	KC_8	10000	Et_2O	66 h	85.7

S4. X-Ray Crystal Structure Data

	Compound 1	**Compound 2**$(THF)_3$	**Compound 3**$(Et_2O)_3$
CCDC No.	2193855	2193856	2193857
Formula	$C_{27}H_{46}BrCoNP_2$	$C_{60}H_{114}Co_2KN_4O_3P_4$	$C_{78}H_{156}Co_2KN_6O_9P_4$
Formula weight	585.43	1220.39	1602.92
Temp. (K)	179.99(10)	180.00(10)	120.00(10)
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$I2/a$	$C2/c$
a (Å)	9.8615(3)	24.7989(7)	28.9250(7)
b (Å)	15.4191(4)	13.3737(3)	18.5369(4)
c (Å)	19.5790(5)	22.8232(6)	17.6376(4)
α(°)	90	90	90
β(°)	101.827(2)	117.199(4)	103.471(2)
γ(°)	90	90	90
V [Å^3]	2913.89(14)	6732.4(4)	9196.7(4)
Z	4	4	4
ρ_{calcd}(g·cm^{-3})	1.334	1.204	1.158
μ(mm^{-1})	2.085	0.692	0.527
F(000)	1228.0	2636.0	3484.0
Collected data	25300	25916	33343
Unique data	6627 [R(int) = 0.0232]	7712 [R(int) = 0.0250]	10505 [R(int) = 0.0217]
GOF on F^2	1.039	1.052	1.067
Final R indexes [I > 2σ(I)]	R_1 = 0.0275 ωR_2 = 0.0648	R_1 = 0.0482 0.1314	R_1 = 0.0419 ωR_2 = 0.1071
R indexes (all data)	R_1 = 0.0362 ωR_2 = 0.0675	R_1 = 0.0587 ωR_2 = 0.1375	R_1 = 0.0506 ωR_2 = 0.1121
Completeness	0.992	0.998	0.996

S5. Calculations

In our system, the energy difference for the doublet and quartet states is significant (23.3

kcal/mol), thus, the ground state of **3** should be doublet. We tried to investigate the electronic structure of **3** with several different broken symmetry states by employing the TPSSh/def2SVP level with Gaussian 16. However, the final converged results are the same regardless of the initial guess used (<S2> = 0.81). Thus, our calculation in this manuscript is reasonable.

We performed the AdNDP analysis for the α and β orbitals separately. To make it clear, the 2c1e Co-Co bond (α), 2c1e Co-Co bond (β), and 6c1e bond (β) were shown in figure S9. The shapes of the Co-Co (α) and Co-Co (β) 2c1e bonds match perfectly. Thus, we think there is a 2c2e Co-Co bond in complex **3**. The remaining 6c1e bond (β) could be regarded as a delocalized metal-ligand pi-type bond. However, the overlap between the two Co centers cannot be ignored. The FBO of the Co-Co bond was 0.38 (α spin) and 0.60 (β spin), respectively.

****

Input file of 3

```
! r2SCAN-3c SlowConv opt freq tightSCF noautostart miniprint nopop
%maxcore    9000
%pal nprocs      16 end
* xyz      -1      2
Co       -1.13262400     -0.22880300     -0.44930200
P        -0.32500800      1.75975300     -0.06936400
P        -3.04842000     -0.41590500      0.53663600
N        -1.60132000     -0.37527100     -2.16631500
N        -1.88935800     -0.46073200     -3.25624300
C        -0.27838500      2.96470200     -1.53072800
H         0.23529800      3.88520200     -1.20261600
C        -0.87432500      2.98124300      1.27531500
H        -1.68347500      3.60839300      0.86208000
C        -1.41777200      2.26617500      2.51555900
H        -2.25388900      1.61639100      2.24214600
H        -0.63913600      1.60697000      2.91984000
C        -4.22519000      1.05450900      0.36326600
H        -3.54170200      1.91539100      0.43249800
C        -4.19770000     -1.88743700      0.20733400
H        -5.22788400     -1.58518700      0.45941500
C         0.50640700      2.38062700     -2.70821000
H         0.03262100      1.44457500     -3.02730000
H         1.51660700      2.11599700     -2.38510600
```

C	-4.14284000	-2.31522200	-1.26420800
H	-3.10079800	-2.56338700	-1.50289900
H	-4.41571700	-1.48886300	-1.92854200
C	-5.66862600	2.42546600	-1.18612200
H	-4.96719900	3.27174400	-1.14294800
H	-6.14485000	2.45748500	-2.17501200
C	0.55811200	3.35369700	-3.88965000
H	1.10528300	4.26180500	-3.58990200
H	1.11704900	2.90623500	-4.72287900
C	-4.88289000	1.12112100	-1.01911800
H	-5.57685900	0.27538400	-1.13613700
H	-4.12177000	1.02740500	-1.80287000
C	-1.69181500	3.34735500	-1.99703500
H	-2.26866800	3.78661300	-1.17317200
H	-2.21499700	2.42747400	-2.29342800
C	-5.03428100	-3.53001800	-1.53715900
H	-6.08687500	-3.26430800	-1.35207300
H	-4.95974300	-3.81512700	-2.59478300
C	-6.71962300	2.57768400	-0.08371100
H	-7.25856100	3.52817300	-0.19402100
H	-7.46607200	1.77529900	-0.18811700
C	-1.86221500	3.26081000	3.59322100
H	-2.70375800	3.85886600	3.20865400
H	-2.23393300	2.71989000	4.47419900
C	-6.08029800	2.48706100	1.30423800
H	-6.84899100	2.56168900	2.08542900
H	-5.40095000	3.34118400	1.44389100
C	-0.85061100	3.74126000	-4.34551600
H	-1.36135800	2.84196800	-4.72033600
H	-0.80628700	4.45803400	-5.17724800
C	-5.27712900	1.19040300	1.46832400
H	-4.79310300	1.17346300	2.45357600
H	-5.96412000	0.33103300	1.43619300
C	0.27906800	3.90712400	1.69330600
H	1.08730100	3.28045300	2.09481000
H	0.69156900	4.43474900	0.82412500
C	-0.71994000	4.19818900	3.99035200
H	0.08147200	3.60437800	4.45422600
H	-1.05880400	4.92526300	4.74125300
C	-3.81174200	-3.07552100	1.09905400
H	-2.76176000	-3.33518300	0.89583600

H	-3.87068600	-2.79367000	2.15841700
C	-4.64700300	-4.70678100	-0.64056900
H	-5.30422000	-5.56772600	-0.82310600
H	-3.62403600	-5.02390200	-0.89269800
C	-0.15621800	4.91582200	2.76227700
H	0.69193500	5.55333700	3.04860800
H	-0.92797300	5.58014200	2.34352300
C	-1.65759500	4.32029200	-3.18155900
H	-2.68089100	4.55580200	-3.50629000
H	-1.19888300	5.26811400	-2.85955200
C	-4.69349000	-4.29966600	0.83304000
H	-4.37526000	-5.13463400	1.47175400
H	-5.73295800	-4.06511300	1.10993200
H	-3.12696900	-0.49640800	1.95953700
Co	1.13352400	0.22985500	0.45059400
P	0.32592700	-1.75865300	0.07033900
P	3.04968500	0.41739500	-0.53456500
N	1.60138400	0.37600600	2.16784700
N	1.88880300	0.46098400	3.25797500
C	0.27898200	-2.96397800	1.53138800
H	-0.23433200	-3.88450100	1.20275400
C	0.87569600	-2.97962300	-1.27460400
H	1.68452300	-3.60711000	-0.86125500
C	1.41999500	-2.26391600	-2.51411400
H	2.25589600	-1.61423000	-2.23979300
H	0.64161500	-1.60451800	-2.91856900
C	4.22668900	-1.05276600	-0.36081600
H	3.54342700	-1.91376100	-0.43086400
C	4.19842100	1.88928900	-0.20510100
H	5.22864300	1.58767900	-0.45779100
C	-0.50658800	-2.38054700	2.70867000
H	-0.03308100	-1.44466700	3.02859600
H	-1.51660900	-2.11579800	2.38510300
C	4.14395100	2.31648500	1.26662100
H	3.10185200	2.56385200	1.50589300
H	4.41771800	1.49006300	1.93051700
C	5.66921700	-2.42396400	1.18919400
H	4.96799500	-3.27036600	1.14516700
H	6.14468400	-2.45624800	2.17844100
C	-0.55891800	-3.35425800	3.88955100
H	-1.10569600	-4.26232100	3.58895000

H	-1.11850800	-2.90735500	4.72264200
C	4.88335100	-1.11971600	1.02204300
H	5.57706800	-0.27388500	1.13988100
H	4.12159600	-1.02641400	1.80523500
C	1.69223100	-3.34646200	1.99838000
H	2.26971400	-3.78524100	1.17470400
H	2.21499100	-2.42656500	2.29548400
C	5.03463400	3.53182700	1.53962200
H	6.08733500	3.26700500	1.35388200
H	4.96041400	3.81644100	2.59740100
C	6.72109700	-2.57556300	0.08753800
H	7.26014100	-3.52598300	0.19791700
H	7.46730200	-1.77306500	0.19281800
C	1.86510900	-3.25800600	-3.59199800
H	2.70633800	-3.85634000	-3.20717700
H	2.23747500	-2.71665000	-4.47243500
C	6.08282700	-2.48456400	-1.30087300
H	6.85214000	-2.55874900	-2.08149600
H	5.40376700	-3.33877900	-1.44136000
C	0.84959200	-3.74173600	4.34616000
H	1.35985200	-2.84251800	4.72182000
H	0.80489000	-4.45897200	5.17747300
C	5.27950700	-1.18801900	-1.46511100
H	4.79623100	-1.17083100	-2.45072600
H	5.96627500	-0.32850200	-1.43212400
C	-0.27754300	-3.90512400	-1.69383000
H	-1.08547400	-3.27815600	-2.09547500
H	-0.69062400	-4.43324900	-0.82522800
C	0.72300800	-4.19506100	-3.99039300
H	-0.07801300	-3.60092800	-4.45453100
H	1.06229900	-4.92180500	-4.74142100
C	3.81126300	3.07743300	-1.09624500
H	2.76111300	3.33612300	-0.89262600
H	3.87013300	2.79602500	-2.15572800
C	4.64597800	4.70865500	0.64371500
H	5.30259000	5.57005300	0.82629200
H	3.62287800	5.02484400	0.89647500
C	0.15835000	-4.91326600	-2.76308100
H	-0.68966700	-5.55054200	-3.05034300
H	0.92974900	-5.57788800	-2.34414700
C	1.65751900	-4.31994100	3.18244700

H	2.68067100	-4.55530900	3.50774000
H	1.19930600	-5.26774500	2.85967700
C	4.69211800	4.30218700	-0.83008100
H	4.37291900	5.13715700	-1.46830900
H	5.73166000	4.06861200	-1.10752200
H	3.12861900	0.49786700	-1.95744900

*

****

Optimized geometry of 3

CARTESIAN COORDINATES (ANGSTROEM)

Co	-1.131616	-0.234854	-0.451281
P	-0.325154	1.754355	-0.072436
P	-3.046780	-0.422057	0.536234
N	-1.601673	-0.382753	-2.167746
N	-1.890663	-0.469375	-3.257321
C	-0.279474	2.958500	-1.534506
H	0.237923	3.877620	-1.208352
C	-0.873781	2.976461	1.272042
H	-1.688022	3.598646	0.861289
C	-1.407383	2.261830	2.516808
H	-2.241994	1.607706	2.249363
H	-0.623618	1.607021	2.918388
C	-4.218394	1.053209	0.372002
H	-3.530183	1.911095	0.431253
C	-4.204110	-1.885003	0.197294
H	-5.233835	-1.575033	0.441661
C	0.499522	2.371413	-2.714362
H	0.021404	1.436933	-3.031658
H	1.509702	2.103257	-2.394502
C	-4.142100	-2.310391	-1.274489
H	-3.100264	-2.565829	-1.506349
H	-4.404227	-1.480410	-1.938943
C	-5.672595	2.425262	-1.166166
H	-4.967005	3.268542	-1.133683
H	-6.159572	2.456012	-2.149843
C	0.550769	3.343990	-3.896214
H	1.101856	4.250375	-3.598412

H	1.105619	2.894483	-4.731072
C	-4.890723	1.118053	-1.003356
H	-5.589444	0.274740	-1.110178
H	-4.138469	1.018543	-1.794876
C	-1.693135	3.345295	-1.996534
H	-2.266146	3.786521	-1.171053
H	-2.219950	2.426908	-2.291073
C	-5.041112	-3.517677	-1.556000
H	-6.092882	-3.243660	-1.378578
H	-4.960836	-3.801924	-2.613441
C	-6.710604	2.586080	-0.052691
H	-7.246355	3.538678	-0.160305
H	-7.461855	1.786830	-0.146087
C	-1.850677	3.256819	3.594642
H	-2.697097	3.850020	3.213291
H	-2.215086	2.716151	4.478824
C	-6.056445	2.497172	1.328468
H	-6.816143	2.577917	2.117810
H	-5.371698	3.348606	1.457775
C	-0.858109	3.736011	-4.347765
H	-1.372907	2.838293	-4.720811
H	-0.814102	4.452479	-5.179777
C	-5.257547	1.197321	1.488018
H	-4.762903	1.181118	2.468005
H	-5.948915	0.341154	1.466047
C	0.277172	3.909086	1.681785
H	1.090652	3.287414	2.080388
H	0.682398	4.436747	0.809210
C	-0.710787	4.200500	3.983505
H	0.095991	3.611559	4.444274
H	-1.049034	4.927597	4.734660
C	-3.834432	-3.077478	1.090048
H	-2.785312	-3.345888	0.894073
H	-3.898650	-2.796701	2.149385
C	-4.670521	-4.698885	-0.658151
H	-5.333495	-5.554043	-0.846962
H	-3.648421	-5.024242	-0.902882
C	-0.157274	4.918091	2.750796
H	0.689297	5.560381	3.031095
H	-0.934531	5.577680	2.334750
C	-1.659603	4.317828	-3.181418

H	-2.683165	4.556481	-3.503001
H	-1.196902	5.264274	-2.861074
C	-4.724634	-4.293609	0.815687
H	-4.418372	-5.132233	1.455459
H	-5.764077	-4.050488	1.085159
H	-3.124449	-0.511102	1.958653
Co	1.134439	0.225546	0.448250
P	0.328629	-1.763555	0.067197
P	3.051341	0.414873	-0.535486
N	1.601845	0.372437	2.165597
N	1.889090	0.458024	3.255710
C	0.281435	-2.970192	1.527236
H	-0.225934	-3.892975	1.195644
C	0.879487	-2.982639	-1.279169
H	1.687188	-3.611383	-0.865598
C	1.426098	-2.264862	-2.516494
H	2.261221	-1.615472	-2.239600
H	0.648326	-1.604948	-2.921398
C	4.232289	-1.050872	-0.353476
H	3.551928	-1.914208	-0.422352
C	4.197069	1.889540	-0.208335
H	5.227548	1.590348	-0.462892
C	-0.512433	-2.391486	2.701303
H	-0.044288	-1.454253	3.024873
H	-1.521848	-2.130229	2.373129
C	4.144690	2.315084	1.263814
H	3.102284	2.558527	1.505816
H	4.423050	1.488681	1.926108
C	5.674919	-2.411171	1.205884
H	4.976712	-3.260112	1.163047
H	6.147625	-2.438084	2.196615
C	-0.566596	-3.367003	3.880573
H	-1.107537	-4.277204	3.575879
H	-1.132644	-2.923820	4.711278
C	4.885014	-1.110287	1.031546
H	5.575270	-0.261384	1.148550
H	4.120416	-1.016959	1.811968
C	1.694171	-3.346036	2.001072
H	2.278175	-3.781072	1.180070
H	2.210659	-2.423787	2.301892
C	5.031889	3.533133	1.536112

H	6.085047	3.271981	1.347866
H	4.958977	3.816490	2.594321
C	6.730438	-2.563466	0.107792
H	7.272253	-3.511697	0.223296
H	7.473729	-1.758156	0.212184
C	1.873583	-3.257057	-3.595113
H	2.714093	-3.855929	-3.209555
H	2.247691	-2.714196	-4.473885
C	6.095910	-2.479737	-1.282811
H	6.867726	-2.554214	-2.060931
H	5.420082	-3.336701	-1.422140
C	0.841312	-3.748406	4.344093
H	1.345215	-2.847288	4.723760
H	0.795685	-4.467054	5.174134
C	5.288841	-1.186456	-1.454092
H	4.808524	-1.174244	-2.441228
H	5.972694	-0.324574	-1.421967
C	-0.273034	-3.907241	-1.702296
H	-1.080076	-3.279636	-2.104631
H	-0.687909	-4.436871	-0.835451
C	0.732430	-4.193536	-3.997345
H	-0.067650	-3.598745	-4.462258
H	1.073327	-4.919118	-4.748766
C	3.805119	3.077296	-1.098011
H	2.754519	3.332713	-0.892782
H	3.863370	2.796934	-2.157796
C	4.637523	4.709481	0.642107
H	5.291439	5.572986	0.824386
H	3.613756	5.021828	0.896949
C	0.165251	-4.913640	-2.772332
H	-0.681902	-5.550662	-3.062583
H	0.935873	-5.578782	-2.352792
C	1.658208	-4.321027	3.183884
H	2.680818	-4.551654	3.514241
H	1.206484	-5.270730	2.857576
C	4.682553	4.304549	-0.832131
H	4.359665	5.139087	-1.469060
H	5.722369	4.074504	-1.111480
H	3.132270	0.490365	-1.958513

Optimized geometry of Jones-Co-N2-PtBu

CARTESIAN COORDINATES (ANGSTROEM)

Co	-1.119635	-0.211751	-0.258140
N	-1.920844	-0.381601	-1.830321
N	-2.406915	-0.487889	-2.838110
P	0.327898	-1.845810	0.088736
P	-0.333142	1.844197	-0.066921
Co	1.113557	0.210737	0.282126
N	1.909921	0.379194	1.856779
N	2.393288	0.485721	2.865851
C	0.618278	-3.003751	-1.421821
C	1.687117	-4.083617	-1.213200
H	1.892413	-4.575046	-2.174302
H	2.628400	-3.661250	-0.847106
H	1.365851	-4.861863	-0.516938
C	1.088177	-2.104056	-2.572003
H	0.418022	-1.256047	-2.735067
H	2.086911	-1.709899	-2.364515
H	1.138580	-2.689549	-3.499954
C	-0.701556	-3.672790	-1.840400
H	-0.532272	-4.282448	-2.739167
H	-1.099990	-4.329768	-1.063796
H	-1.465200	-2.929420	-2.077904
C	0.354379	-2.925308	1.679973
C	-0.101032	-2.022807	2.838953
H	-0.927728	-1.373627	2.550659
H	-0.419436	-2.646125	3.685320
H	0.709965	-1.385402	3.191380
C	-0.600358	-4.122933	1.594944
H	-0.612510	-4.649527	2.559091
H	-1.624936	-3.802148	1.375477
H	-0.300182	-4.846754	0.833754
C	1.772705	-3.411099	2.022813
H	2.134262	-4.192473	1.352969
H	2.483823	-2.578608	1.998798
H	1.774342	-3.822974	3.041715
C	4.285524	-0.815997	-0.345160
H	4.289531	-1.052520	0.723307
H	3.962248	-1.709626	-0.886091

H	5.300809	-0.547868	-0.660142
C	4.023605	1.975050	0.085257
H	4.120282	1.839570	1.165899
H	5.024505	2.055004	-0.353848
H	3.477061	2.905915	-0.091264
C	-0.356159	2.920807	-1.660003
C	-0.624282	3.005433	1.440820
C	-4.289968	0.819741	0.370575
H	-3.966656	1.715300	0.908289
H	-4.294478	1.052704	-0.698678
H	-5.305148	0.552571	0.686649
C	-4.029149	-1.973102	-0.048650
H	-3.480476	-2.902708	0.128136
H	-5.028255	-2.053331	0.394455
H	-4.130077	-1.840731	-1.129301
P	-3.090739	-0.554206	0.680643
P	3.086520	0.559014	-0.651172
C	3.408967	0.904321	-2.443673
H	2.893731	0.192176	-3.092609
H	3.063236	1.910265	-2.695999
H	4.486970	0.845267	-2.631721
C	-3.410841	-0.893292	2.474728
H	-4.488147	-0.828522	2.664923
H	-3.070010	-1.900840	2.727494
H	-2.890681	-0.182926	3.121610
C	0.696359	3.672558	1.860192
H	0.525178	4.290098	2.753180
H	1.455410	2.927628	2.107309
H	1.101455	4.321533	1.080327
C	-1.097944	2.109635	2.592436
H	-2.100860	1.724333	2.388455
H	-0.434531	1.255749	2.752929
H	-1.140197	2.695368	3.520642
C	-1.690091	4.087588	1.228091
H	-1.897403	4.579658	2.188429
H	-1.364736	4.864999	0.532743
H	-2.631075	3.667254	0.858864
C	0.095977	2.013866	-2.816798
H	-0.716748	1.376932	-3.166166
H	0.414362	2.634192	-3.665400
H	0.921751	1.363838	-2.527760

C	0.602517	4.115452	-1.577621
H	1.625915	3.792154	-1.356412
H	0.617121	4.639258	-2.543284
H	0.303879	4.842538	-0.818952
C	-1.772719	3.410794	-2.004600
H	-2.487951	2.581938	-1.975591
H	-2.129779	4.197690	-1.338834
H	-1.773350	3.817119	-3.025714

****

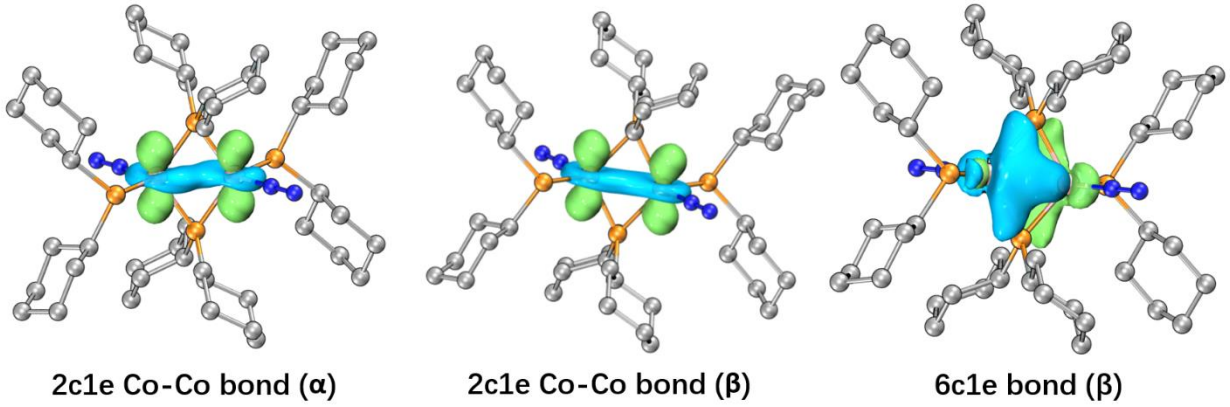
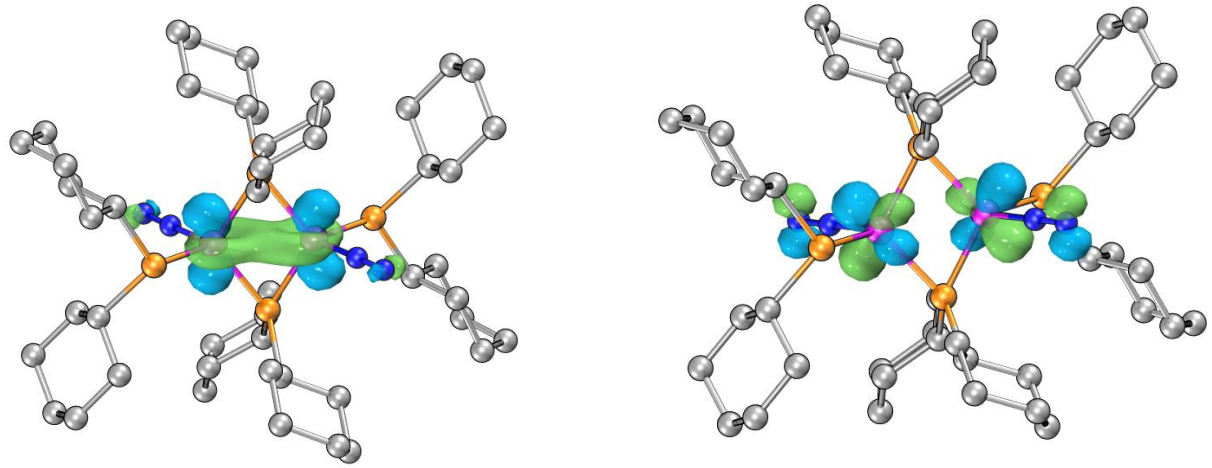
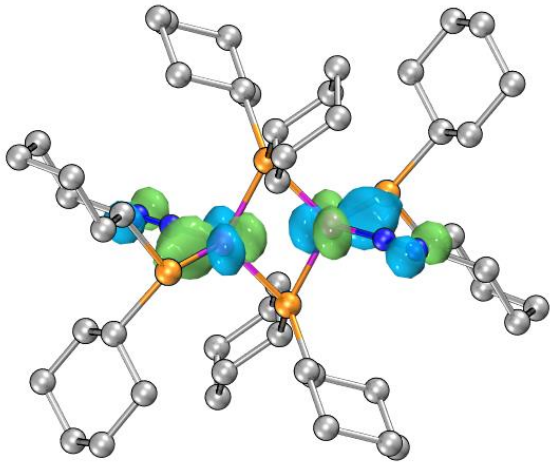
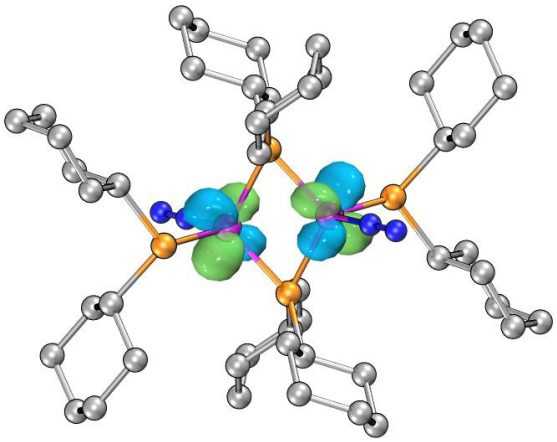


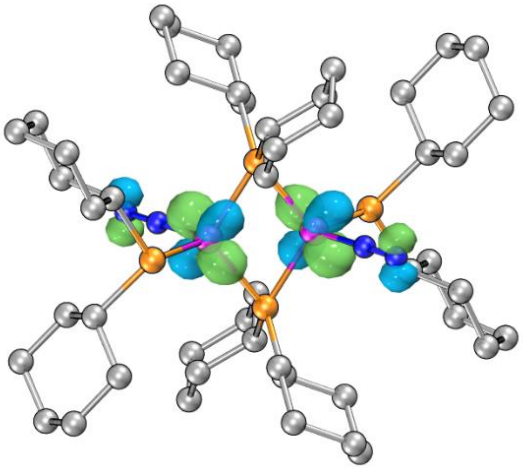
Figure S9. AdNDP analysis of **3**. 2c1e Co-Co bond (α), 2c1e Co-Co bond (β) and 6c1e bond (β) of **3**

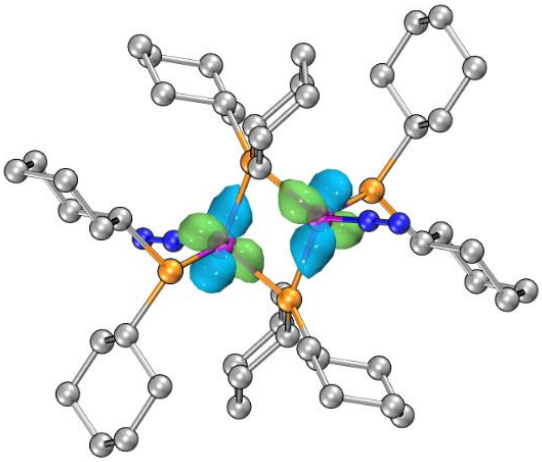
****

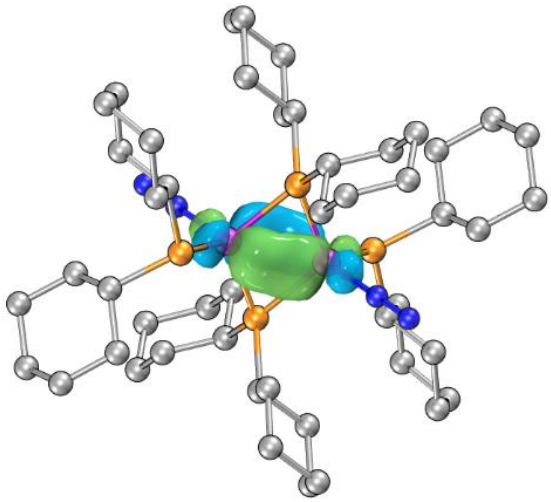


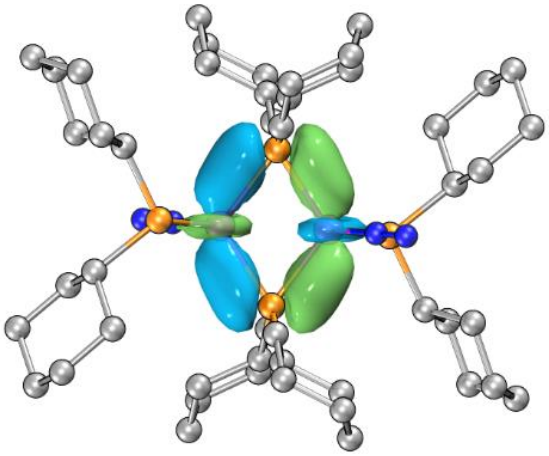












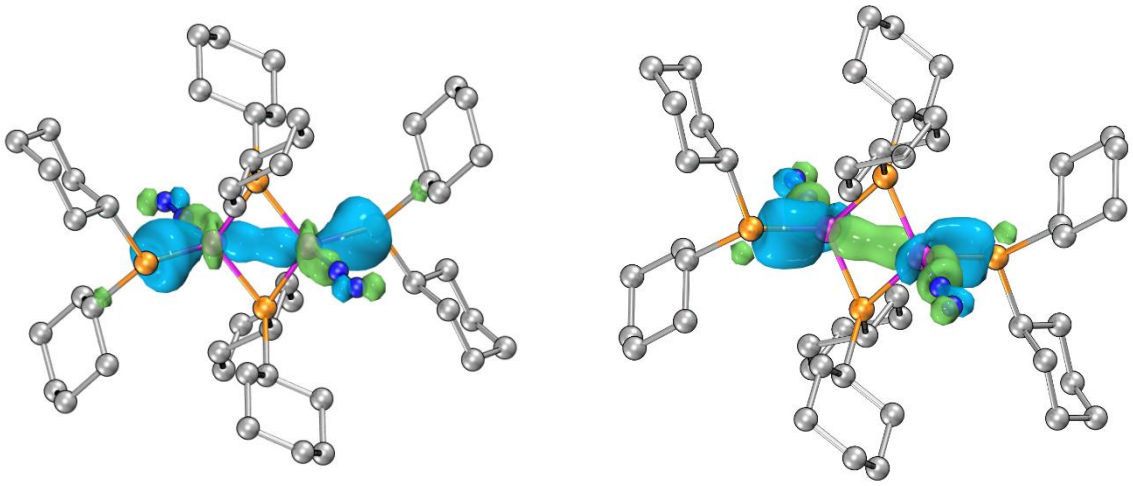
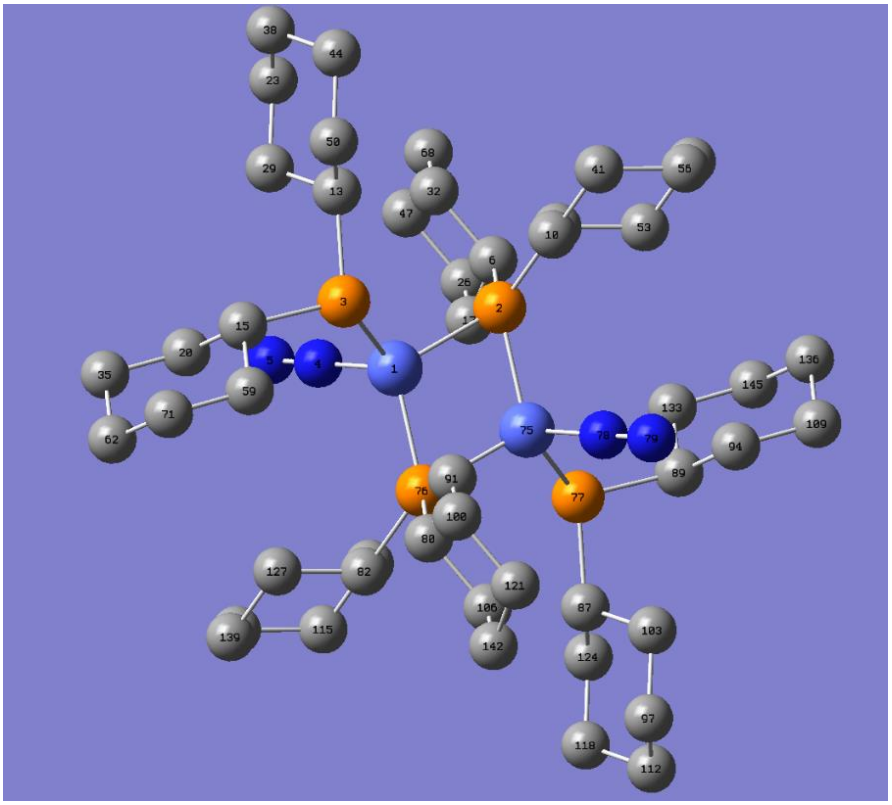


Figure S10. Frontier orbitals of **3** from SOMO-1 to SOMO-11. To pair the α and β orbitals generated by the open shell calculations, biorthogonalization was performed based on the canonical orbitals by the Multiwfn software.

****

Fuzzy atom bond order of 3



#	1:	1(Co)	2(P)	Alpha:	0.534476 Beta:	0.560523 Total: 1.094998
#	2:	1(Co)	3(P)	Alpha:	0.614181 Beta:	0.631830 Total: 1.246011
#	3:	1(Co)	4(N)	Alpha:	0.652178 Beta:	0.688630 Total: 1.340808
#	4:	1(Co)	5(N)	Alpha:	0.208497 Beta:	0.224766 Total: 0.433263
#	5:	1(Co)	13(C)	Alpha:	0.029459 Beta:	0.032099 Total: 0.061557
#	6:	1(Co)	15(C)	Alpha:	0.026812 Beta:	0.029264 Total: 0.056076
#	7:	1(Co)	74(H)	Alpha:	0.027109 Beta:	0.024450 Total: 0.051559
#	8:	1(Co)	75(Co)	Alpha:	0.378028 Beta:	0.600453 Total: 0.978480
#	9:	1(Co)	76(P)	Alpha:	0.541562 Beta:	0.565999 Total: 1.107561
#	10:	2(P)	3(P)	Alpha:	0.028806 Beta:	0.027972 Total: 0.056778
#	11:	2(P)	6(C)	Alpha:	0.503446 Beta:	0.500770 Total: 1.004217
#	12:	2(P)	7(H)	Alpha:	0.029405 Beta:	0.029119 Total: 0.058524
#	13:	2(P)	8(C)	Alpha:	0.503359 Beta:	0.500592 Total: 1.003951
#	14:	2(P)	9(H)	Alpha:	0.029312 Beta:	0.029041 Total: 0.058353
#	15:	2(P)	10(C)	Alpha:	0.055242 Beta:	0.055330 Total: 0.110572
#	16:	2(P)	17(C)	Alpha:	0.056957 Beta:	0.057067 Total: 0.114024
#	17:	2(P)	32(C)	Alpha:	0.060140 Beta:	0.060026 Total: 0.120166
#	18:	2(P)	53(C)	Alpha:	0.062375 Beta:	0.062240 Total: 0.124615
#	19:	2(P)	75(Co)	Alpha:	0.541499 Beta:	0.565946 Total: 1.107445
#	20:	2(P)	76(P)	Alpha:	0.040600 Beta:	0.031977 Total: 0.072577

```
#    21:    3(P )   13(C ) Alpha:    0.511774 Beta:    0.509968 Total:    1.021742
#    22:    3(P )   14(H ) Alpha:    0.032113 Beta:    0.032211 Total:    0.064324
#    23:    3(P )   15(C ) Alpha:    0.509590 Beta:    0.507797 Total:    1.017387
#    24:    3(P )   16(H ) Alpha:    0.027945 Beta:    0.027775 Total:    0.055720
#    25:    3(P )   20(C ) Alpha:    0.058774 Beta:    0.058835 Total:    0.117609
#    26:    3(P )   29(C ) Alpha:    0.058263 Beta:    0.058158 Total:    0.116421
#    27:    3(P )   50(C ) Alpha:    0.053052 Beta:    0.052376 Total:    0.105429
#    28:    3(P )   59(C ) Alpha:    0.062882 Beta:    0.062625 Total:    0.125507
#    29:    3(P )   74(H ) Alpha:    0.426857 Beta:    0.423390 Total:    0.850247
#    30:    4(N )    5(N ) Alpha:    1.305394 Beta:    1.281413 Total:    2.586807
#    31:    6(C )    7(H ) Alpha:    0.391000 Beta:    0.391592 Total:    0.782592
#    32:    6(C )   17(C ) Alpha:    0.512898 Beta:    0.513194 Total:    1.026093
#    33:    6(C )   26(C ) Alpha:    0.034955 Beta:    0.035041 Total:    0.069995
#    34:    6(C )   32(C ) Alpha:    0.513311 Beta:    0.514056 Total:    1.027367
#    35:    6(C )   68(C ) Alpha:    0.034408 Beta:    0.034498 Total:    0.068906
#    36:    8(C )    9(H ) Alpha:    0.390708 Beta:    0.391260 Total:    0.781969
#    37:    8(C )   10(C ) Alpha:    0.513920 Beta:    0.514223 Total:    1.028143
#    38:    8(C )   41(C ) Alpha:    0.034822 Beta:    0.034906 Total:    0.069727
#    39:    8(C )   53(C ) Alpha:    0.512853 Beta:    0.513621 Total:    1.026474
#    40:    8(C )   65(C ) Alpha:    0.034596 Beta:    0.034685 Total:    0.069281
#    41:   10(C )   11(H ) Alpha:    0.401546 Beta:    0.401416 Total:    0.802962
#    42:   10(C )   12(H ) Alpha:    0.400304 Beta:    0.400273 Total:    0.800577
#    43:   10(C )   41(C ) Alpha:    0.553808 Beta:    0.553799 Total:    1.107607
#    44:   10(C )   53(C ) Alpha:    0.035425 Beta:    0.035469 Total:    0.070894
#    45:   10(C )   56(C ) Alpha:    0.038586 Beta:    0.038585 Total:    0.077172
#    46:   13(C )   14(H ) Alpha:    0.380214 Beta:    0.380011 Total:    0.760225
#    47:   13(C )   23(C ) Alpha:    0.036192 Beta:    0.036220 Total:    0.072412
#    48:   13(C )   29(C ) Alpha:    0.515545 Beta:    0.515734 Total:    1.031279
#    49:   13(C )   44(C ) Alpha:    0.036577 Beta:    0.036637 Total:    0.073214
#    50:   13(C )   50(C ) Alpha:    0.524168 Beta:    0.524158 Total:    1.048326
#    51:   15(C )   16(H ) Alpha:    0.393480 Beta:    0.393384 Total:    0.786864
#    52:   15(C )   20(C ) Alpha:    0.514254 Beta:    0.514410 Total:    1.028664
#    53:   15(C )   35(C ) Alpha:    0.034980 Beta:    0.035018 Total:    0.069998
#    54:   15(C )   59(C ) Alpha:    0.517278 Beta:    0.517486 Total:    1.034763
#    55:   15(C )   71(C ) Alpha:    0.034913 Beta:    0.034956 Total:    0.069869
#    56:   17(C )   18(H ) Alpha:    0.398369 Beta:    0.398333 Total:    0.796702
#    57:   17(C )   19(H ) Alpha:    0.404522 Beta:    0.404368 Total:    0.808891
#    58:   17(C )   26(C ) Alpha:    0.552892 Beta:    0.552864 Total:    1.105756
#    59:   17(C )   32(C ) Alpha:    0.034740 Beta:    0.034780 Total:    0.069519
#    60:   17(C )   47(C ) Alpha:    0.038651 Beta:    0.038647 Total:    0.077298
#    61:   20(C )   21(H ) Alpha:    0.395291 Beta:    0.395183 Total:    0.790474
```

```
#    62:   20(C )   22(H ) Alpha:   0.408921 Beta:   0.408921 Total:   0.817842
#    63:   20(C )   35(C ) Alpha:   0.553555 Beta:   0.553583 Total:   1.107139
#    64:   20(C )   59(C ) Alpha:   0.035057 Beta:   0.035051 Total:   0.070108
#    65:   20(C )   62(C ) Alpha:   0.038908 Beta:   0.038907 Total:   0.077815
#    66:   23(C )   24(H ) Alpha:   0.420082 Beta:   0.420080 Total:   0.840162
#    67:   23(C )   25(H ) Alpha:   0.432509 Beta:   0.432525 Total:   0.865034
#    68:   23(C )   29(C ) Alpha:   0.553393 Beta:   0.553436 Total:   1.106828
#    69:   23(C )   38(C ) Alpha:   0.558534 Beta:   0.558530 Total:   1.117063
#    70:   23(C )   44(C ) Alpha:   0.039067 Beta:   0.039066 Total:   0.078133
#    71:   26(C )   27(H ) Alpha:   0.425361 Beta:   0.425392 Total:   0.850753
#    72:   26(C )   28(H ) Alpha:   0.431849 Beta:   0.431859 Total:   0.863708
#    73:   26(C )   47(C ) Alpha:   0.557634 Beta:   0.557624 Total:   1.115258
#    74:   26(C )   68(C ) Alpha:   0.039401 Beta:   0.039398 Total:   0.078799
#    75:   29(C )   30(H ) Alpha:   0.413015 Beta:   0.413022 Total:   0.826036
#    76:   29(C )   31(H ) Alpha:   0.406309 Beta:   0.406238 Total:   0.812547
#    77:   29(C )   38(C ) Alpha:   0.039072 Beta:   0.039072 Total:   0.078143
#    78:   29(C )   50(C ) Alpha:   0.034826 Beta:   0.034832 Total:   0.069658
#    79:   32(C )   33(H ) Alpha:   0.417639 Beta:   0.417629 Total:   0.835268
#    80:   32(C )   34(H ) Alpha:   0.402087 Beta:   0.402036 Total:   0.804123
#    81:   32(C )   47(C ) Alpha:   0.038559 Beta:   0.038563 Total:   0.077123
#    82:   32(C )   68(C ) Alpha:   0.554491 Beta:   0.554641 Total:   1.109131
#    83:   35(C )   36(H ) Alpha:   0.426450 Beta:   0.426475 Total:   0.852924
#    84:   35(C )   37(H ) Alpha:   0.431509 Beta:   0.431524 Total:   0.863033
#    85:   35(C )   62(C ) Alpha:   0.558240 Beta:   0.558236 Total:   1.116477
#    86:   35(C )   71(C ) Alpha:   0.039575 Beta:   0.039574 Total:   0.079150
#    87:   38(C )   39(H ) Alpha:   0.435128 Beta:   0.435115 Total:   0.870243
#    88:   38(C )   40(H ) Alpha:   0.426247 Beta:   0.426247 Total:   0.852494
#    89:   38(C )   44(C ) Alpha:   0.558535 Beta:   0.558507 Total:   1.117042
#    90:   38(C )   50(C ) Alpha:   0.038380 Beta:   0.038377 Total:   0.076757
#    91:   41(C )   42(H ) Alpha:   0.424714 Beta:   0.424744 Total:   0.849457
#    92:   41(C )   43(H ) Alpha:   0.431516 Beta:   0.431525 Total:   0.863041
#    93:   41(C )   56(C ) Alpha:   0.558281 Beta:   0.558272 Total:   1.116553
#    94:   41(C )   65(C ) Alpha:   0.039424 Beta:   0.039421 Total:   0.078845
#    95:   44(C )   45(H ) Alpha:   0.434208 Beta:   0.434214 Total:   0.868422
#    96:   44(C )   46(H ) Alpha:   0.424253 Beta:   0.424250 Total:   0.848503
#    97:   44(C )   50(C ) Alpha:   0.555197 Beta:   0.555211 Total:   1.110408
#    98:   47(C )   48(H ) Alpha:   0.421363 Beta:   0.421354 Total:   0.842717
#    99:   47(C )   49(H ) Alpha:   0.436121 Beta:   0.436120 Total:   0.872241
#   100:   47(C )   68(C ) Alpha:   0.558107 Beta:   0.558117 Total:   1.116224
#   101:   50(C )   51(H ) Alpha:   0.423374 Beta:   0.423295 Total:   0.846669
#   102:   50(C )   52(H ) Alpha:   0.419311 Beta:   0.419324 Total:   0.838634
```

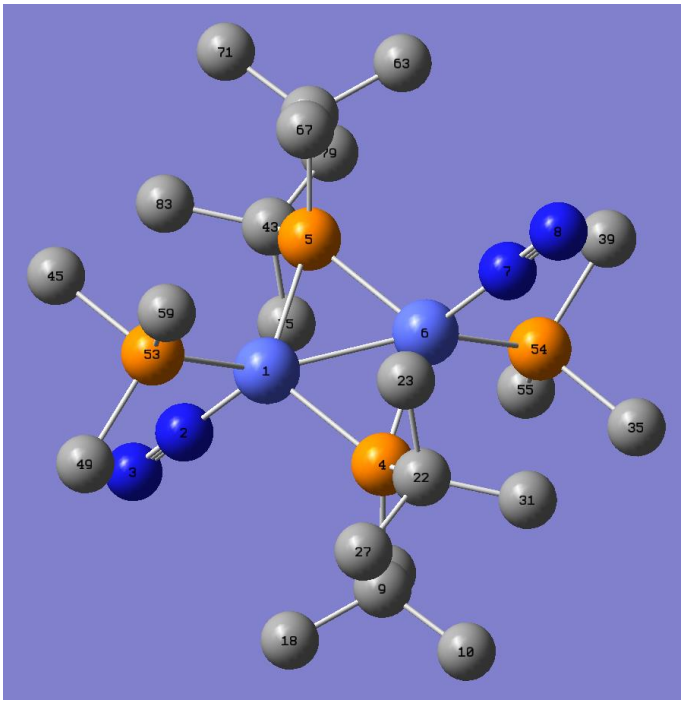
```
#   103:    53(C )    54(H ) Alpha:    0.403176 Beta:    0.403124 Total:    0.806300
#   104:    53(C )    55(H ) Alpha:    0.417983 Beta:    0.417969 Total:    0.835952
#   105:    53(C )    56(C ) Alpha:    0.038951 Beta:    0.038955 Total:    0.077907
#   106:    53(C )    65(C ) Alpha:    0.554529 Beta:    0.554685 Total:    1.109214
#   107:    56(C )    57(H ) Alpha:    0.422155 Beta:    0.422148 Total:    0.844303
#   108:    56(C )    58(H ) Alpha:    0.435983 Beta:    0.435982 Total:    0.871965
#   109:    56(C )    65(C ) Alpha:    0.557944 Beta:    0.557957 Total:    1.115901
#   110:    59(C )    60(H ) Alpha:    0.403303 Beta:    0.403293 Total:    0.806596
#   111:    59(C )    61(H ) Alpha:    0.421376 Beta:    0.421389 Total:    0.842765
#   112:    59(C )    62(C ) Alpha:    0.038746 Beta:    0.038743 Total:    0.077489
#   113:    59(C )    71(C ) Alpha:    0.554206 Beta:    0.554246 Total:    1.108452
#   114:    62(C )    63(H ) Alpha:    0.435559 Beta:    0.435557 Total:    0.871117
#   115:    62(C )    64(H ) Alpha:    0.421107 Beta:    0.421107 Total:    0.842214
#   116:    62(C )    71(C ) Alpha:    0.558065 Beta:    0.558059 Total:    1.116125
#   117:    65(C )    66(H ) Alpha:    0.432742 Beta:    0.432804 Total:    0.865546
#   118:    65(C )    67(H ) Alpha:    0.426261 Beta:    0.426279 Total:    0.852540
#   119:    68(C )    69(H ) Alpha:    0.432455 Beta:    0.432513 Total:    0.864967
#   120:    68(C )    70(H ) Alpha:    0.426478 Beta:    0.426497 Total:    0.852975
#   121:    71(C )    72(H ) Alpha:    0.432360 Beta:    0.432383 Total:    0.864743
#   122:    71(C )    73(H ) Alpha:    0.426352 Beta:    0.426336 Total:    0.852688
#   123:    75(Co)    76(P ) Alpha:    0.534460 Beta:    0.560519 Total:    1.094979
#   124:    75(Co)    77(P ) Alpha:    0.614192 Beta:    0.631845 Total:    1.246036
#   125:    75(Co)    78(N ) Alpha:    0.652165 Beta:    0.688643 Total:    1.340808
#   126:    75(Co)    79(N ) Alpha:    0.208490 Beta:    0.224770 Total:    0.433260
#   127:    75(Co)    87(C ) Alpha:    0.029459 Beta:    0.032099 Total:    0.061558
#   128:    75(Co)    89(C ) Alpha:    0.026812 Beta:    0.029264 Total:    0.056076
#   129:    75(Co)   148(H ) Alpha:    0.027109 Beta:    0.024452 Total:    0.051561
#   130:    76(P )    77(P ) Alpha:    0.028789 Beta:    0.027953 Total:    0.056742
#   131:    76(P )    80(C ) Alpha:    0.503454 Beta:    0.500779 Total:    1.004233
#   132:    76(P )    81(H ) Alpha:    0.029411 Beta:    0.029126 Total:    0.058537
#   133:    76(P )    82(C ) Alpha:    0.503362 Beta:    0.500594 Total:    1.003956
#   134:    76(P )    83(H ) Alpha:    0.029312 Beta:    0.029042 Total:    0.058354
#   135:    76(P )    84(C ) Alpha:    0.055254 Beta:    0.055341 Total:    0.110594
#   136:    76(P )    91(C ) Alpha:    0.056956 Beta:    0.057066 Total:    0.114022
#   137:    76(P )   106(C ) Alpha:    0.060132 Beta:    0.060017 Total:    0.120149
#   138:    76(P )   127(C ) Alpha:    0.062362 Beta:    0.062227 Total:    0.124589
#   139:    77(P )    87(C ) Alpha:    0.511786 Beta:    0.509981 Total:    1.021767
#   140:    77(P )    88(H ) Alpha:    0.032119 Beta:    0.032217 Total:    0.064335
#   141:    77(P )    89(C ) Alpha:    0.509597 Beta:    0.507805 Total:    1.017402
#   142:    77(P )    90(H ) Alpha:    0.027945 Beta:    0.027775 Total:    0.055720
#   143:    77(P )    94(C ) Alpha:    0.058775 Beta:    0.058837 Total:    0.117612
```

144: 77(P) 103(C) Alpha: 0.058261 Beta: 0.058157 Total: 0.116418
145: 77(P) 124(C) Alpha: 0.053042 Beta: 0.052366 Total: 0.105408
146: 77(P) 133(C) Alpha: 0.062919 Beta: 0.062662 Total: 0.125581
147: 77(P) 148(H) Alpha: 0.426856 Beta: 0.423389 Total: 0.850246
148: 78(N) 79(N) Alpha: 1.305405 Beta: 1.281411 Total: 2.586816
149: 80(C) 81(H) Alpha: 0.390995 Beta: 0.391588 Total: 0.782583
150: 80(C) 91(C) Alpha: 0.512898 Beta: 0.513195 Total: 1.026093
151: 80(C) 100(C) Alpha: 0.034958 Beta: 0.035044 Total: 0.070003
152: 80(C) 106(C) Alpha: 0.513314 Beta: 0.514058 Total: 1.027372
153: 80(C) 142(C) Alpha: 0.034410 Beta: 0.034500 Total: 0.068909
154: 82(C) 83(H) Alpha: 0.390712 Beta: 0.391264 Total: 0.781976
155: 82(C) 84(C) Alpha: 0.513908 Beta: 0.514211 Total: 1.028119
156: 82(C) 115(C) Alpha: 0.034821 Beta: 0.034905 Total: 0.069727
157: 82(C) 127(C) Alpha: 0.512864 Beta: 0.513632 Total: 1.026496
158: 82(C) 139(C) Alpha: 0.034599 Beta: 0.034688 Total: 0.069287
159: 84(C) 85(H) Alpha: 0.401521 Beta: 0.401391 Total: 0.802911
160: 84(C) 86(H) Alpha: 0.400335 Beta: 0.400304 Total: 0.800639
161: 84(C) 115(C) Alpha: 0.553809 Beta: 0.553800 Total: 1.107609
162: 84(C) 127(C) Alpha: 0.035426 Beta: 0.035470 Total: 0.070896
163: 84(C) 130(C) Alpha: 0.038588 Beta: 0.038587 Total: 0.077174
164: 87(C) 88(H) Alpha: 0.380225 Beta: 0.380022 Total: 0.760248
165: 87(C) 97(C) Alpha: 0.036192 Beta: 0.036220 Total: 0.072412
166: 87(C) 103(C) Alpha: 0.515547 Beta: 0.515735 Total: 1.031282
167: 87(C) 118(C) Alpha: 0.036578 Beta: 0.036638 Total: 0.073215
168: 87(C) 124(C) Alpha: 0.524172 Beta: 0.524163 Total: 1.048335
169: 89(C) 90(H) Alpha: 0.393493 Beta: 0.393397 Total: 0.786890
170: 89(C) 94(C) Alpha: 0.514260 Beta: 0.514416 Total: 1.028676
171: 89(C) 109(C) Alpha: 0.034980 Beta: 0.035018 Total: 0.069998
172: 89(C) 133(C) Alpha: 0.517260 Beta: 0.517468 Total: 1.034727
173: 89(C) 145(C) Alpha: 0.034910 Beta: 0.034953 Total: 0.069863
174: 91(C) 92(H) Alpha: 0.398396 Beta: 0.398361 Total: 0.796757
175: 91(C) 93(H) Alpha: 0.404481 Beta: 0.404327 Total: 0.808809
176: 91(C) 100(C) Alpha: 0.552891 Beta: 0.552862 Total: 1.105753
177: 91(C) 106(C) Alpha: 0.034743 Beta: 0.034783 Total: 0.069526
178: 91(C) 121(C) Alpha: 0.038653 Beta: 0.038650 Total: 0.077303
179: 94(C) 95(H) Alpha: 0.395287 Beta: 0.395178 Total: 0.790465
180: 94(C) 96(H) Alpha: 0.408949 Beta: 0.408950 Total: 0.817899
181: 94(C) 109(C) Alpha: 0.553551 Beta: 0.553579 Total: 1.107130
182: 94(C) 133(C) Alpha: 0.035051 Beta: 0.035045 Total: 0.070095
183: 94(C) 136(C) Alpha: 0.038907 Beta: 0.038906 Total: 0.077813
184: 97(C) 98(H) Alpha: 0.420084 Beta: 0.420082 Total: 0.840167

185: 97(C) 99(H) Alpha: 0.432509 Beta: 0.432525 Total: 0.865034
186: 97(C) 103(C) Alpha: 0.553390 Beta: 0.553433 Total: 1.106823
187: 97(C) 112(C) Alpha: 0.558533 Beta: 0.558528 Total: 1.117061
188: 97(C) 118(C) Alpha: 0.039066 Beta: 0.039065 Total: 0.078131
189: 100(C) 101(H) Alpha: 0.425363 Beta: 0.425395 Total: 0.850758
190: 100(C) 102(H) Alpha: 0.431850 Beta: 0.431859 Total: 0.863709
191: 100(C) 121(C) Alpha: 0.557635 Beta: 0.557625 Total: 1.115261
192: 100(C) 142(C) Alpha: 0.039399 Beta: 0.039396 Total: 0.078795
193: 103(C) 104(H) Alpha: 0.413014 Beta: 0.413021 Total: 0.826035
194: 103(C) 105(H) Alpha: 0.406294 Beta: 0.406224 Total: 0.812518
195: 103(C) 112(C) Alpha: 0.039073 Beta: 0.039073 Total: 0.078145
196: 103(C) 124(C) Alpha: 0.034827 Beta: 0.034833 Total: 0.069660
197: 106(C) 107(H) Alpha: 0.417648 Beta: 0.417638 Total: 0.835287
198: 106(C) 108(H) Alpha: 0.402095 Beta: 0.402045 Total: 0.804140
199: 106(C) 121(C) Alpha: 0.038556 Beta: 0.038560 Total: 0.077117
200: 106(C) 142(C) Alpha: 0.554492 Beta: 0.554642 Total: 1.109134
201: 109(C) 110(H) Alpha: 0.426451 Beta: 0.426476 Total: 0.852927
202: 109(C) 111(H) Alpha: 0.431511 Beta: 0.431526 Total: 0.863037
203: 109(C) 136(C) Alpha: 0.558239 Beta: 0.558235 Total: 1.116473
204: 109(C) 145(C) Alpha: 0.039575 Beta: 0.039574 Total: 0.079149
205: 112(C) 113(H) Alpha: 0.435129 Beta: 0.435115 Total: 0.870244
206: 112(C) 114(H) Alpha: 0.426257 Beta: 0.426256 Total: 0.852513
207: 112(C) 118(C) Alpha: 0.558536 Beta: 0.558508 Total: 1.117044
208: 112(C) 124(C) Alpha: 0.038380 Beta: 0.038378 Total: 0.076758
209: 115(C) 116(H) Alpha: 0.424714 Beta: 0.424744 Total: 0.849457
210: 115(C) 117(H) Alpha: 0.431518 Beta: 0.431527 Total: 0.863045
211: 115(C) 130(C) Alpha: 0.558281 Beta: 0.558272 Total: 1.116552
212: 115(C) 139(C) Alpha: 0.039422 Beta: 0.039419 Total: 0.078842
213: 118(C) 119(H) Alpha: 0.434210 Beta: 0.434217 Total: 0.868427
214: 118(C) 120(H) Alpha: 0.424249 Beta: 0.424246 Total: 0.848495
215: 118(C) 124(C) Alpha: 0.555195 Beta: 0.555208 Total: 1.110403
216: 121(C) 122(H) Alpha: 0.421363 Beta: 0.421354 Total: 0.842716
217: 121(C) 123(H) Alpha: 0.436121 Beta: 0.436121 Total: 0.872242
218: 121(C) 142(C) Alpha: 0.558108 Beta: 0.558118 Total: 1.116226
219: 124(C) 125(H) Alpha: 0.423382 Beta: 0.423303 Total: 0.846685
220: 124(C) 126(H) Alpha: 0.419312 Beta: 0.419325 Total: 0.838638
221: 127(C) 128(H) Alpha: 0.403172 Beta: 0.403121 Total: 0.806293
222: 127(C) 129(H) Alpha: 0.418004 Beta: 0.417990 Total: 0.835994
223: 127(C) 130(C) Alpha: 0.038949 Beta: 0.038953 Total: 0.077902
224: 127(C) 139(C) Alpha: 0.554528 Beta: 0.554685 Total: 1.109213
225: 130(C) 131(H) Alpha: 0.422158 Beta: 0.422152 Total: 0.844310

#	226:	130(C)	132(H) Alpha:	0.435984	Beta:	0.435984	Total: 0.871968
#	227:	130(C)	139(C) Alpha:	0.557946	Beta:	0.557959	Total: 1.115905
#	228:	133(C)	134(H) Alpha:	0.403283	Beta:	0.403272	Total: 0.806555
#	229:	133(C)	135(H) Alpha:	0.421376	Beta:	0.421389	Total: 0.842764
#	230:	133(C)	136(C) Alpha:	0.038743	Beta:	0.038740	Total: 0.077483
#	231:	133(C)	145(C) Alpha:	0.554205	Beta:	0.554245	Total: 1.108450
#	232:	136(C)	137(H) Alpha:	0.435557	Beta:	0.435555	Total: 0.871112
#	233:	136(C)	138(H) Alpha:	0.421077	Beta:	0.421076	Total: 0.842153
#	234:	136(C)	145(C) Alpha:	0.558063	Beta:	0.558057	Total: 1.116120
#	235:	139(C)	140(H) Alpha:	0.432746	Beta:	0.432809	Total: 0.865555
#	236:	139(C)	141(H) Alpha:	0.426260	Beta:	0.426278	Total: 0.852538
#	237:	142(C)	143(H) Alpha:	0.432456	Beta:	0.432514	Total: 0.864969
#	238:	142(C)	144(H) Alpha:	0.426482	Beta:	0.426501	Total: 0.852984
#	239:	145(C)	146(H) Alpha:	0.432355	Beta:	0.432378	Total: 0.864732
#	240:	145(C)	147(H) Alpha:	0.426355	Beta:	0.426339	Total: 0.852694

Fuzzy atom bond order of Jones-Co-N2-PtBu



#	1:	1(Co)	2(N)	1.28612718
#	2:	1(Co)	3(N)	0.40021316
#	3:	1(Co)	4(P)	1.04634694
#	4:	1(Co)	5(P)	1.04746634
#	5:	1(Co)	6(Co)	1.30866478
#	6:	1(Co)	45(C)	0.06556405

```
#      7:          1(Co)    49(C )     0.05854445
#      8:          1(Co)    53(P )     1.13011519
#      9:          1(Co)    54(P )     0.06088464
#     10:          1(Co)    59(C )     0.05015158
#     11:          2(N )     3(N )     2.61253894
#     12:          2(N )    53(P )     0.08342229
#     13:          4(P )     5(P )     0.08796103
#     14:          4(P )     6(Co)     1.04719316
#     15:          4(P )     9(C )     0.95461335
#     16:          4(P )    10(C )     0.10540660
#     17:          4(P )    14(C )     0.13059980
#     18:          4(P )    18(C )     0.11979153
#     19:          4(P )    22(C )     0.95718208
#     20:          4(P )    23(C )     0.12745641
#     21:          4(P )    27(C )     0.11590864
#     22:          4(P )    31(C )     0.11662910
#     23:          5(P )     6(Co)     1.04667849
#     24:          5(P )    43(C )     0.95724784
#     25:          5(P )    44(C )     0.95467860
#     26:          5(P )    63(C )     0.11997564
#     27:          5(P )    67(C )     0.13053810
#     28:          5(P )    71(C )     0.10535351
#     29:          5(P )    75(C )     0.12751008
#     30:          5(P )    79(C )     0.11572830
#     31:          5(P )    83(C )     0.11660025
#     32:          6(Co)     7(N )     1.28628474
#     33:          6(Co)     8(N )     0.40018696
#     34:          6(Co)    35(C )     0.06566217
#     35:          6(Co)    39(C )     0.05839095
#     36:          6(Co)    53(P )     0.06095512
#     37:          6(Co)    54(P )     1.13006159
#     38:          6(Co)    55(C )     0.05014628
#     39:          7(N )     8(N )     2.61246918
#     40:          7(N )    54(P )     0.08331706
#     41:          9(C )    10(C )     1.04348627
#     42:          9(C )    14(C )     1.01790940
#     43:          9(C )    18(C )     1.02852025
#     44:         10(C )    11(H )     0.87587939
#     45:         10(C )    12(H )     0.86691228
#     46:         10(C )    13(H )     0.86757214
#     47:         10(C )    14(C )     0.09776395
```

#	48:	10(C)	18(C)	0.09237003
#	49:	14(C)	15(H)	0.82656895
#	50:	14(C)	16(H)	0.84066297
#	51:	14(C)	17(H)	0.87222893
#	52:	14(C)	18(C)	0.09009255
#	53:	18(C)	19(H)	0.87503543
#	54:	18(C)	20(H)	0.86403339
#	55:	18(C)	21(H)	0.83447726
#	56:	22(C)	23(C)	1.01202994
#	57:	22(C)	27(C)	1.03973864
#	58:	22(C)	31(C)	1.03137215
#	59:	23(C)	24(H)	0.81598842
#	60:	23(C)	25(H)	0.87189609
#	61:	23(C)	26(H)	0.82728836
#	62:	23(C)	27(C)	0.09445446
#	63:	23(C)	31(C)	0.09992606
#	64:	27(C)	28(H)	0.87722285
#	65:	27(C)	29(H)	0.86386440
#	66:	27(C)	30(H)	0.86595697
#	67:	27(C)	31(C)	0.08984402
#	68:	31(C)	32(H)	0.86462105
#	69:	31(C)	33(H)	0.85415209
#	70:	31(C)	34(H)	0.87371039
#	71:	35(C)	36(H)	0.84890297
#	72:	35(C)	37(H)	0.85348931
#	73:	35(C)	38(H)	0.87299777
#	74:	35(C)	54(P)	1.13581710
#	75:	36(H)	54(P)	0.07213241
#	76:	37(H)	54(P)	0.07382218
#	77:	38(H)	54(P)	0.06747706
#	78:	39(C)	40(H)	0.84059173
#	79:	39(C)	41(H)	0.87110347
#	80:	39(C)	42(H)	0.85465099
#	81:	39(C)	54(P)	1.13754826
#	82:	39(C)	55(C)	0.05382090
#	83:	40(H)	54(P)	0.06915520
#	84:	41(H)	54(P)	0.06869601
#	85:	42(H)	54(P)	0.07547045
#	86:	43(C)	75(C)	1.01194982
#	87:	43(C)	79(C)	1.03974064
#	88:	43(C)	83(C)	1.03127738

#	89:	44(C)	63(C)	1.02836297
#	90:	44(C)	67(C)	1.01798827
#	91:	44(C)	71(C)	1.04338523
#	92:	45(C)	46(H)	0.85345379
#	93:	45(C)	47(H)	0.84881729
#	94:	45(C)	48(H)	0.87297898
#	95:	45(C)	53(P)	1.13583120
#	96:	46(H)	53(P)	0.07383297
#	97:	47(H)	53(P)	0.07211221
#	98:	48(H)	53(P)	0.06747688
#	99:	49(C)	50(H)	0.85462808
#	100:	49(C)	51(H)	0.87109071
#	101:	49(C)	52(H)	0.84074854
#	102:	49(C)	53(P)	1.13746321
#	103:	49(C)	59(C)	0.05396786
#	104:	50(H)	53(P)	0.07547930
#	105:	51(H)	53(P)	0.06863965
#	106:	52(H)	53(P)	0.06916798
#	107:	53(P)	59(C)	1.14261294
#	108:	53(P)	60(H)	0.07210593
#	109:	53(P)	61(H)	0.07363766
#	110:	53(P)	62(H)	0.07091295
#	111:	54(P)	55(C)	1.14275119
#	112:	54(P)	56(H)	0.07106398
#	113:	54(P)	57(H)	0.07356668
#	114:	54(P)	58(H)	0.07210692
#	115:	55(C)	56(H)	0.85407878
#	116:	55(C)	57(H)	0.85140677
#	117:	55(C)	58(H)	0.86551687
#	118:	59(C)	60(H)	0.86542101
#	119:	59(C)	61(H)	0.85139640
#	120:	59(C)	62(H)	0.85396896
#	121:	63(C)	64(H)	0.87507117
#	122:	63(C)	65(H)	0.83444721
#	123:	63(C)	66(H)	0.86388983
#	124:	63(C)	67(C)	0.09020743
#	125:	63(C)	71(C)	0.09249667
#	126:	67(C)	68(H)	0.84081936
#	127:	67(C)	69(H)	0.82644886
#	128:	67(C)	70(H)	0.87217439
#	129:	67(C)	71(C)	0.09784094

#	130:	71(C)	72(H)	0.87579967
#	131:	71(C)	73(H)	0.86750734
#	132:	71(C)	74(H)	0.86683087
#	133:	75(C)	76(H)	0.82715363
#	134:	75(C)	77(H)	0.87183001
#	135:	75(C)	78(H)	0.81587431
#	136:	75(C)	79(C)	0.09429448
#	137:	75(C)	83(C)	0.10001089
#	138:	79(C)	80(H)	0.86370822
#	139:	79(C)	81(H)	0.87721747
#	140:	79(C)	82(H)	0.86615458
#	141:	79(C)	83(C)	0.08989741
#	142:	83(C)	84(H)	0.85417492
#	143:	83(C)	85(H)	0.86463759
#	144:	83(C)	86(H)	0.87367077

S6. References

[1] F. Neese, *WIREs Comput. Mol. Sci*., 2012, **2**, 73-78.

[2] F. Neese, *WIREs Comput. Mol. Sci*., 2018, **8**, e1327.

[3] J. W. Furness, A. D. Kaplan, J. Ning, J. P. Perdew, J. Sun, *J. Phys. Chem. Lett*., 2020, **11**, 8208-8215.

[4] E. Caldeweyher, C. Bannwarth, S. Grimme, *J. Chem. Phys*., 2017, **147**, 034112.

[5] S.-H. Chong, S. Ham, *J. Chem. Phys*., 2012, **137**, 154101.

[6] T. Lu, F. Chen, *J. Comput. Chem*., 2012, **33**, 580-592.

[7] D. Y. Zubarev, Z. A. I. Boldyrev, *Phys. Chem. Chem. Phys*., 2008, **10**, 5207-5217.

[8] L. B. Schenkel, J. A. Ellman, *Org. Lett*. 2003, **5**, 545-548.

[9] S. Chakraborty, G. Leitus, D. Milstein, *Angew. Chem. Int. Ed*. 2017, **56**, 2074-2078.