Supporting Information for:

Coinage metal *tris*(dialkylamido)imidophosphorane complexes as transmetallation reagents for cerium complexes

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General Considerations

Unless otherwise stated, all reagents were obtained from commercial suppliers, and the syntheses and manipulations were conducted under argon with exclusion of dioxygen (O_2) and H_2O using Schlenk techniques or in an inert atmosphere box (Vigor) under a dinitrogen (<0.1 ppm O_2/H_2O) atmosphere. All glassware was stored in an oven over-night (>8 h) at a temperature of ca. 160˚C prior to use. Celite and molecular sieves were dried under vacuum at a temperature >250 °C for a minimum of 24 h. C_6D_6 was stored over 3 Å molecular sieves and then vacuum-transferred from purple sodium/benzophenone prior to use. Diethyl ether, *n*-pentane, *n*-hexane, benzene, toluene, and tetrahydrofuran (THF) were purged with UHP-grade argon (Airgas) and passed through columns containing Q-5 and molecular sieves in a solvent purification system (JC Meyer Solvent Systems). All solvents in the glovebox were stored in bottles over 3 Å molecular sieves. The reagents $CeI_3(THF)_4$, K[NP(pip)$_3$] and K[NP*] were prepared by published procedures.[1-3] NMR spectra were obtained on a Bruker Advance III 400 MHz spectrometer at 298 K, unless otherwise noted. ^{1}H, ^{13}C, and ^{31}P NMR chemical shifts are reported in δ, parts per million. All NMR samples were prepared in C_6D_6 (unless otherwise noted) and ^{1}H NMR are references to the residual ^{1}H resonances of C_6D_6.[4] ^{13}C NMR are referenced to the ^{13}C resonance of the C_6D_6.[4] The peak position is listed, followed by the peak multiplicity, integration value, and proton assignment, where applicable. The multiplicity and shape are indicated by one or more of the following abbreviations: s (singlet); d (doublet); t (triplet); q (quartet); m (multiplet); br (broad). Elemental analyses were determined at Robertson Microlit Laboratories (Ledgewood, NJ). Infrared (IR) samples were taken on a Bruker ALPHA FTIR spectrometer from 400 to 4000 cm^{-1}. IR samples were prepared as Nujol mulls sandwiched between two KBr plates. The peaks are listed in wavenumber [cm^{-1}] and intensity by using the following abbreviations: vw (very weak); w (weak); m (medium); s (strong); vs (very strong); br (broad). Crystals suitable for X-ray diffraction were covered in paratone oil in a glove box and transferred to the diffractometer in a 20-mL capped vial. Crystals were mounted on a loop with paratone oil on a Bruker D8 VENTURE diffractometer. The crystals were cooled and kept at T = 100(2) K during data collections. The structures were solved with the ShelXT structure solution program using the Intrinsic Phasing solution method and by using Olex2 as the graphical interface.[5, 6] The model was refined with version 2014/7 of XL using Least Squares minimization.[7] Structures were visualized in Mercury and graphics were generated with POV-ray.[8, 9]

Complexes **1-Cu**, **1-Ag**, **2-Cu**, and **2-Ag** were found to be stable to light after isolation and not special precautions to exclude light were taken to store them (except to be placed in the freezer when not in use) or in subsequent reactions.

Synthetic Procedures

Synthesis of 1-Cu

Inside a glovebox, 2 mL of THF was added to a 20 mL scintillation vial charged with CuCl (0.096 g, 0.952 mmol) and a stir bar. A solution of K[PN*] (0.311 g, 0.952 mmol) in 12 mL of THF was added and the reaction mixture was stirred for 24 hours in the absence of light. The mixture was filtered through a pipet packed with glass filter paper and Celite. The filtrate was reduced *in vacuo* to a residue and triturated three times with 2-3 mL of pentane. The residue was then extracted into approximately 10 mL of THF and filtered through pipet packed with glass filter paper and Celite. The filtrate was then concentrated *in vacuo* until saturated and placed in the freezer at −35 °C for 24 hours, during which time, colorless crystals formed. Decantation and removal of volatiles yielded the title compound in 62% yield (0.207 g). The product was recrystallized from THF at −35 °C to provide X-ray quality crystals. ^{1}H NMR (400.13 MHz, C_6D_6): δ 3.51(q, 4H), 3.13 (m, 2 H), 2.90 (m, 2 H), 1.56 (s, 18 H), 1.25 (t, 6 H). ^{31}P{^{1}H} NMR (161.98 MHz, C_6D_6): δ 15.41 (s). ^{13}C NMR (100.61 MHz, C_6D_6): δ 52.22 (s), 40.59 (d), 40.27 (s), 29.04 (s), 13.45 (s). IR (cm^{-1}): ν 1267 (m), 1251 (m), 1211 (s), 1190 (s), 1163 (m), 1152 (s), 1094 (w), 1056(s), 1029 (s), 978 (m), 932 (m), 869 (m), 800 (m), 771 (vw), 706 (s), 638 (w). Elem. Anal. Found (calculated) for $C_{56}H_{128}Cu_4N_{16}P_4$: C 45.75 (47.91) H 8.48 (9.19), N 14.76 (15.96). Elemental percentages consistently low on multiple burns.

Synthesis of 1-Ag

Inside a glovebox, 2 mL of THF and a stir bar were added to a 20 mL scintillation vial charged with AgI (0.223 g, 0.949 mmol). A solution of K[PN*] (0.310 g, 0.949 mmol) in 12 mL of THF was added and the mixture allowed to stir for 24 hours in the absence of light. The mixture was filtered through a pipet packed with glass filter paper and Celite. The filtrate was reduced *in vacuo* to a residue and triturated three times with 2-3 mL of pentane. The residue was then extracted into approximately 10 mL of THF and filtered through pipet packed with glass filter paper and Celite. The filtrate was then concentrated *in vacuo* until saturated and placed in the freezer at −35 °C for 24 hours, during which time, colorless crystals formed. Decantation and removal of volatiles yielded the title compound in 64% yield (0.240 g). The product was recrystallized from THF at −35 °C to provide X-ray quality crystals. ^{1}H NMR (400.13 MHz, C_6D_6): δ 3.40(sextet, 4H), 3.16 (m, 2 H), 2.91 (m, 2 H), 1.55 (s, 18 H), 1.26 (t, 6 H). ^{31}P{^{1}H} NMR (161.98 MHz, C_6D_6): δ 18.10 (t). ^{13}C NMR (100.61 MHz, C_6D_6): δ 52.29 (s), 40.95 (m), 40.79 (s), 28.97 (s), 14.07 (s). IR (cm^{-1}): ν 2042 (vw), 1599(m), 1577 (m), 1304 (vw), 1262 (m), 1207 (s), 1180 (w), 1148 (w), 1115 (vw), 1093 (vw), 1049 (s), 1022 (s), 968 (m), 909 (m), 864 (vw), 790 (w), 676 (m). Elem. Anal. Found (calculated) for $C_{56}H_{128}Ag_4N_{16}P_4$: C 42.50 (42.54) H 7.96 (8.16), N 14.45 (14.17).

Synthesis of 2-Cu

Inside a glovebox, 2 mL of THF and a stir bar were added to a 20 mL scintillation vial charged with CuCl (0.031 g, 0.309 mmol). A solution of K[NP(pip)$_3$] (0.104 g, 0.309 mmol) in 8 mL of THF was added and the mixture stirred for 24 hours in the absence of light. The mixture was filtered through a pipet packed with glass filter paper and Celite. The filtrate was reduced *in vacuo* to a residue and triturated three times with 2-3 mL of pentane. The residue was then extracted into approximately 10 mL of THF and filtered through pipet packed with glass filter paper and Celite. The filtrate was then concentrated *in vacuo* until saturated and placed in the freezer at −35 °C for 24 hours, during which time, colorless crystals formed. Decantation and removal of volatiles yielded the title compound in 78% yield (0.087 g). ^{1}H NMR (400.13 MHz, C_6D_6): δ 3.33(br-s, 48H), 1.57 (br-s, 72 H). ^{31}P{^{1}H} NMR (161.98 MHz, C_6D_6): δ 26.95 (s). ^{13}C NMR (100.61 MHz, C_6D_6): δ 46.70 (s), 27.05 (d), 25.47 (s). IR (cm^{-1}): ν 2064 (m), 1332 (s), 1275 (m), 1259 (m), 1215 (s), 1200 (vw), 1161 (vs), 1120 (s), 1062 (vs), 1027 (m), 945 (vs), 854 (m), 835 (m), 809 (m), 671 (w), 628 (vw).Elem. Anal. Found (calculated) for $C_{60}H_{120}Cu_4N_{16}P_4$: C 49.09 (49.91) H 8.73 (8.38), N 14.79 (15.52).

Synthesis of 2-Ag

Inside a glovebox, 20 mL of THF and a stir bar were added to a 100 mL round-bottomed flask charged with AgI (0.751 g, 3.201 mmol). A solution of K[NP(pip)$_3$] (1.077 g, 3.201 mmol) in 40 mL of THF was added and the mixture was stirred for 24 hours in the absence of light. The mixture was filtered through a pipet packed with glass filter paper and Celite. The filtrate was reduced *in vacuo* to a residue and triturated three times with 10 mL of pentane. The residue was then extracted into approximately 40 mL of THF and filtered through pipet packed with glass filter paper and Celite. The filtrate was then concentrated *in vacuo* until saturated and placed in the freezer at −35 °C for 24 hours, during which time, colorless crystals formed. Decantation and removal of volatiles yielded the title compound in 72% yield (0.934 g). The product was recrystallized from THF at −35 °C to provide X-ray quality crystals. ^{1}H NMR (400.13 MHz, C_6D_6): δ 3.27(br-s, 48 H), 1.54 (br-s, 72 H). ^{31}P{^{1}H} NMR (161.98 MHz, C_6D_6): δ 29.13 (t). ^{13}C NMR (100.61 MHz, C_6D_6): δ 46.60 (s), 27.09 (d), 25.40 (s). IR (cm^{-1}): ν 1329 (s), 1274 (m), 1259 (m), 1217 (s), 1201 (vw), 1162 (vs), 1123 (s), 1108 (m), 1059 (vs), 1027 (m), 940 (vs), 854 (m), 833 (m), 809 (m), 798 (w), 666 (w), 582 (vw). Elem Anal. Found (calculated) for $C_{60}H_{120}Ag_4N_{16}P_4$: C 44.91 (44.46) H 7.32 (7.46), N 13.59 (13.82).

Synthesis of 1-Ce

Inside a glovebox, 2 mL of THF and a stir bar were added to a 20 mL scintillation vial charged with $CeI_3(THF)_4$ (0.231 g, 0.286 mmol). A solution of K[NP(pip)$_3$] (0.289 g, 0.858 mmol) in 10 mL of THF was added and the mixture was stirred for 24 hours. The mixture was filtered through a pipet packed with glass filter paper and Celite. The filtrate was reduced *in vacuo* to a residue and triturated three times with 2-3 mL of pentane. The residue was then extracted into approximately 10 mL of THF and filtered through pipet packed with glass filter paper and Celite. The filtrate was then concentrated *in vacuo* until saturated and placed in the freezer at −35 °C for 24 hours, during which time, colorless crystals formed. Decantation and removal of volatiles yielded the title compound in 91% yield (0.273 g). The product was recrystallized from pentane at −35 °C to provide X-ray quality crystals. ^{1}H NMR (400.13 MHz, C_6D_6): δ 10.91 (br-s), 3.98 (br-s), 3.10 (br-s), -3.30

(br-s), -5.64 (br-s), -19.73 (br-s). $^{31}P\{^{1}H\}$ NMR (161.98 MHz, C_6D_6): δ 143.50 (br-s), -18.52 (br-s). ^{13}C NMR (100.61 MHz, C_6D_6): δ 53.26 (s), 31.16 (s), 28.38 (s), 18.08 (s), 15.05 (s). IR (cm^{-1}): ν 1328 (w), 1310 (vw), 1259 (m), 1203 (s), 1167 (vs), 1125 (s), 1057 (vs), 1028 (m), 937 (vs), 853 (m), 834 (m), 810 (m), 800 (w), 704 (s), 665 (w), 562 (vw). Elem Anal. Elem Anal. Found (calculated) for $C_{90}H_{180}Ce_2N_{24}P_6$: C 51.73 (52.36) H 8.86 (8.79), N 15.32 (16.28).

Reaction of 2-Ag with 1-Ce (Synthesis of $[Ce(NP(pip)_3)]_4$ through Route A)
Inside a glovebox, 2 mL of THF and a stir bar were added to a 20 mL scintillation vial charged with **1-Ce** (0.105 g, 0.051 mmol). A solution of **2-Ag** (0.041 g, 0.025 mmol) in 10 mL of THF was added and the mixture was stirred for 24 hours. The mixture was reduced to a residue *in vacuo*, triturated three times with 3mL *n*-pentane, dissolved in 10 mL of *n*-pentane, and filtered through a pipet filter packed with glass filter paper and Celite. The filtrate was concentrated *in vacuo* and placed in the freezer at −35 °C for 24 hours, during which time, yellow crystals of the previously reported compound $[Ce(NP(pip)_3)_4]$ grew (0.124 g, 92%). $^{31}P\{^{1}H\}$ NMR (161.98 MHz, C_6D_6): δ -12.30 (s).[3]

Reaction of 2-Ag with Ce^0 Shavings (Synthesis of $[Ce(NP(pip)_3)]_4$ through Route B)
Inside a glovebox, 2 mL of THF and a stir bar were added to a 20 mL scintillation vial charged with fresh Ce^0 shavings (0.013 g, 0.093 mmol). A solution of **2-Ag** (0.150 g, 0.093 mmol) in 11 mL of THF was added and the mixture was stirred for 48 hours. The mixture was dried *in vacuo*, triturated three times with 2 mL of *n*-pentane, dissolved in 10 mL of toluene, and filtered through a pipet filter packed with glass filter paper and Celite. The filtrate was concentrated *in vacuo* and placed in the freezer at −35 °C for 36 hours, during which time, yellow crystals of the previously reported compound $[Ce(NP(pip)_3)_4]$ grew (0.025 g, 20% isolated yield, 23% spectroscopic conversion). $^{31}P\{^{1}H\}$ NMR (161.98 MHz, C_6D_6): δ -12.30 (s).[3]

Reaction of 2-Cu with 1-Ce
Inside a glovebox, 2 mL of THF and a stir bar were added to a 20 mL scintillation vial charged with **1-Ce** (0.036 g, 0.018 mmol). A solution of **2-Cu** (0.009 g, 0.025 mmol) in 3 mL of THF was added and the reaction mixture was stirred for 24 hours. The mixture was filtered through a pipet packed with glass filter paper and Celite. The filtrate was reduced *in vacuo* to a residue and triturated three times with 2-3 mL of pentane. The residue was then extracted into approximately 6 mL of THF and filtered through pipet packed with glass filter paper and Celite. The filtrate was then reduced to a residue *in vacuo*. $^{31}P\{^{1}H\}$ NMR spectrum revealed the presence of only **2-Cu** and **1-Ce**.

Reaction of 2-Cu with Ce^0 Shavings
Inside a glovebox, 2 mL of THF and a stir bar were added to a 20 mL scintillation vial charged with fresh Ce^0 shavings (0.006 g, 0.043 mmol. A solution of **2-Cu** (0.062g, 0.043 mmol) in 5 mL of THF was added and the mixture was stirred for 48 hours. The mixture was filtered through a pipet packed with glass filter paper and Celite. The filtrate was reduced *in vacuo* to a residue and triturated three times with 2-3 mL of pentane. The residue was then extracted into approximately 6 mL of THF and filtered through pipet

packed with glass filter paper and Celite. The filtrate was then reduced to a residue *in vacuo*. $^{31}P\{^{1}H\}$ NMR spectrum revealed the presence of only **2-Cu**.

NMR Spectra of Reported Compounds

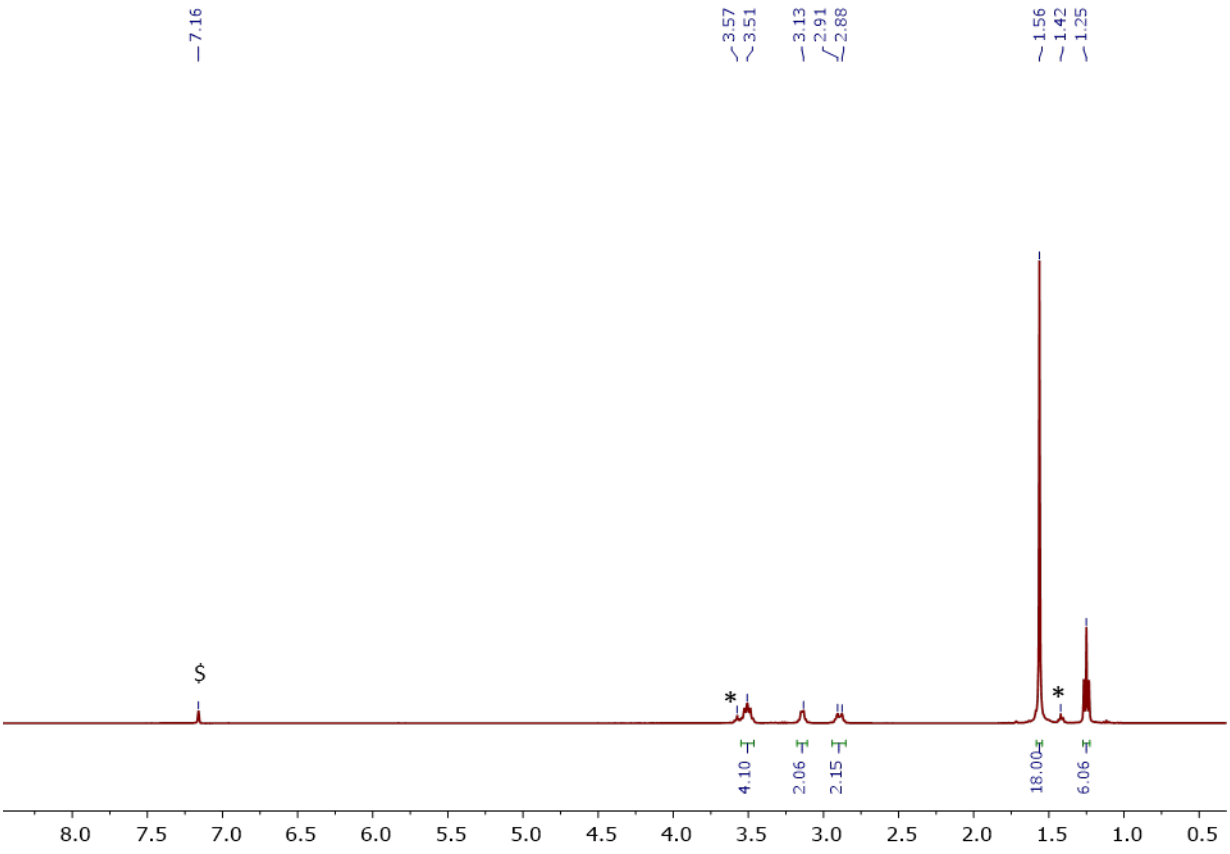

Figure S1. ^{1}H NMR of **1-Cu** in C_6D_6. C_6D_5H is noted as $. Residual THF noted as *.

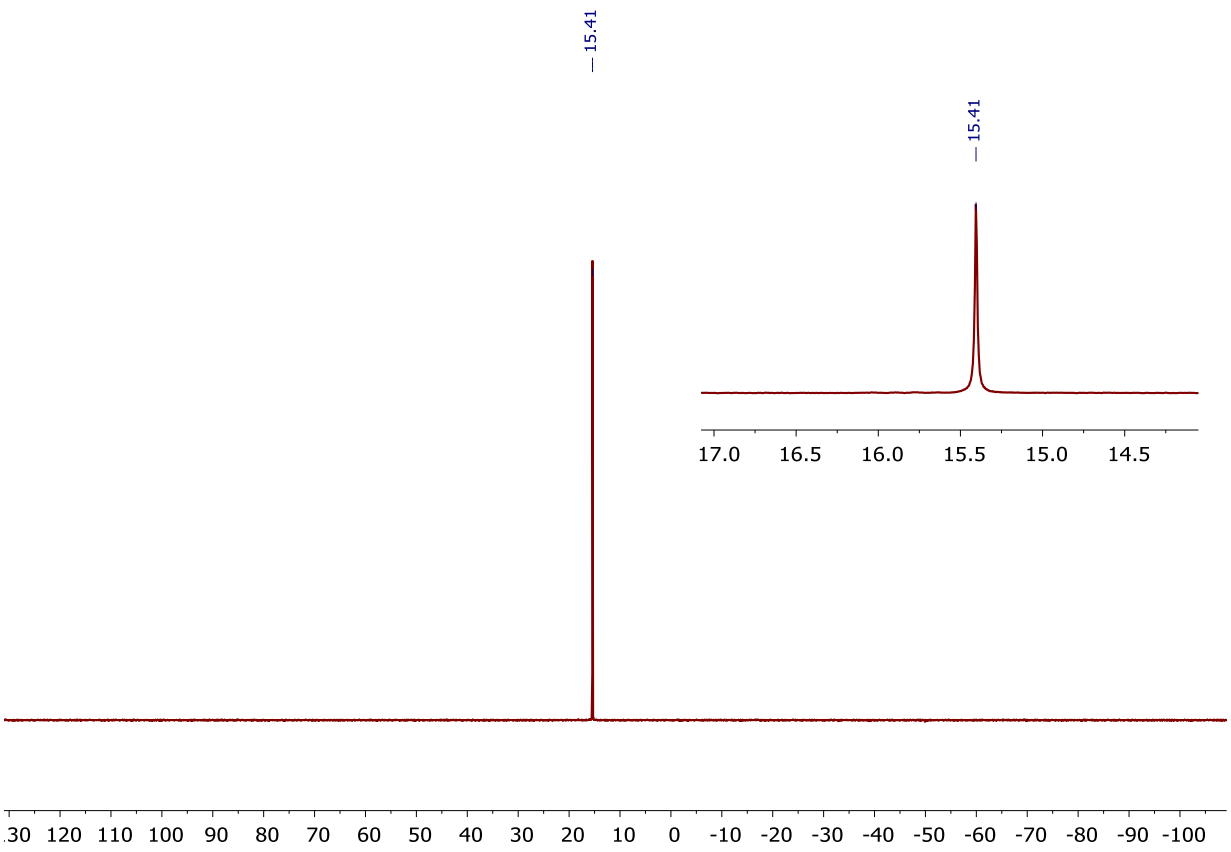

Figure S2. $^{31}P\{^{1}H\}$ NMR of **1-Cu** in C_6D_6.

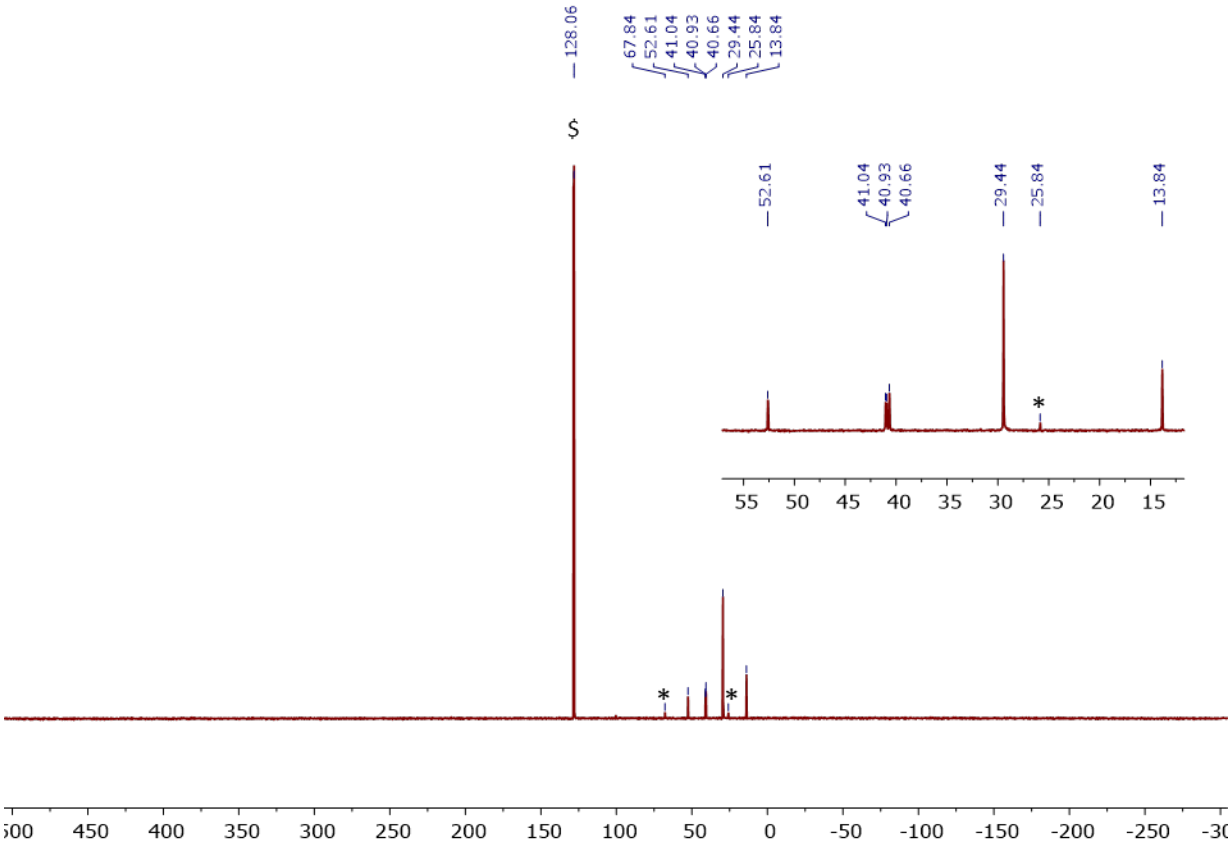

Figure S3. ^{13}C NMR of **1-Cu** in C_6D_6. C_6D_5H is noted as $. Residual THF noted as *. Inset shows a zoom-in of the observed signals for clarity.

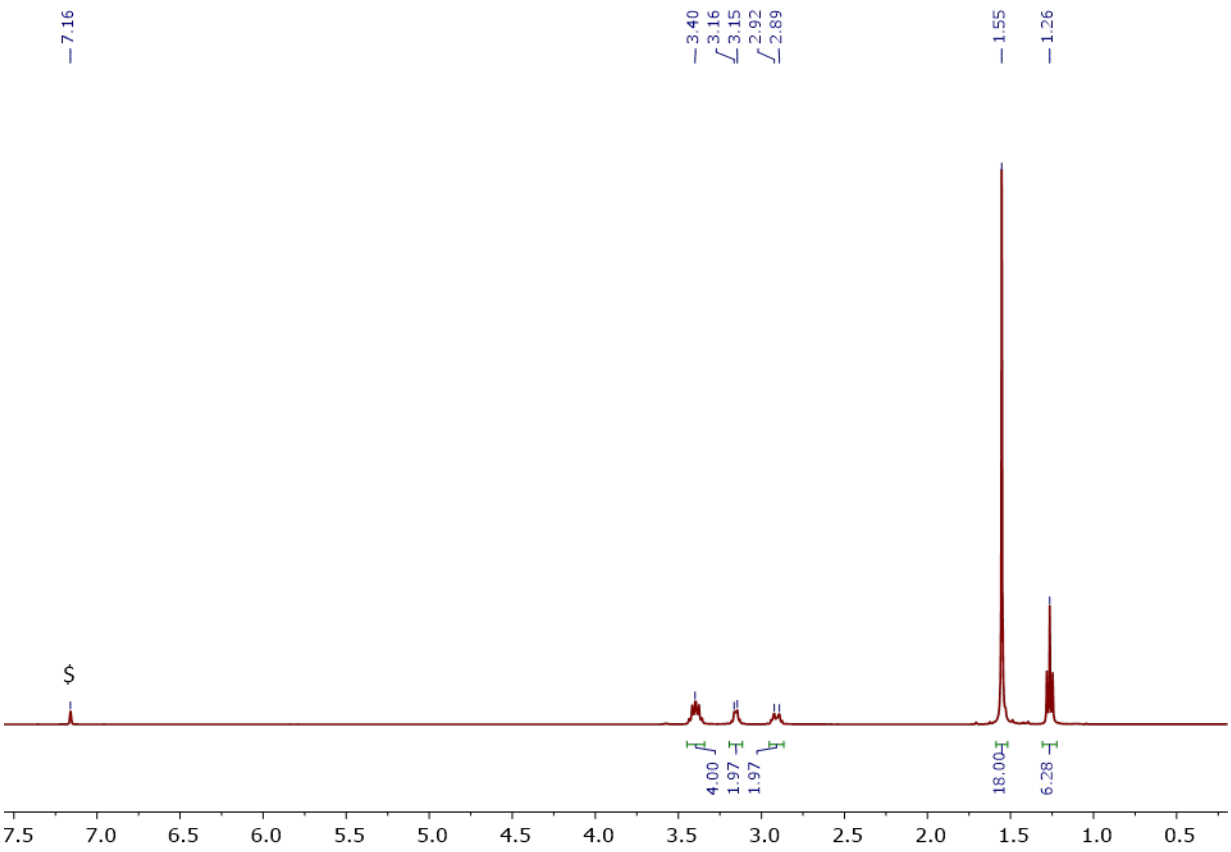

Figure S4. ^{1}H NMR of **1-Ag** in C_6D_6. C_6D_5H is noted as $.

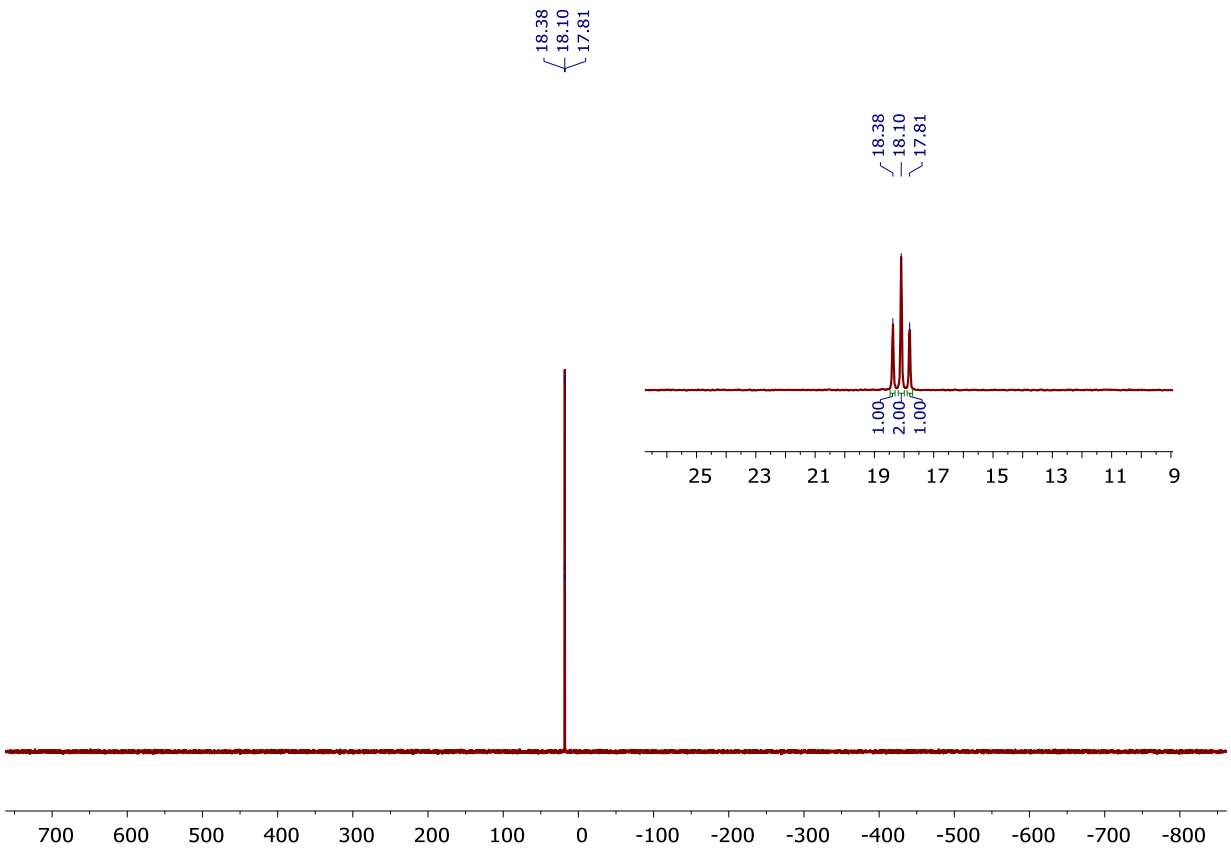

Figure S5. $^{31}P\{^{1}H\}$ NMR of **1-Ag** in C_6D_6.

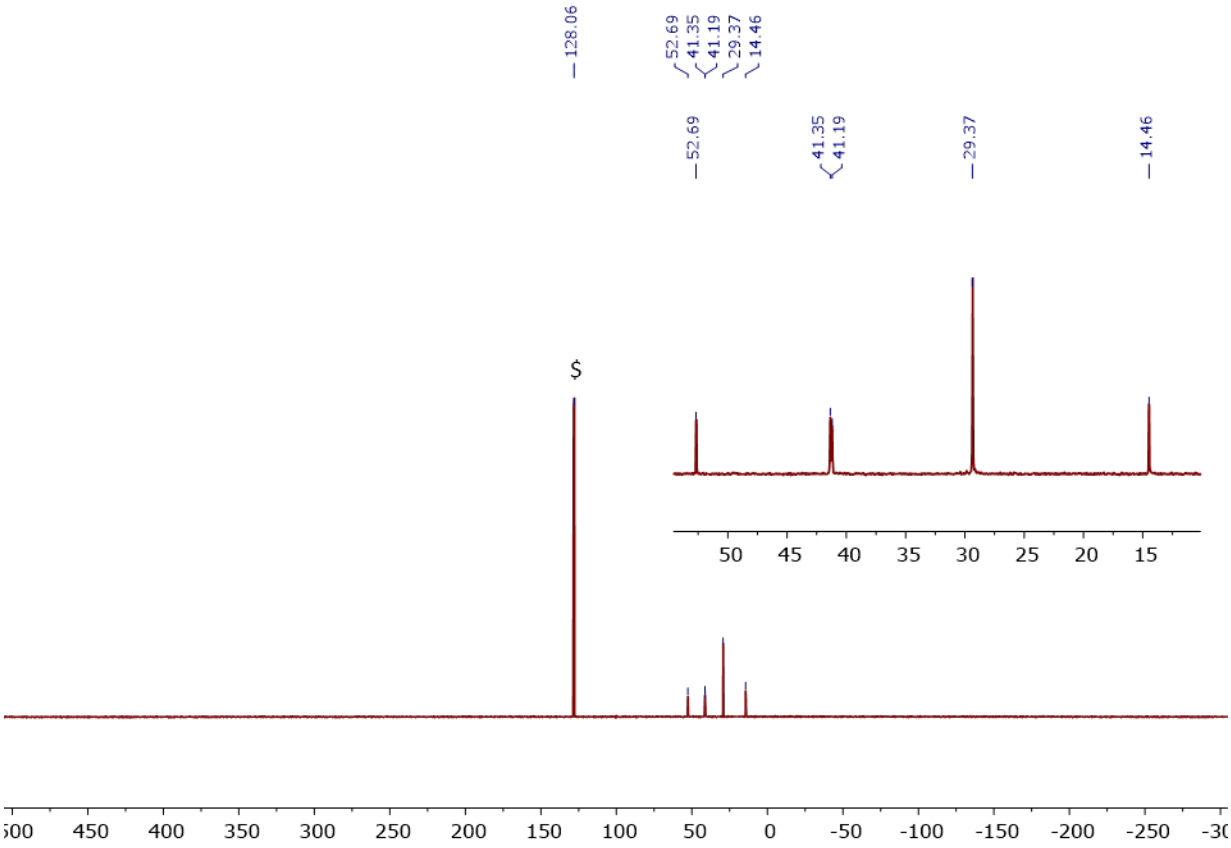

Figure S6. ^{13}C NMR of **1-Ag** in C_6D_6. C_6D_5H is noted as $. Inset shows a zoom-in of the observed signals for clarity.

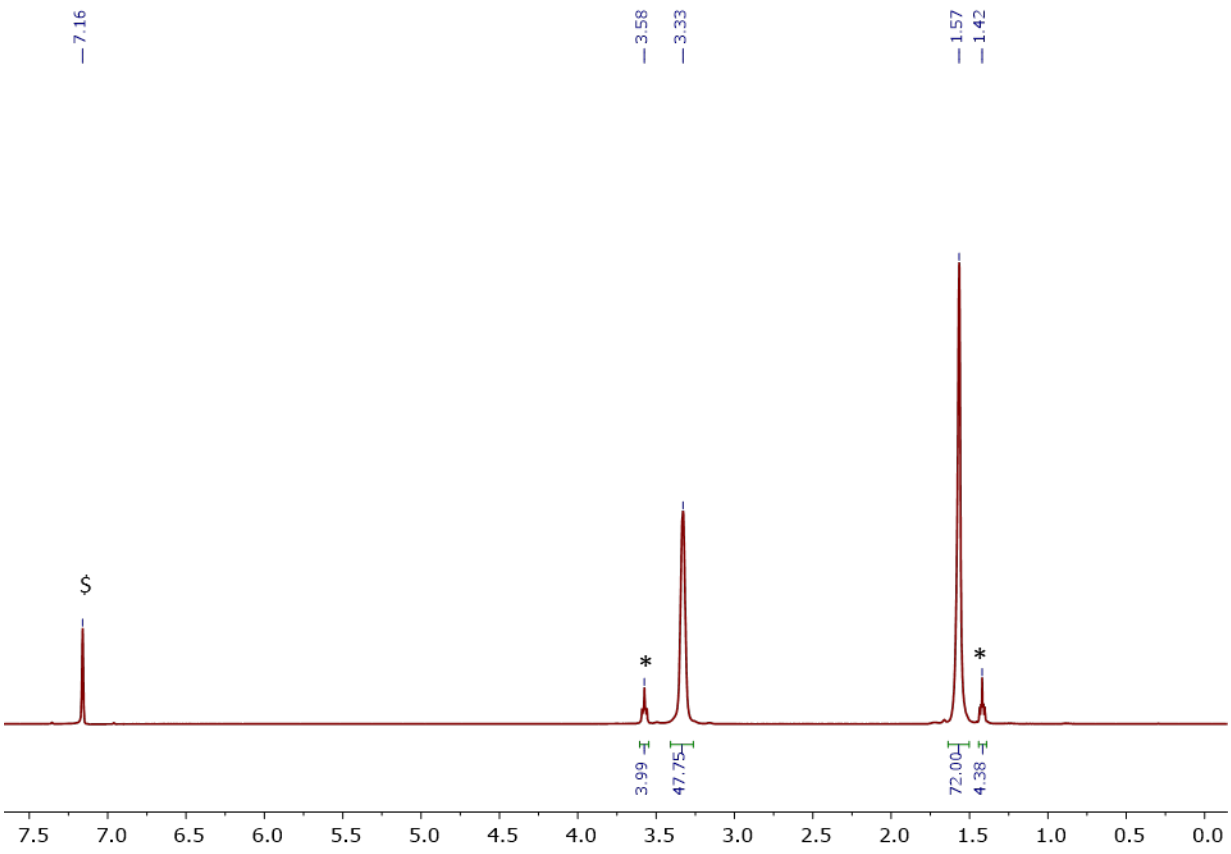

Figure S7. ^{1}H NMR of **2-Cu** in C_6D_6. C_6D_5H is noted as $. Residual THF noted as *.

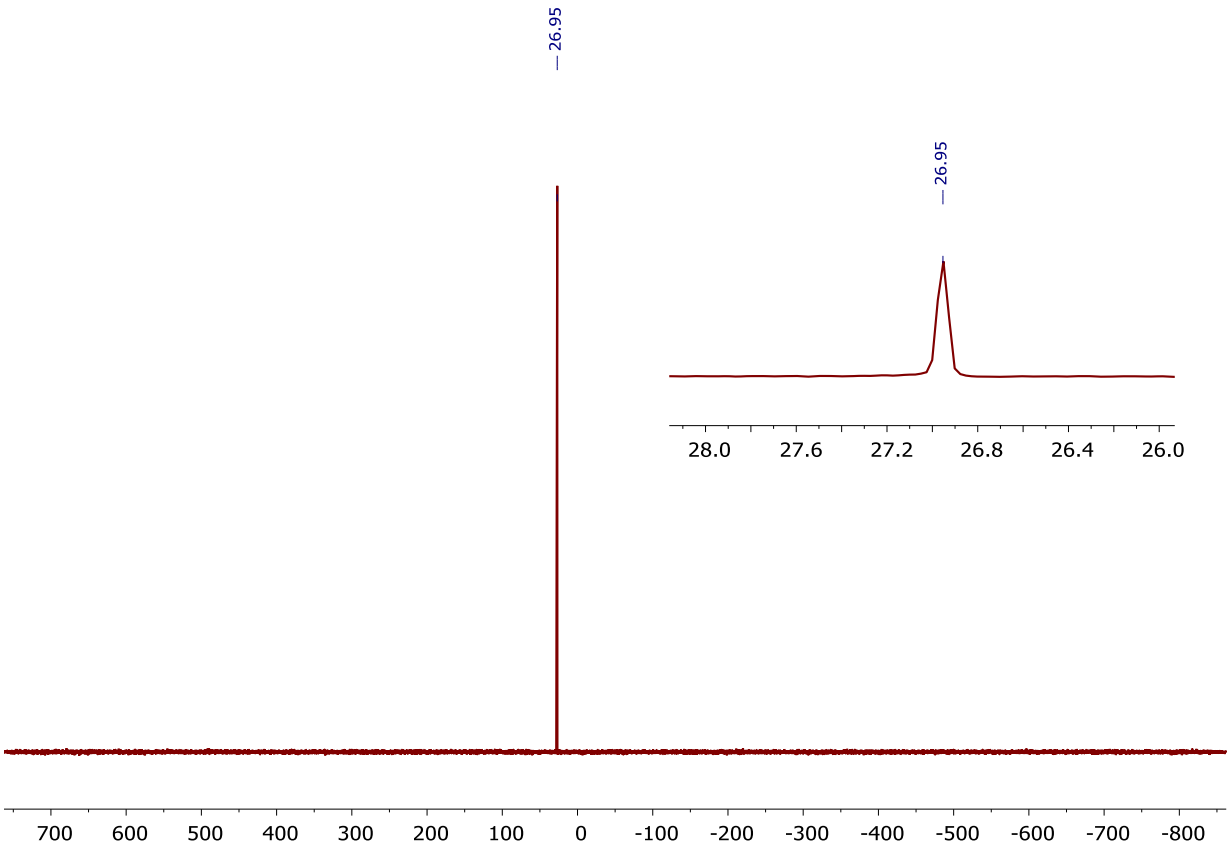

Figure S8. $^{31}P\{^{1}H\}$ NMR of **2-Cu** in C_6D_6.

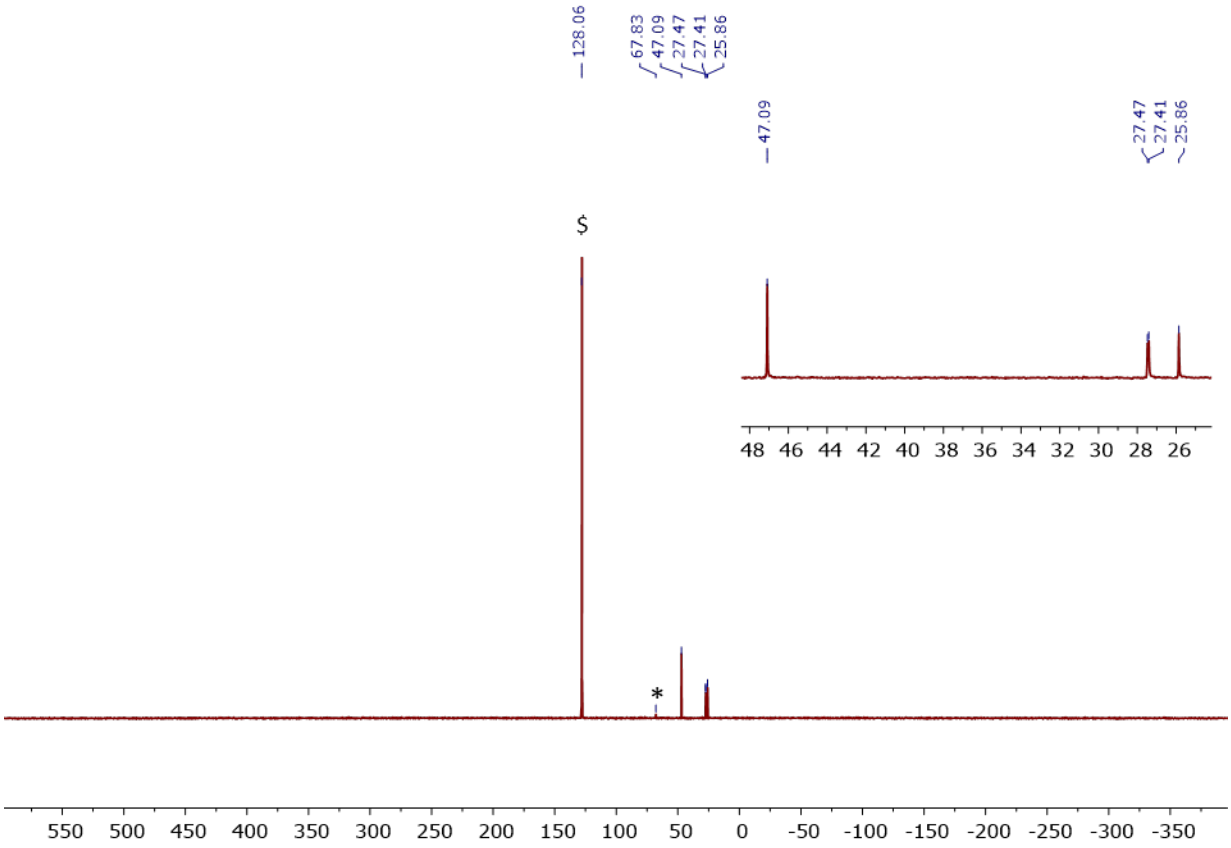

Figure S9. ^{13}C NMR of **2-Cu** in C_6D_6. C_6D_5H is noted as $. Residual THF noted as *. Inset shows a zoom-in of the observed signals for clarity.

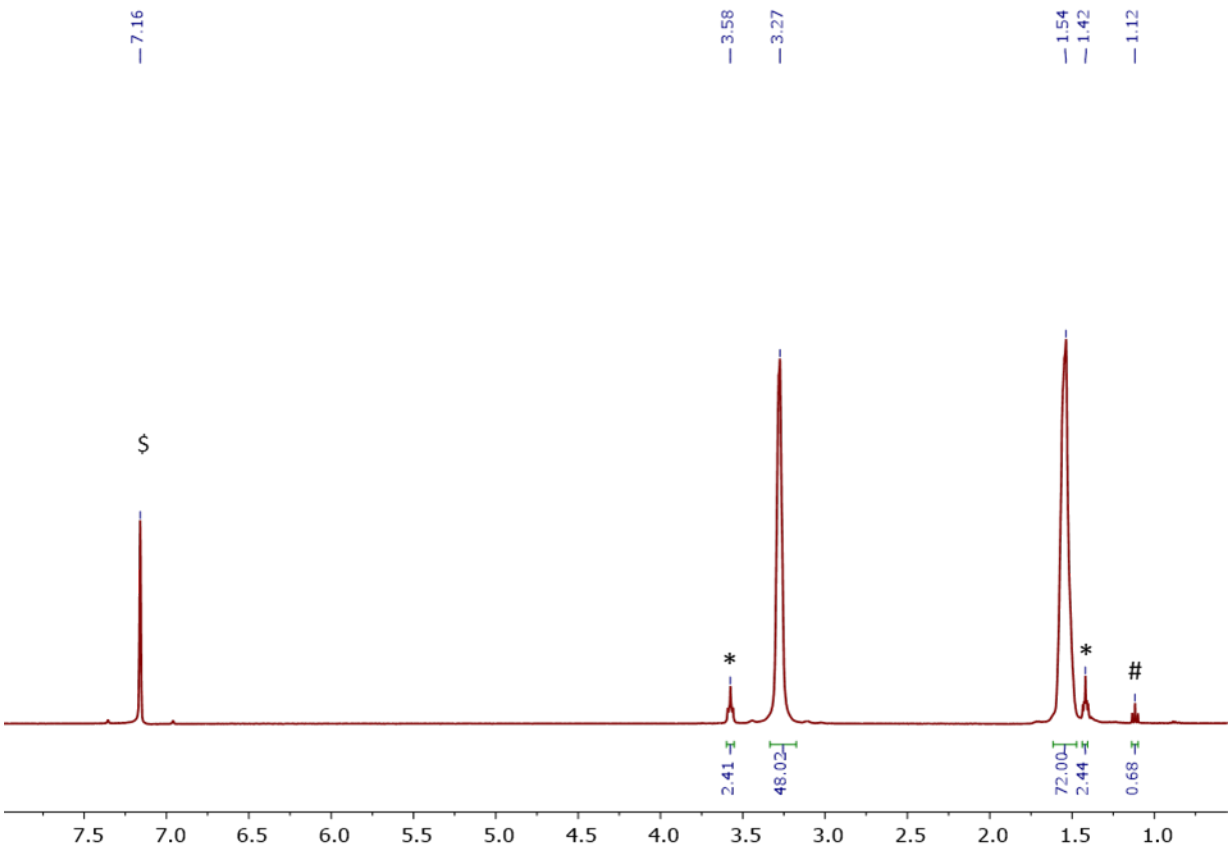

Figure S10. ^{1}H NMR of **2-Ag** in C_6D_6. C_6D_5H is noted as $. Residual THF noted as *. Residual Et_2O noted as #.

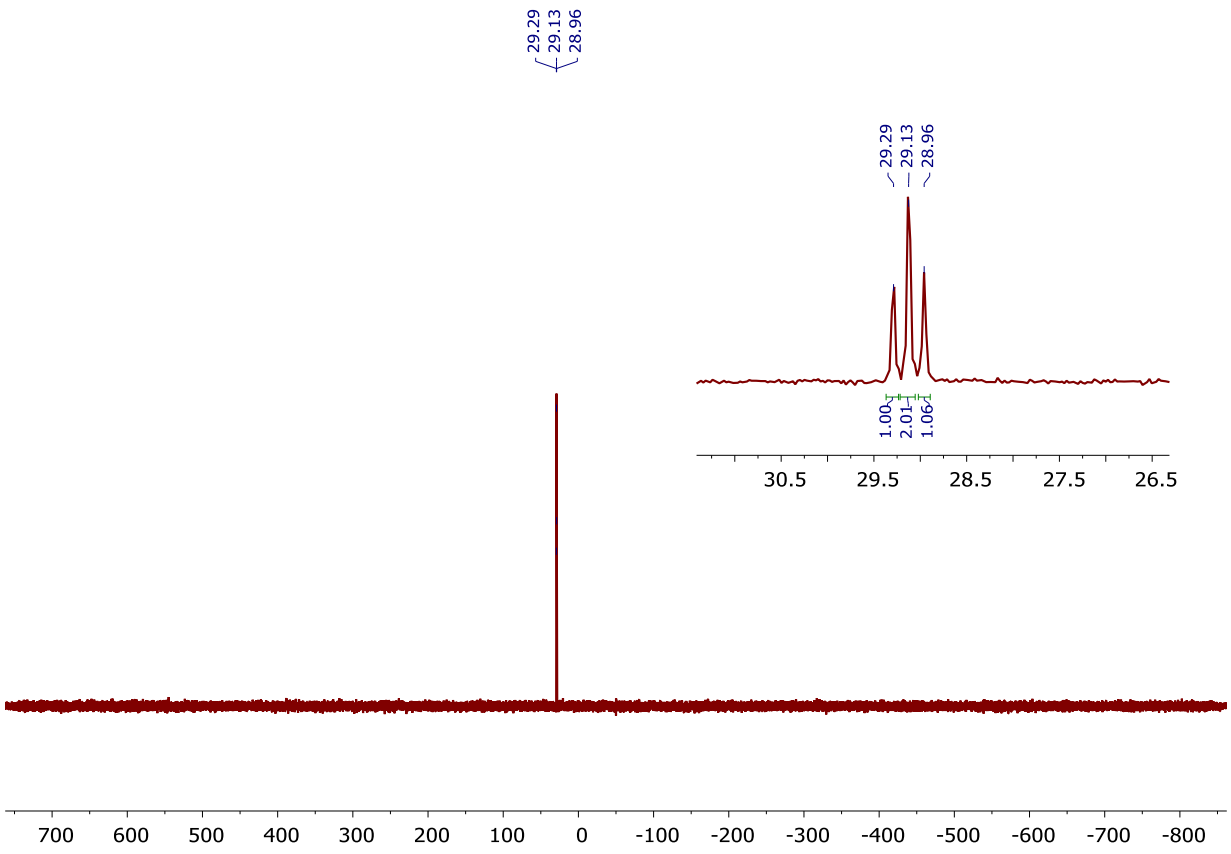

Figure S11. $^{31}P\{^{1}H\}$ NMR of **2-Ag** in C_6D_6.

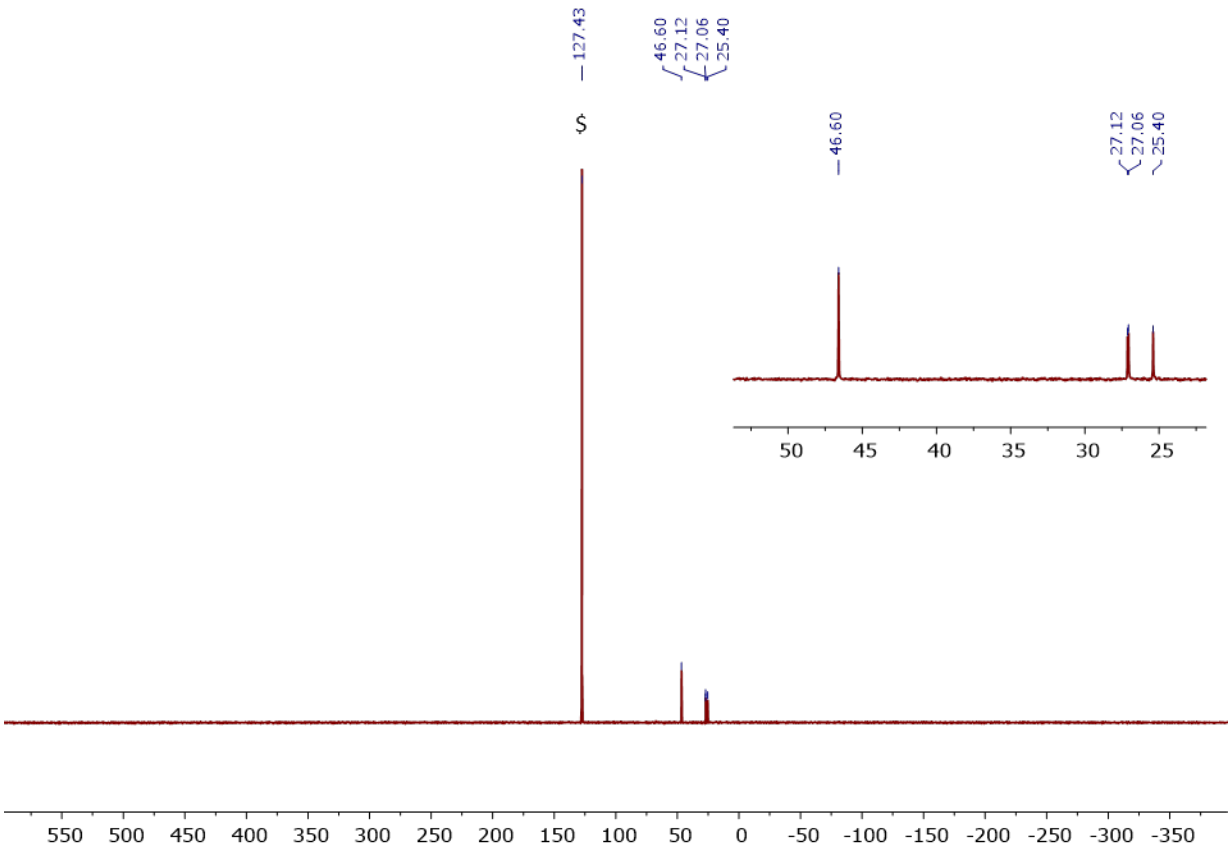

Figure S12. ^{13}C NMR of **2-Ag** in C_6D_6. C_6D_5H is noted as $. Inset shows a zoom-in of the observed signals for clarity.

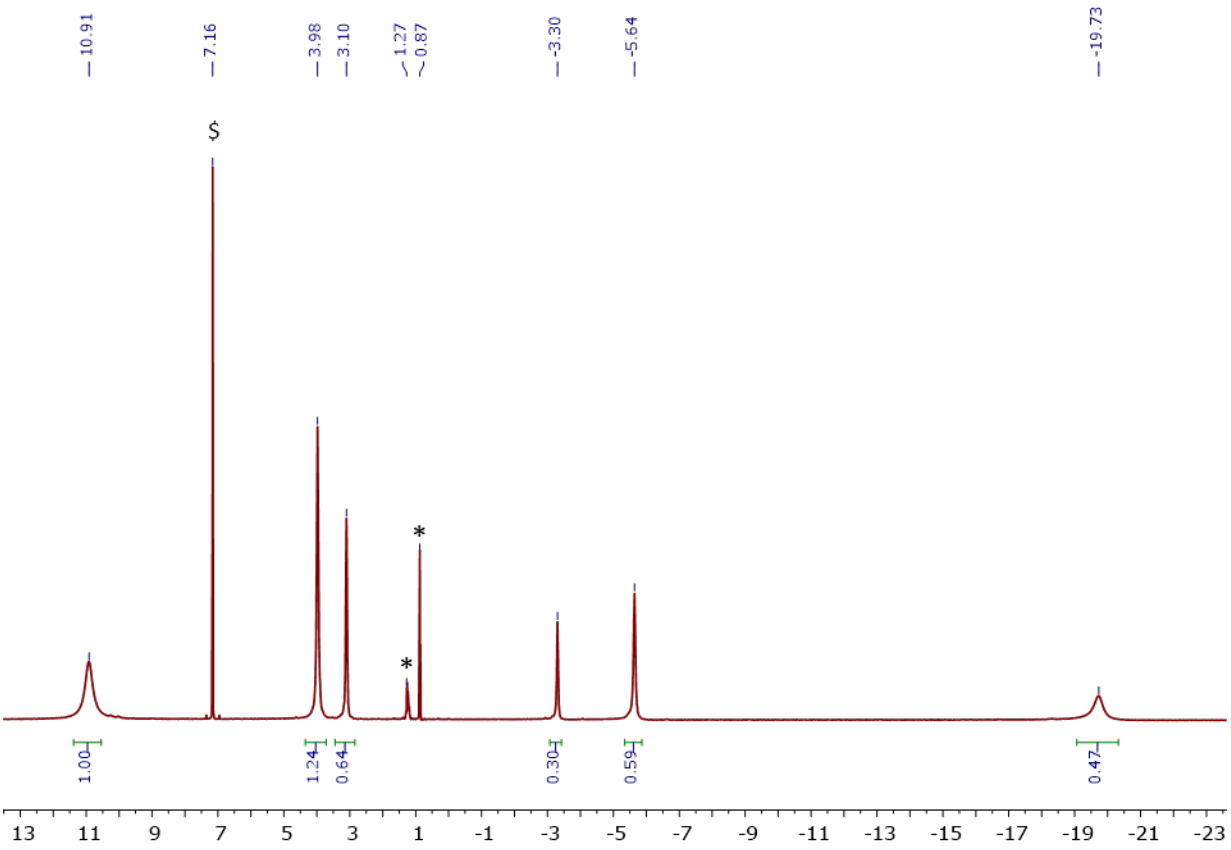

Figure S13. ^{1}H NMR of **1-Ce** in C_6D_6. Peak of residual C_6D_5H noted as $. Residual pentane noted as *.

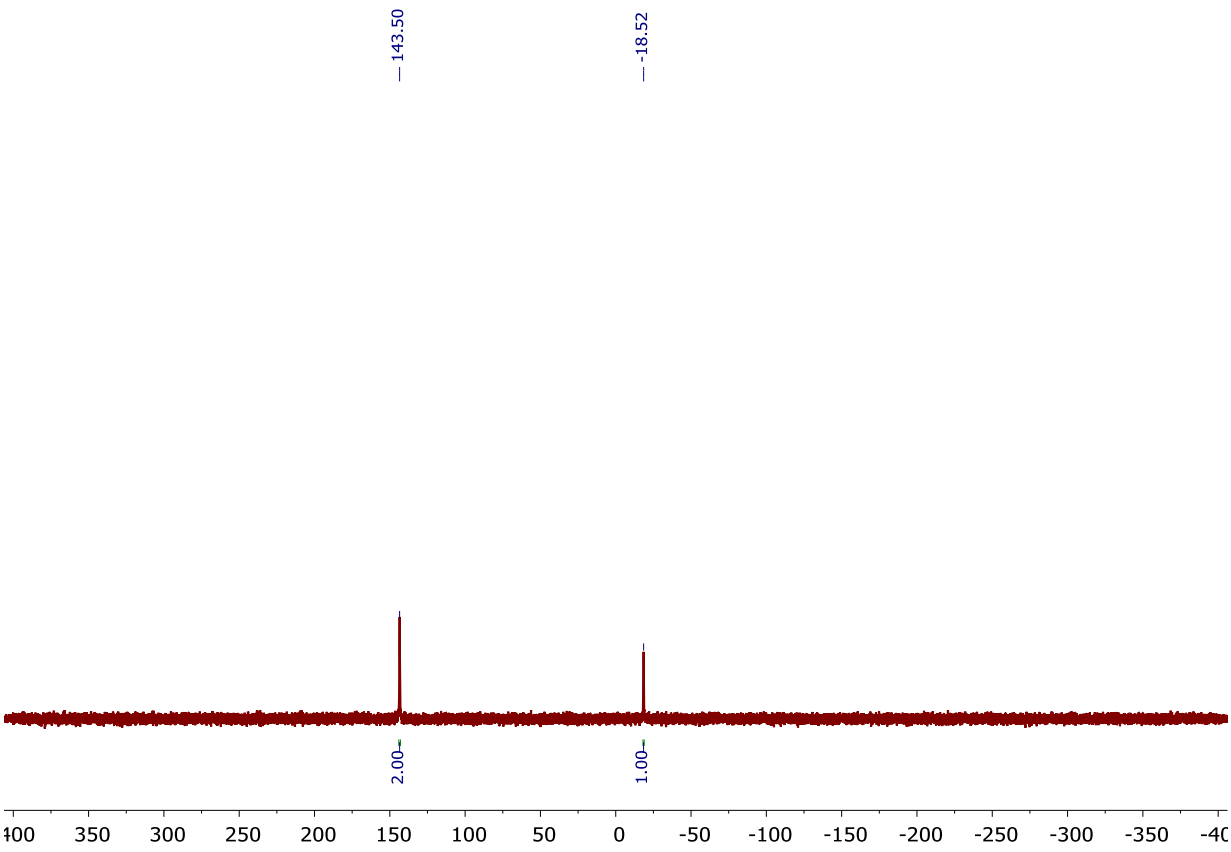

Figure S14. $^{31}P\{^{1}H\}$ NMR of **1-Ce** in C_6D_6.

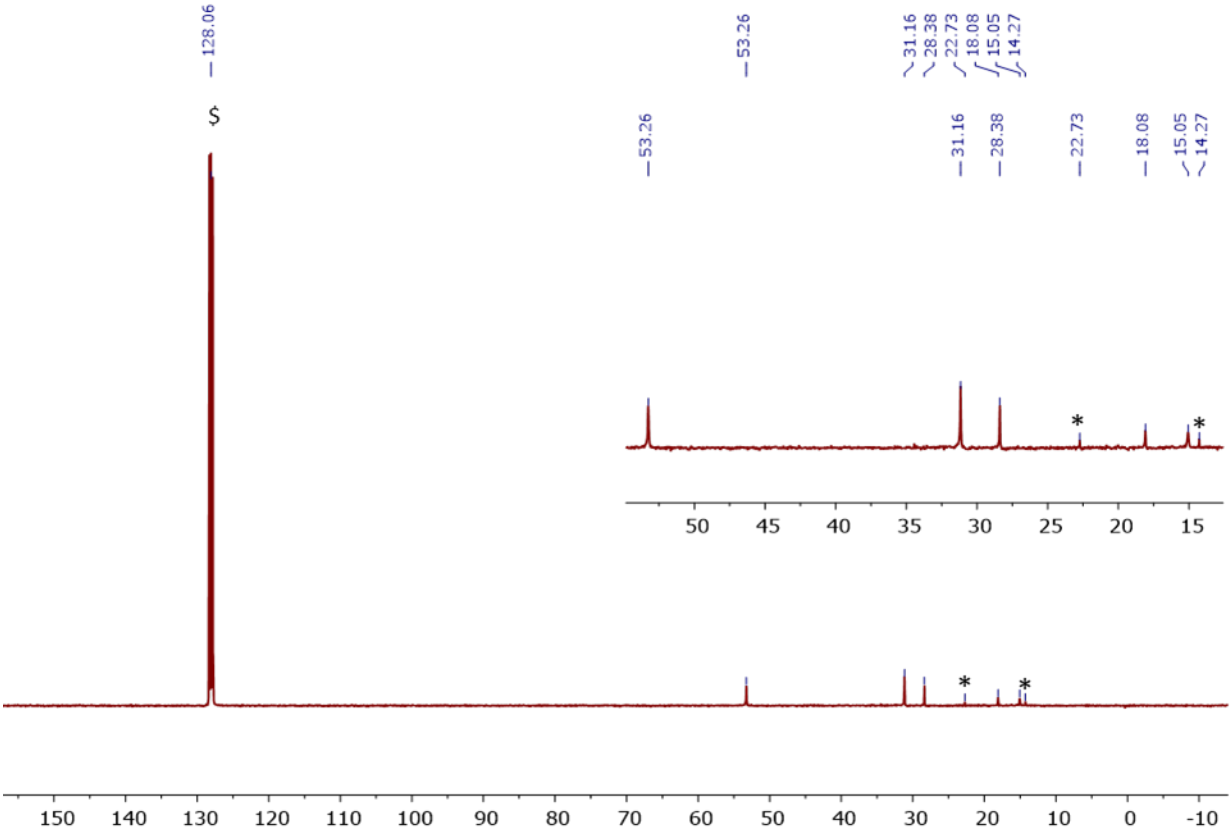

Figure S15. ^{13}C NMR of **1-Ce** in C_6D_6. Peak of residual C_6D_5H noted as $. Residual pentane noted as *. Inset shows a zoom-in of the observed signals for clarity.

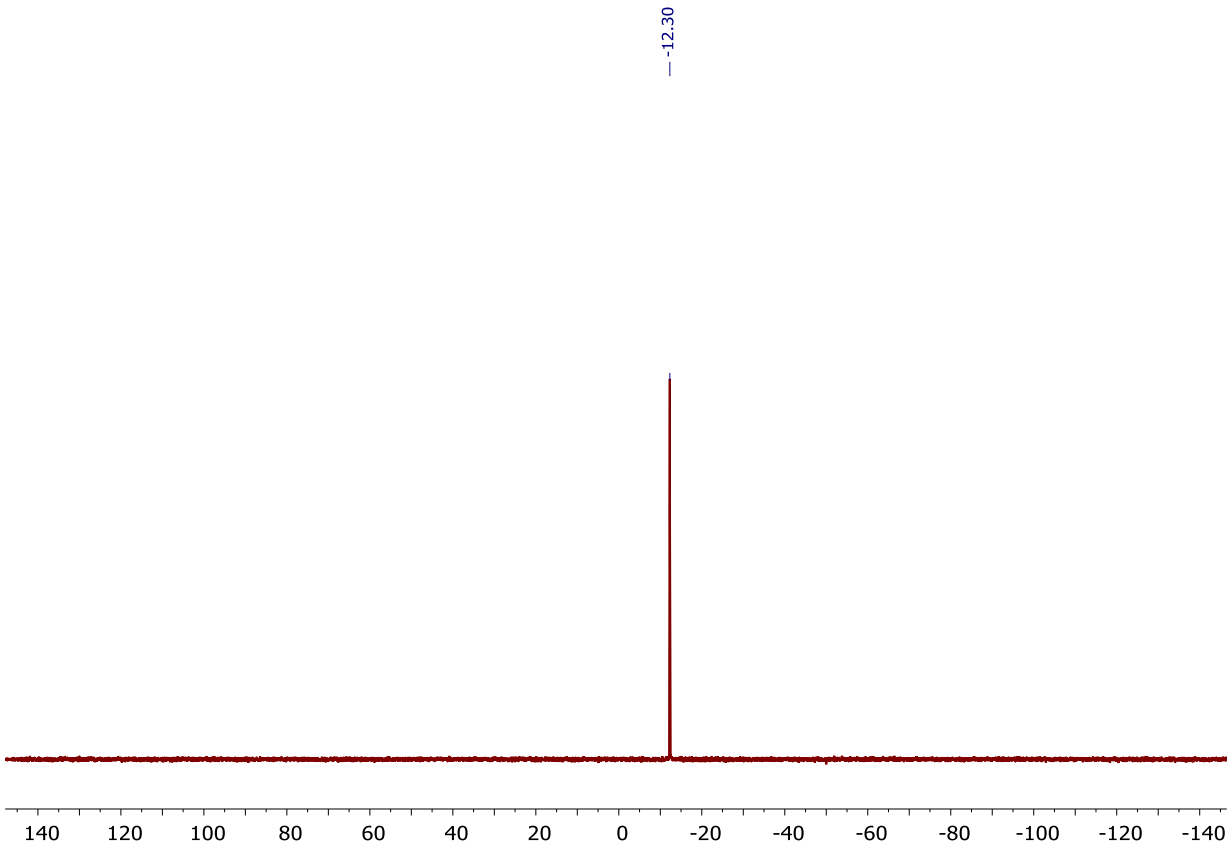

Figure S16. $^{31}P\{^{1}H\}$ NMR of $[Ce(NP(pip)_3)_4]$ in C_6D_6. The $[Ce(NP(pip)_3)_4]$ was obtained from the reaction between **2-Ag** and **1-Ce**.

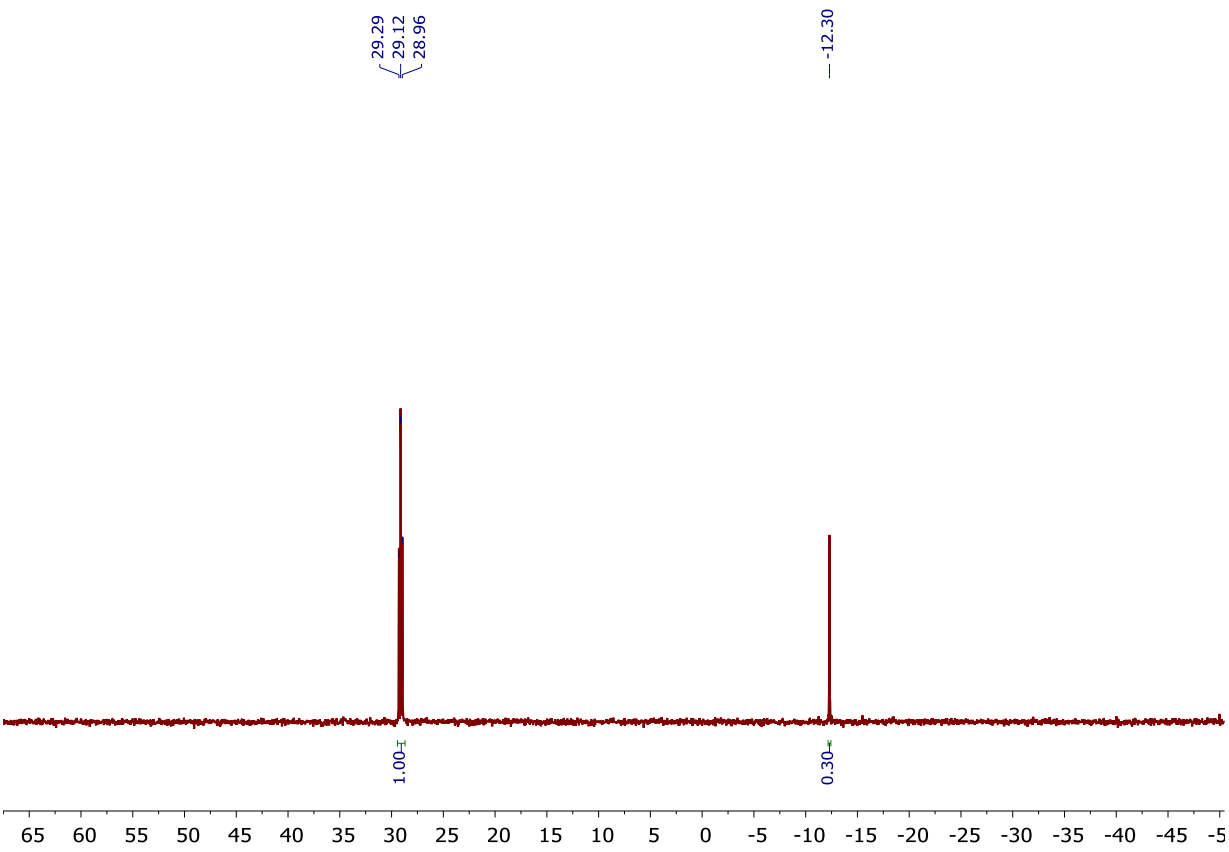

Figure S17. $^{31}P\{^{1}H\}$ NMR of the reaction mixture from the reaction between **2-Ag** and Ce^{0} shavings in C_6D_6.

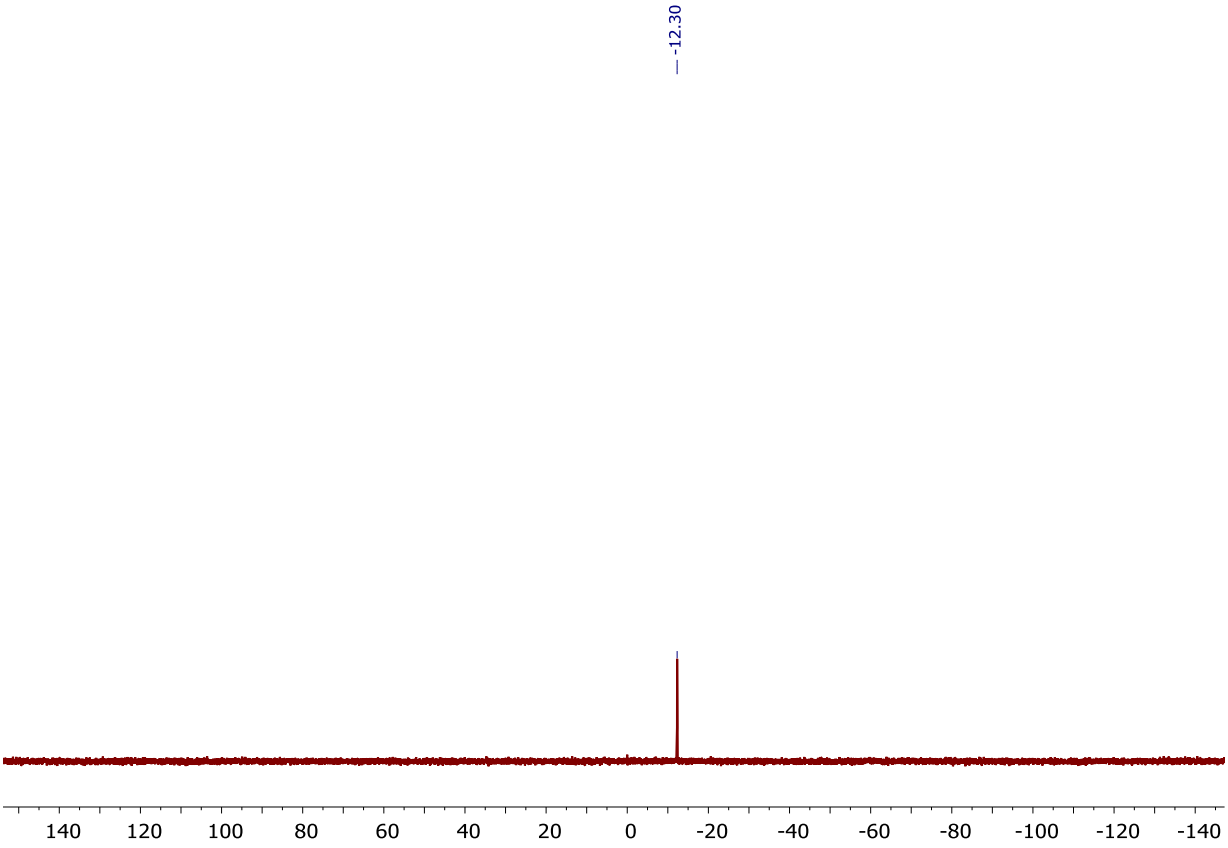

Figure S18. $^{31}P\{^{1}H\}$ NMR of $[Ce(NP(pip)_3)_4]$ in C_6D_6. The $[Ce(NP(pip)_3)_4]$ was obtained from the reaction between **2-Ag** and Ce^0 shavings.

Crystallographic Analyses

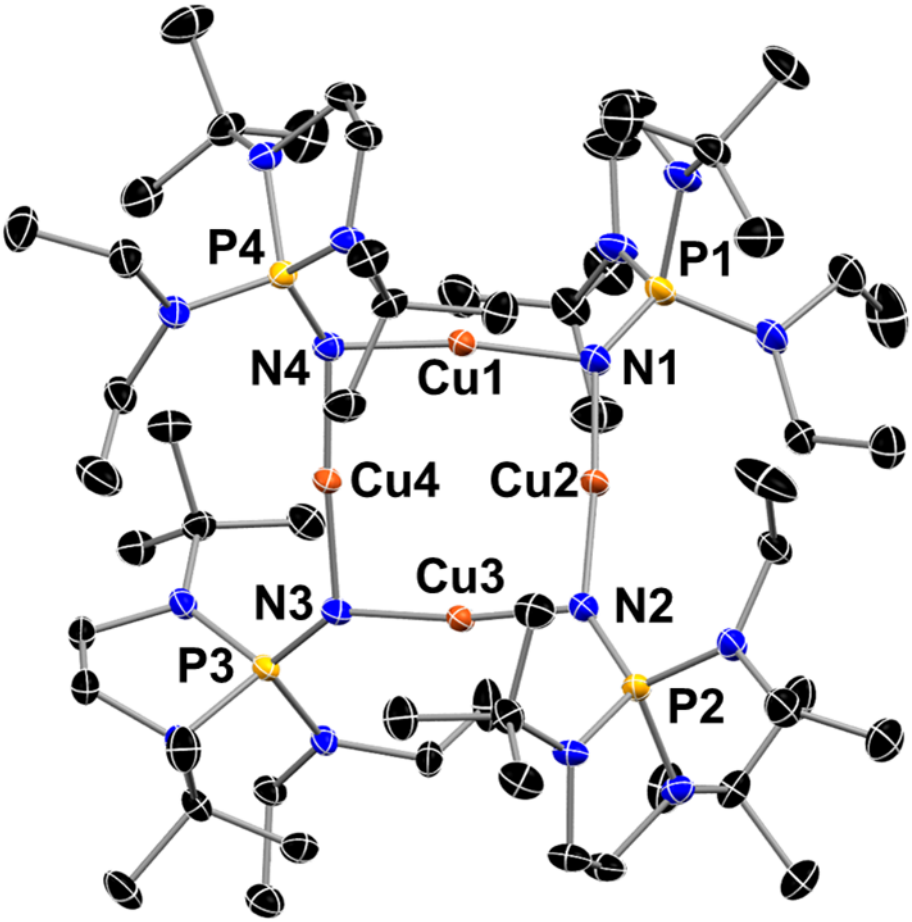

Figure S19. Molecular structure of **1-Cu** with thermal ellipsoids shown at 50% probability. An uncoordinated molecule of THF and H atoms are omitted for clarity.

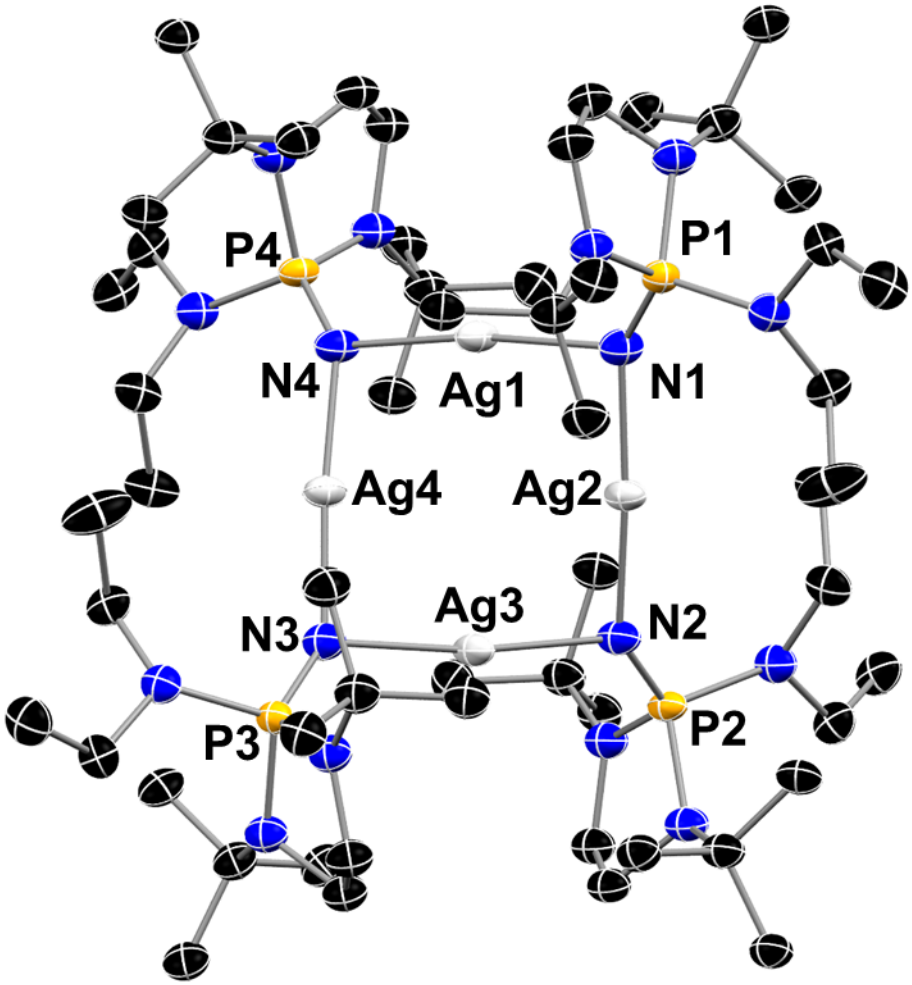

Figure S20. Molecular structure of **1-Ag** with thermal ellipsoids shown at 50% probability and H atoms are omitted for clarity.

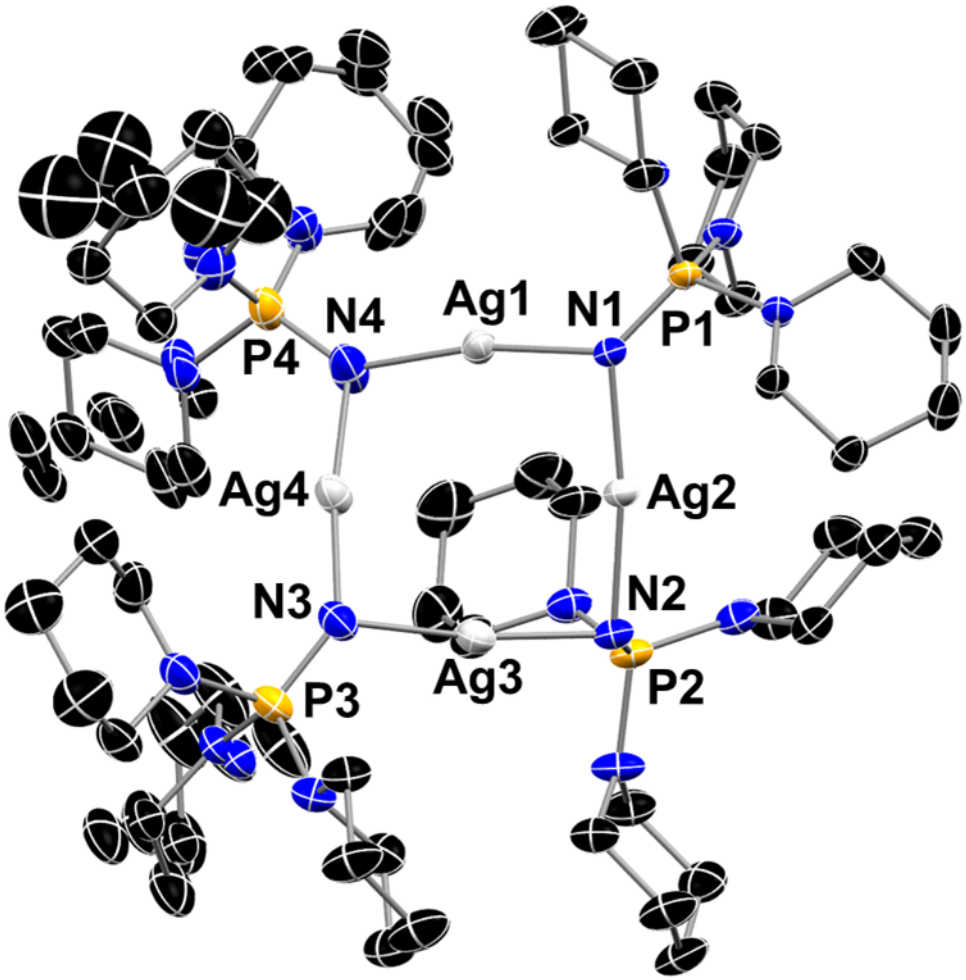

Figure S21. Molecular structure of **2-Ag** with thermal ellipsoids shown at 50% probability and H atoms are omitted for clarity.

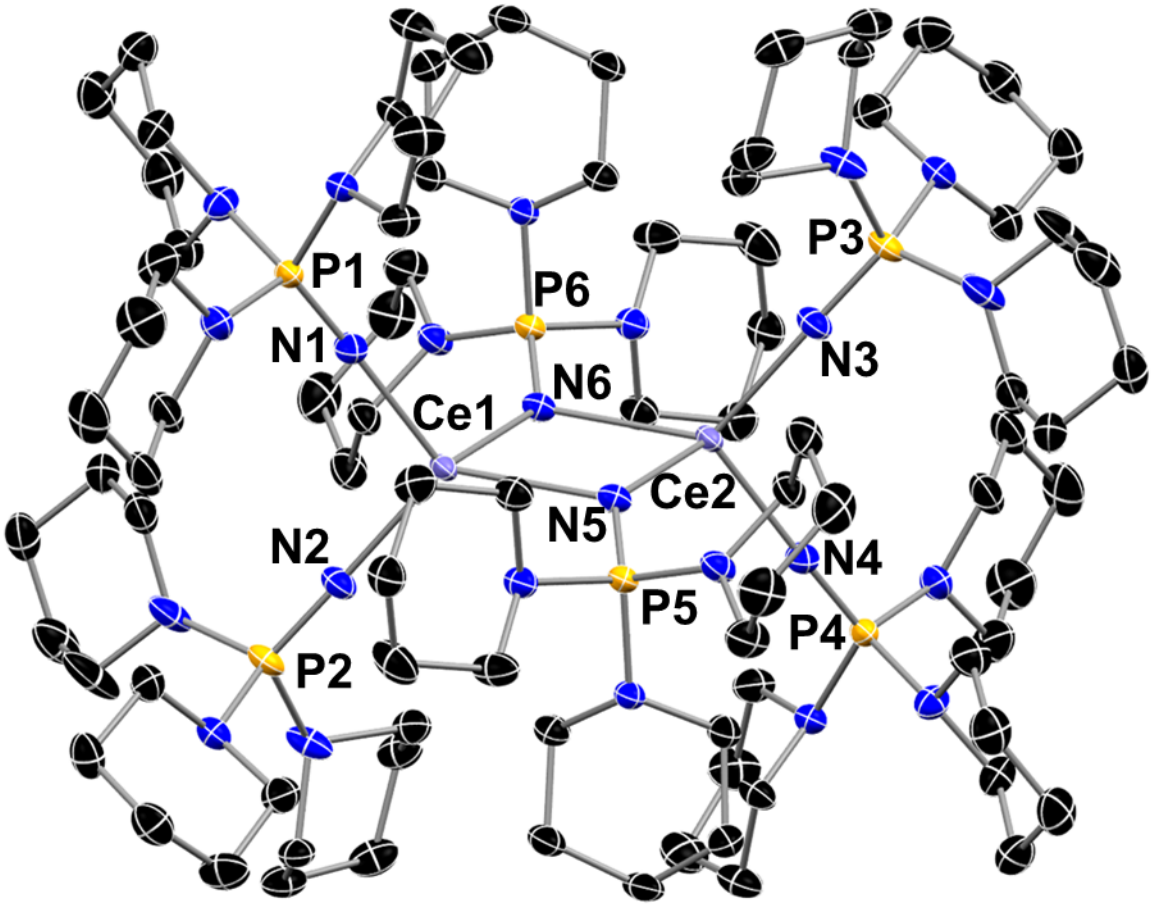

Figure S22. Molecular structure of **1-Ce** with thermal ellipsoids shown at 50% probability and H atoms are omitted for clarity.

Table S1. Crystallographic Data and Structure Refinement for **1-Cu**

	1-Cu
Empirical Formula	$C_{240}H_{548}Cu_{16}N_{64}O_4P_{16}$
Formula Weight	5907.55
Temperature (K)	99.99
Crystal System	monoclinic
Space Group	$P2_1/n$
a/Å	13.463(2)
b/Å	22.899(4)
c/Å	24.461(4)
α/°	90
β/°	93.561(7)
γ/°	90
Volume/Å3	7526(2)
Z	1
Z'	0.25
ρ(g/cm3)	1.303
μ(mm-1)	1.248
F(000)	3172.0
Crystal Size/mm3	0.324 x 0.108 x 0.088
Radiation	MoKα (λ=0.71073)
2θ range for data collection(°)	4.674 to 56.758
Index Ranges	-17 ≤ h ≤ 17, -30 ≤ k ≤30, -32 ≤ 1 ≤ 32
Reflections Collected	74391
Independent Reflections	18628 [Rint = 0.0756, Rsigma = 0.0731]]
Data/Restraints/Parameters	18628/31/805
Goodness-of-Fit on F2	1.014
Final R Indexes [I>=2σ (I)]	R1=0.0451, wR2=0.0953
Final R Indexes [all data]	R1=0.0791, wR2=0.1123
Largest Diff. Peak/Hole/ (e Å3)	0.62/-0.79
Flack Parameter	-
Completeness to 2θ	99

Table S2: Bond Lengths in Å for **1-Cu**.

Atom	Atom	Length/Å
Cu3	Cu2	2.6119(6)
Cu3	Cu4	2.6703(6)
Cu3	N5	1.856(2)
Cu3	N9	1.857(2)
Cu1	Cu2	2.6445(6)
Cu1	Cu4	2.6321(6)
Cu1	N1	1.865(2)
Cu1	N13	1.868(2)
Cu2	N5	1.869(2)
Cu2	N1	1.862(2)
Cu4	N9	1.868(3)
Cu4	N13	1.878(2)
P1	N1	1.541(2)
P1	N2	1.665(2)
P1	N4	1.671(3)
P1	N3	1.707(2)
P4	N13	1.539(2)
P4	N15	1.703(3)
P4	N16	1.678(2)
P4	N14	1.665(3)
P2	N5	1.541(3)
P2	N7	1.701(3)
P2	N8	1.672(2)
P2	N6	1.664(2)
P3	N9	1.540(2)
P3	N10	1.670(3)
P3	N11	1.687(3)
P3	N12	1.684(3)
N2	C3	1.469(3)
N2	C2	1.458(4)
N7	C19	1.485(4)
N7	C22	1.463(4)
N8	C24	1.476(4)
N8	C23	1.459(4)
N4	C11	1.493(4)
N4	C10	1.461(4)
N3	C5	1.492(4)
N3	C9	1.462(4)
N6	C16	1.464(4)
N6	C17	1.469(4)
N15	C47	1.491(4)
N15	C51	1.463(4)
N16	C53	1.484(4)
N16	C52	1.452(4)
N10	C30	1.453(4)
N10	C31	1.469(4)
N14	C44	1.466(4)
N14	C45	1.465(4)
N11	C33	1.490(4)
N11	C37	1.449(4)
N12	C39	1.485(4)
N12	C38	1.435(4)
C11	C14	1.524(4)
C11	C12	1.538(4)
C11	C13	1.530(4)
C24	C27	1.530(4)
C24	C25	1.531(4)
C24	C26	1.534(4)
C5	C7	1.528(4)
C5	C6	1.537(4)
C5	C8	1.535(4)
C3	C4	1.516(4)
C19	C20	1.532(5)
C19	C01I	1.530(5)
C19	C21	1.520(4)
C54	C53	1.530(4)
C30	C29	1.522(4)
C10	C9	1.509(4)
C53	C55	1.526(4)
C53	C56	1.526(4)
C16	C15	1.504(5)
C2	C1	1.527(4)
C33	C36	1.524(5)
C33	C35	1.530(5)
C33	C34	1.525(4)
C52	C51	1.520(4)
C23	C22	1.511(4)
C44	C43	1.519(5)
C47	C48	1.529(5)
C47	C50	1.525(5)
C47	C49	1.529(5)
C40	C39	1.529(5)
C45	C46	1.518(5)
C17	C18	1.518(5)
C39	C42	1.523(5)
C39	C41	1.534(4)
C37	C38	1.463(5)
C31	C32	1.498(5)
O1	C60	1.378(7)
O1	C57	1.481(8)
C60	C59B	1.418(13)
C60	C59A	1.688(13)
C57	C58B	1.590(16)
C57	C58A	1.463(14)
C59B	C58B	1.332(12)
C59A	C58A	1.331(12)

Table S3: Bond Angles in ° for **1-Cu**.

Atom	Atom	Atom	Angle/°
Cu2	Cu3	Cu4	91.66(2)
C30	N10	C31	115.7(3)

N5	Cu3	Cu2	45.70(7)	C31	N10	P3	119.4(2)
N5	Cu3	Cu4	131.71(8)	C44	N14	P4	119.4(2)
N5	Cu3	N9	175.01(11)	C45	N14	P4	123.9(2)
N9	Cu3	Cu2	129.31(8)	C45	N14	C44	116.7(2)
N9	Cu3	Cu4	44.35(8)	C33	N11	P3	125.6(2)
Cu4	Cu1	Cu2	91.79(2)	C37	N11	P3	111.3(2)
N1	Cu1	Cu2	44.75(8)	C37	N11	C33	117.1(3)
N1	Cu1	Cu4	129.14(8)	C39	N12	P3	126.7(2)
N1	Cu1	N13	174.13(11)	C38	N12	P3	113.6(2)
N13	Cu1	Cu2	132.41(8)	C38	N12	C39	119.0(3)
N13	Cu1	Cu4	45.52(8)	N4	C11	C14	110.6(2)
Cu3	Cu2	Cu1	88.683(19)	N4	C11	C12	109.1(2)
N5	Cu2	Cu3	45.28(7)	N4	C11	C13	109.9(2)
N5	Cu2	Cu1	127.45(8)	C14	C11	C12	108.8(2)
N1	Cu2	Cu3	127.67(7)	C14	C11	C13	108.9(3)
N1	Cu2	Cu1	44.83(7)	C13	C11	C12	109.6(3)
N1	Cu2	N5	172.16(11)	N8	C24	C27	109.8(2)
Cu1	Cu4	Cu3	87.71(2)	N8	C24	C25	111.1(2)
N9	Cu4	Cu3	44.03(7)	N8	C24	C26	109.5(3)
N9	Cu4	Cu1	126.63(8)	C27	C24	C25	108.4(3)
N9	Cu4	N13	171.13(11)	C27	C24	C26	109.9(3)
N13	Cu4	Cu3	127.25(8)	C25	C24	C26	108.1(2)
N13	Cu4	Cu1	45.20(7)	N3	C5	C7	110.4(2)
N1	P1	N2	112.23(13)	N3	C5	C6	111.3(3)
N1	P1	N4	117.83(13)	N3	C5	C8	107.9(2)
N1	P1	N3	119.80(13)	C7	C5	C6	109.5(3)
N2	P1	N4	107.96(12)	C7	C5	C8	108.0(3)
N2	P1	N3	104.63(12)	C8	C5	C6	109.7(3)
N4	P1	N3	92.03(12)	N2	C3	C4	115.0(2)
N13	P4	N15	118.62(13)	N7	C19	C20	110.0(3)
N13	P4	N16	119.33(13)	N7	C19	C01I	108.7(2)
N13	P4	N14	112.45(13)	N7	C19	C21	111.8(3)
N16	P4	N15	91.99(12)	C01I	C19	C20	108.5(3)
N14	P4	N15	105.20(13)	C21	C19	C20	107.6(3)
N14	P4	N16	106.74(13)	C21	C19	C01I	110.2(3)
N5	P2	N7	120.07(13)	N10	C30	C29	113.6(3)
N5	P2	N8	118.20(13)	N4	C10	C9	104.8(2)
N5	P2	N6	112.37(13)	N16	C53	C54	108.5(2)
N8	P2	N7	91.92(12)	N16	C53	C55	111.1(2)
N6	P2	N7	105.41(13)	N16	C53	C56	110.1(2)
N6	P2	N8	106.35(12)	C55	C53	C54	108.5(3)
N9	P3	N10	112.53(14)	C56	C53	C54	109.7(3)
N9	P3	N11	119.77(14)	C56	C53	C55	108.9(3)
N9	P3	N12	118.25(14)	N3	C9	C10	104.9(2)
N10	P3	N11	103.98(14)	N6	C16	C15	114.4(3)
N10	P3	N12	107.74(14)	N2	C2	C1	114.6(3)
N12	P3	N11	92.03(12)	N11	C33	C36	110.9(3)
Cu3	N5	Cu2	89.03(11)	N11	C33	C35	110.4(3)
P2	N5	Cu3	144.99(15)	N11	C33	C34	108.5(3)
P2	N5	Cu2	125.89(14)	C36	C33	C35	109.0(3)
Cu3	N9	Cu4	91.62(11)	C36	C33	C34	108.3(3)
P3	N9	Cu3	141.78(17)	C34	C33	C35	109.6(3)
P3	N9	Cu4	126.19(15)	N16	C52	C51	105.7(2)
Cu2	N1	Cu1	90.42(10)	N8	C23	C22	105.6(2)
P1	N1	Cu1	126.57(15)	N7	C22	C23	104.6(2)
P1	N1	Cu2	142.20(16)	N14	C44	C43	114.4(3)

C3	N2	P1	120.21(19)	N15	C47	C48	109.5(3)
C2	N2	P1	124.77(19)	N15	C47	C50	111.6(3)
C2	N2	C3	115.0(2)	N15	C47	C49	108.3(2)
C19	N7	P2	123.9(2)	C50	C47	C48	108.6(3)
C22	N7	P2	108.7(2)	C50	C47	C49	110.2(3)
C22	N7	C19	116.5(2)	C49	C47	C48	108.6(3)
C24	N8	P2	127.4(2)	N14	C45	C46	114.0(3)
C23	N8	P2	113.8(2)	N15	C51	C52	104.2(2)
C23	N8	C24	118.4(2)	N6	C17	C18	115.1(3)
Cu1	N13	Cu4	89.29(11)	N12	C39	C40	110.2(3)
P4	N13	Cu1	138.99(15)	N12	C39	C42	110.7(3)
P4	N13	Cu4	121.97(14)	N12	C39	C41	108.9(3)
C11	N4	P1	128.92(19)	C40	C39	C41	109.7(3)
C10	N4	P1	114.04(19)	C42	C39	C40	108.8(3)
C10	N4	C11	116.9(2)	C42	C39	C41	108.5(3)
C5	N3	P1	123.03(19)	N11	C37	C38	107.5(3)
C9	N3	P1	108.90(19)	N10	C31	C32	114.2(3)
C9	N3	C5	115.9(2)	N12	C38	C37	108.4(3)
C16	N6	P2	124.1(2)	C60	O1	C57	109.5(5)
C16	N6	C17	115.9(2)	O1	C60	C59B	105.9(7)
C17	N6	P2	119.8(2)	O1	C60	C59A	100.5(6)
C47	N15	P4	123.24(19)	O1	C57	C58B	98.7(6)
C51	N15	P4	109.18(19)	C58A	C57	O1	105.5(7)
C51	N15	C47	115.8(2)	C58B	C59B	C60	106.2(12)
C53	N16	P4	127.4(2)	C59B	C58B	C57	105.6(11)
C52	N16	P4	113.74(19)	C58A	C59A	C60	107.5(10)
C52	N16	C53	118.8(2)	C59A	C58A	C57	106.5(11)
C30	N10	P3	124.8(2)				

Table S4. Crystallographic Data and Structure Refinement for **1-Ag**

	1-Ag
Empirical Formula	$C_{56}H_{128}Ag_4N_{16}P_4$
Formula Weight	1581.10
Temperature (K)	100.2
Crystal System	orthorhombic
Space Group	Pbcn
a/Å	18.3095(17)
b/Å	17.4338(17)
c/Å	26.753(2)
α/°	90
β/°	90
γ/°	90
Volume/Å3	8539.7(13)
Z	4
Z'	0.5
ρ(g/cm3)	1.230
μ(mm-1)	1.017
F(000)	3296.0
Crystal Size/mm3	0.268 x 0.246 x 0.24
Radiation	MoKα (λ=0.71073)
2θ range for data collection(°)	4.436 to 61.016
Index Ranges	-24 ≤ h ≤ 26, -24 ≤ k ≤24, -36≤ 1 ≤ 38
Reflections Collected	91258
Independent Reflections	13006 [Rint = 0.0639, Rsigma = 0.0401]
Data/Restraints/Parameters	13006/912/724
Goodness-of-Fit on F2	1.080
Final R Indexes [I>=2σ (I)]	R1=0.0703, wR2=0.1844
Final R Indexes [all data]	R1=0.1014, wR2=0.2160
Largest Diff. Peak/Hole/ (e Å3)	2.15/-2.10
Flack Parameter	-
Completeness to 2θ	100

Table S5: Bond Lengths in Å for **1-Ag**.

Atom	Atom	Length/Å
N1_1	P1_1	1.537(3)
N1_1	Ag1_5	2.074(8)
N1_1	Ag2_5	2.089(8)
P1_1	N2_1	1.695(3)
P1_1	N3_1	1.682(4)
P1_1	N4_1	1.672(4)
N2_1	C1_1	1.463(5)
N2_1	C3_1	1.493(5)
N3_1	C2_1	1.457(5)
N3_1	C7_1	1.483(5)
C1_1	C2_1	1.524(5)
C3_1	C4_1	1.548(6)
C3_1	C5_1	1.526(6)
C3_1	C6_1	1.527(6)
C7_1	C8_1	1.530(6)
C7_1	C9_1	1.544(7)
C7_1	C10_1	1.519(8)
N4_1	C11_1	1.470(5)
N4_1	C13_1	1.471(6)
C11_1	C12_1	1.465(8)
C13_1	C14_1	1.532(7)
N1_2	P1_2	1.537(3)
N1_2	Ag1_6	2.093(8)
N1_2	Ag2_6	2.029(8)
P1_2	N2_2	1.697(3)
P1_2	N3_2	1.683(4)
P1_2	N4_2	1.669(4)
N2_2	C1_2	1.462(5)
N2_2	C3_2	1.494(5)
N3_2	C2_2	1.456(5)
N3_2	C7_2	1.483(5)
C1_2	C2_2	1.524(5)
C3_2	C4_2	1.547(6)
C3_2	C5_2	1.526(6)
C3_2	C6_2	1.528(6)
C7_2	C8_2	1.531(6)
C7_2	C9_2	1.544(7)
C7_2	C10_2	1.519(8)
N4_2	C11_2	1.467(5)
N4_2	C13_2	1.468(6)
C11_2	C12_2	1.464(8)
C13_2	C14_2	1.532(7)
N1_3	P1_3	1.537(3)
N1_3	Ag1_6	2.162(7)
P1_3	N2_3	1.698(3)
P1_3	N3_3	1.681(4)
P1_3	N4_3	1.668(4)
N2_3	C1_3	1.463(5)
N2_3	C3_3	1.496(5)
N3_3	C2_3	1.457(5)
N3_3	C7_3	1.483(5)
C1_3	C2_3	1.525(5)
C3_3	C4_3	1.547(6)
C3_3	C5_3	1.525(6)
C3_3	C6_3	1.528(6)
C7_3	C8_3	1.531(6)
C7_3	C9_3	1.544(7)
C7_3	C10_3	1.519(8)
N4_3	C11_3	1.466(5)
N4_3	C13_3	1.468(6)
C11_3	C12_3	1.465(8)
C13_3	C14_3	1.532(7)
N1_4	P1_4	1.537(3)
N1_4	Ag1_5	2.040(6)
N1_4	Ag2_5[1]	2.067(7)
P1_4	N2_4	1.698(3)
P1_4	N3_4	1.681(4)
P1_4	N4_4	1.669(4)
N2_4	C1_4	1.463(5)
N2_4	C3_4	1.496(5)
N3_4	C2_4	1.456(5)
N3_4	C7_4	1.483(5)
C1_4	C2_4	1.524(5)
C3_4	C4_4	1.547(6)
C3_4	C5_4	1.525(6)
C3_4	C6_4	1.528(6)
C7_4	C8_4	1.531(6)
C7_4	C9_4	1.544(7)
C7_4	C10_4	1.519(8)
N4_4	C11_4	1.468(5)
N4_4	C13_4	1.469(6)
C11_4	C12_4	1.465(8)
C13_4	C14_4	1.532(7)
Ag1_5	Ag2_5[1]	2.9804(5)
Ag1_5	Ag2_5	2.9773(5)
Ag1_6	Ag2_6	2.9773(5)

[1]-X,+Y,1/2-Z

Table S6: Bond Angles in ° for **1-Ag**.

Atom	Atom	Atom	Angle/°
P1_1	N1_1	Ag1_5	119.5(4)
P1_1	N1_1	Ag2_5	140.3(4)
Ag1_5	N1_1	Ag2_5	91.3(3)
N1_1	P1_1	N2_1	117.9(2)
N1_1	P1_1	N3_1	120.0(2)
C1_3	N2_3	C3_3	116.5(3)
C3_3	N2_3	P1_3	122.1(3)
C2_3	N3_3	P1_3	113.6(3)
C2_3	N3_3	C7_3	118.4(4)
C7_3	N3_3	P1_3	128.0(3)

N1_1	P1_1	N4_1	111.9(2)
N3_1	P1_1	N2_1	91.95(18)
N4_1	P1_1	N2_1	106.0(2)
N4_1	P1_1	N3_1	106.6(2)
C1_1	N2_1	P1_1	109.3(3)
C1_1	N2_1	C3_1	116.6(3)
C3_1	N2_1	P1_1	124.0(3)
C2_1	N3_1	P1_1	113.8(3)
C2_1	N3_1	C7_1	117.9(4)
C7_1	N3_1	P1_1	128.3(3)
N2_1	C1_1	C2_1	104.1(3)
N3_1	C2_1	C1_1	104.9(3)
N2_1	C3_1	C4_1	111.4(4)
N2_1	C3_1	C5_1	108.5(4)
N2_1	C3_1	C6_1	110.9(4)
C5_1	C3_1	C4_1	109.2(4)
C5_1	C3_1	C6_1	108.3(4)
C6_1	C3_1	C4_1	108.5(4)
N3_1	C7_1	C8_1	111.2(4)
N3_1	C7_1	C9_1	108.7(4)
N3_1	C7_1	C10_1	109.6(4)
C8_1	C7_1	C9_1	107.9(4)
C10_1	C7_1	C8_1	109.1(4)
C10_1	C7_1	C9_1	110.4(5)
C11_1	N4_1	P1_1	118.2(3)
C11_1	N4_1	C13_1	114.9(4)
C13_1	N4_1	P1_1	122.5(3)
C12_1	C11_1	N4_1	118.0(5)
N4_1	C13_1	C14_1	113.8(5)
P1_2	N1_2	Ag1_6	117.0(4)
P1_2	N1_2	Ag2_6	141.9(4)
Ag2_6	N1_2	Ag1_6	92.5(3)
N1_2	P1_2	N2_2	117.8(2)
N1_2	P1_2	N3_2	119.9(3)
N1_2	P1_2	N4_2	112.1(2)
N3_2	P1_2	N2_2	91.99(18)
N4_2	P1_2	N2_2	106.1(2)
N4_2	P1_2	N3_2	106.7(2)
C1_2	N2_2	P1_2	109.2(3)
C1_2	N2_2	C3_2	116.9(3)
C3_2	N2_2	P1_2	123.2(3)
C2_2	N3_2	P1_2	113.8(3)
C2_2	N3_2	C7_2	118.3(4)
C7_2	N3_2	P1_2	127.9(3)
N2_2	C1_2	C2_2	104.3(3)
N3_2	C2_2	C1_2	105.2(3)
N2_2	C3_2	C4_2	111.5(4)
N2_2	C3_2	C5_2	108.7(4)
N2_2	C3_2	C6_2	110.6(4)
C5_2	C3_2	C4_2	109.4(4)
C5_2	C3_2	C6_2	108.1(4)
C6_2	C3_2	C4_2	108.4(4)
N3_2	C7_2	C8_2	111.0(4)
N3_2	C7_2	C9_2	108.9(4)
N3_2	C7_2	C10_2	109.7(4)
C8_2	C7_2	C9_2	107.8(4)
N2_3	C1_3	C2_3	104.5(3)
N3_3	C2_3	C1_3	104.7(3)
N2_3	C3_3	C4_3	111.3(4)
N2_3	C3_3	C5_3	108.9(4)
N2_3	C3_3	C6_3	110.5(4)
C5_3	C3_3	C4_3	109.5(4)
C5_3	C3_3	C6_3	108.2(4)
C6_3	C3_3	C4_3	108.4(4)
N3_3	C7_3	C8_3	111.1(4)
N3_3	C7_3	C9_3	108.8(4)
N3_3	C7_3	C10_3	109.7(4)
C8_3	C7_3	C9_3	107.8(4)
C10_3	C7_3	C8_3	109.0(4)
C10_3	C7_3	C9_3	110.4(5)
C11_3	N4_3	P1_3	119.4(3)
C11_3	N4_3	C13_3	115.9(4)
C13_3	N4_3	P1_3	123.6(3)
C12_3	C11_3	N4_3	118.2(5)
N4_3	C13_3	C14_3	113.6(5)
P1_4	N1_4	Ag1_5	120.6(4)
P1_4	N1_4	Ag2_5[1]	140.6(4)
Ag1_5	N1_4	Ag2_5[1]	93.1(2)
N1_4	P1_4	N2_4	117.6(2)
N1_4	P1_4	N3_4	120.0(3)
N1_4	P1_4	N4_4	111.8(2)
N3_4	P1_4	N2_4	92.18(18)
N4_4	P1_4	N2_4	106.0(2)
N4_4	P1_4	N3_4	106.9(2)
C1_4	N2_4	P1_4	109.1(3)
C1_4	N2_4	C3_4	116.5(3)
C3_4	N2_4	P1_4	122.3(3)
C2_4	N3_4	P1_4	113.7(3)
C2_4	N3_4	C7_4	118.3(4)
C7_4	N3_4	P1_4	128.0(3)
N2_4	C1_4	C2_4	104.5(3)
N3_4	C2_4	C1_4	105.1(3)
N2_4	C3_4	C4_4	111.4(4)
N2_4	C3_4	C5_4	108.8(4)
N2_4	C3_4	C6_4	110.4(4)
C5_4	C3_4	C4_4	109.5(4)
C5_4	C3_4	C6_4	108.2(4)
C6_4	C3_4	C4_4	108.4(4)
N3_4	C7_4	C8_4	111.1(4)
N3_4	C7_4	C9_4	108.8(4)
N3_4	C7_4	C10_4	109.7(4)
C8_4	C7_4	C9_4	107.8(4)
C10_4	C7_4	C8_4	109.0(4)
C10_4	C7_4	C9_4	110.4(5)
C11_4	N4_4	P1_4	119.0(3)
C11_4	N4_4	C13_4	115.5(4)
C13_4	N4_4	P1_4	123.3(3)
C12_4	C11_4	N4_4	118.0(5)
N4_4	C13_4	C14_4	113.7(5)
N1_1	Ag1_5	Ag2_5[1]	129.4(2)
N1_1	Ag1_5	Ag2_5	44.5(2)
N1_4	Ag1_5	N1_1	171.6(3)

C10_2	C7_2	C8_2	109.0(4)
C10_2	C7_2	C9_2	110.4(5)
C11_2	N4_2	P1_2	118.9(3)
C11_2	N4_2	C13_2	115.9(4)
C13_2	N4_2	P1_2	123.4(3)
C12_2	C11_2	N4_2	118.5(5)
N4_2	C13_2	C14_2	113.8(5)
P1_3	N1_3	Ag1_6	119.3(4)
N1_3	P1_3	N2_3	117.6(2)
N1_3	P1_3	N3_3	119.9(3)
N1_3	P1_3	N4_3	111.9(2)
N3_3	P1_3	N2_3	92.34(19)
N4_3	P1_3	N2_3	106.0(2)
N4_3	P1_3	N3_3	106.8(2)
C1_3	N2_3	P1_3	109.5(3)

N1_4	Ag1_5	Ag2_5[1]	43.82(19)
N1_4	Ag1_5	Ag2_5	127.2(2)
Ag2_5	Ag1_5	Ag2_5[1]	87.661(16)
N1_1	Ag2_5	Ag1_5	44.1(2)
N1_1	Ag2_5	Ag1_5[1]	133.8(2)
N1_41	Ag2_5	N1_1	173.9(3)
N1_41	Ag2_5	Ag1_5	130.6(2)
N1_41	Ag2_5	Ag1_5[1]	43.13(18)
Ag1_5	Ag2_5	Ag1_5[1]	92.331(16)
N1_2	Ag1_6	N1_3	170.4(3)
N1_2	Ag1_6	Ag2_6	42.9(2)
N1_3	Ag1_6	Ag2_6	129.9(2)
N1_2	Ag2_6	Ag1_6	44.6(2)
N1_31	Ag2_6	Ag1_6	136.8(2)

[1]-X,+Y,1/2-Z

Table S7. Crystallographic Data and Structure Refinement for **2-Ag**

	2-Ag
Empirical Formula	$C_{60}H_{120}Ag_4N_{16}P_4$
Formula Weight	1621.07
Temperature (K)	100.0
Crystal System	Monoclinic
Space Group	*C2/c*
a/Å	25.417(4)
b/Å	15.104(2)
c/Å	40.405(8)
α/°	90
β/°	105.657(8)
γ/°	90
Volume/Å3	14935(5)
Z	8
Z'	1
ρ(g/cm3)	1.442
μ(mm-1)	1.165
F(000)	6720.0
Crystal Size/mm3	0.215 x 0.192 x 0.163
Radiation	MoKα (λ=0.71073)
2θ range for data collection(°)	4.384 to 55.236
Index Ranges	-32 ≤ h ≤ 28, -19 ≤ k ≤19, -52≤ 1 ≤ 52
Reflections Collected	52846
Independent Reflections	17175 [Rint = 0.0658, Rsigma = 0.0669]
Data/Restraints/Parameters	17175/97/862
Goodness-of-Fit on F2	1.037
Final R Indexes [I>=2σ (I)]	R1=0.0455, wR2=0.1135
Final R Indexes [all data]	R1=0.0563, wR2=0.1220
Largest Diff. Peak/Hole/ (e Å3)	0.90/-0.63
Flack Parameter	-
Completeness to 2θ	99

Table S8: Bond Lengths in Å for **2-Ag**.

Atom	Atom	Length/Å
Ag1	Ag2	2.9588(5)
Ag1	Ag4	2.9582(5)
Ag1	N1	2.095(3)
Ag1	N13	2.072(3)
Ag2	Ag3	2.9168(5)
Ag2	N1	2.091(3)
Ag2	N5	2.084(3)
Ag3	Ag4	2.9811(5)
Ag3	N5	2.071(3)
Ag3	N9	2.074(4)
Ag4	N9	2.058(4)
Ag4	N13	2.057(3)
P1	N1	1.557(3)
P1	N2	1.687(3)
P1	N3	1.677(4)
P1	N4	1.672(3)
P2	N5	1.542(3)
P2	N6	1.687(4)
P2	N8	1.675(4)
P2	N7A	1.683(10)
P2	N7B	1.686(5)
P3	N9	1.534(4)
P3	N10A	1.686(8)
P3	N11B	1.678(8)
P3	N12A	1.77(3)
P3	N10B	1.668(5)
P3	N11A	1.694(5)
P3	N12B	1.621(14)
P4	N13	1.541(3)
P4	N14	1.692(3)
P4	N15	1.674(3)
P4	N16	1.659(3)
N2	C1	1.488(5)
N2	C5	1.470(6)
N3	C6	1.461(5)
N3	C10	1.467(5)
N4	C11	1.451(5)
N4	C15	1.468(5)
N6	C16	1.483(5)
N6	C20	1.461(5)
N8	C26	1.464(5)
N8	C30	1.452(6)
N14	C46	1.472(5)
N14	C50	1.479(5)
N15	C51	1.470(5)
N15	C55	1.458(5)
N16	C56	1.460(4)

Atom	Atom	Length/Å
C26	C27	1.512(7)
C27	C28	1.505(8)
C28	C29	1.526(8)
C29	C30	1.488(8)
C46	C47	1.526(5)
C47	C48	1.524(6)
C48	C49	1.529(6)
C49	C50	1.526(5)
C51	C52	1.530(6)
C52	C53	1.529(6)
C53	C54	1.537(6)
C54	C55	1.528(6)
C56	C57	1.522(6)
C57	C58	1.535(6)
C58	C59	1.527(6)
C59	C60	1.526(5)
N7A	C21A	1.473(6)
N7A	C25A	1.444(7)
C21A	C22A	1.534(8)
C22A	C23A	1.474(9)
C23A	C24A	1.598(9)
C24A	C25A	1.365(9)
N10A	C31A	1.478(12)
N10A	C35A	1.465(15)
C31A	C32A	1.523(9)
C32A	C33A	1.514(11)
C33A	C34A	1.524(9)
C34A	C35A	1.518(8)
N11B	C36B	1.430(10)
N11B	C40B	1.472(9)
C36B	C37B	1.522(12)
C37B	C38B	1.540(13)
C38B	C39B	1.610(13)
C39B	C40B	1.449(12)
N12A	C45A	1.55(2)
N12A	C41A	1.50(5)
C45A	C44A	1.06(5)
C44A	C43A	1.58(5)
C43A	C42A	1.45(6)
C42A	C41A	1.55(4)
N7B	C21B	1.472(6)
N7B	C25B	1.445(7)
C21B	C22B	1.534(8)
C22B	C23B	1.475(9)
C23B	C24B	1.600(9)
C24B	C25B	1.367(9)
N10B	C31B	1.478(12)

N16	C60	1.464(4)	N10B	C35B	1.465(15)
C1	C2	1.515(6)	C31B	C32B	1.523(9)
C2	C3	1.514(8)	C32B	C33B	1.514(11)
C3	C4	1.537(8)	C33B	C34B	1.524(9)
C4	C5	1.519(6)	C34B	C35B	1.518(8)
C6	C7	1.509(6)	N11A	C36A	1.430(9)
C7	C8	1.531(7)	N11A	C40A	1.472(9)
C8	C9	1.515(7)	C36A	C37A	1.521(12)
C9	C10	1.529(6)	C37A	C38A	1.542(13)
C11	C12	1.512(6)	C38A	C39A	1.611(13)
C12	C13	1.538(7)	C39A	C40A	1.449(12)
C13	C14	1.517(6)	N12B	C41B	1.55(2)
C14	C15	1.503(6)	N12B	C45B	1.419(11)
C16	C17	1.526(6)	C41B	C42B	1.508(15)
C17	C18	1.530(7)	C42B	C43B	1.55(2)
C18	C19	1.525(7)	C43B	C44B	1.52(2)
C19	C20	1.515(6)	C44B	C45B	1.65(2)

S9: Bond Angles in ° for **2-Ag**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
Ag4	Ag1	Ag2	90.713(16)	C6	C7	C8	111.7(4)
N1	Ag1	Ag2	44.96(9)	C9	C8	C7	109.9(4)
N1	Ag1	Ag4	128.53(9)	C8	C9	C10	111.8(4)
N13	Ag1	Ag2	128.15(8)	N3	C10	C9	109.4(4)
N13	Ag1	Ag4	44.03(8)	N4	C11	C12	111.0(4)
N13	Ag1	N1	172.37(12)	C11	C12	C13	111.0(4)
Ag3	Ag2	Ag1	89.709(16)	C14	C13	C12	109.8(4)
N1	Ag2	Ag1	45.07(8)	C15	C14	C13	110.9(4)
N1	Ag2	Ag3	127.72(8)	N4	C15	C14	111.4(4)
N5	Ag2	Ag1	127.89(9)	N6	C16	C17	109.6(4)
N5	Ag2	Ag3	45.25(10)	C16	C17	C18	110.7(4)
N5	Ag2	N1	172.54(12)	C19	C18	C17	110.1(4)
Ag2	Ag3	Ag4	91.084(16)	C20	C19	C18	110.1(4)
N5	Ag3	Ag2	45.58(9)	N6	C20	C19	111.0(4)
N5	Ag3	Ag4	129.38(9)	N8	C26	C27	110.1(4)
N5	Ag3	N9	172.10(14)	C28	C27	C26	111.7(5)
N9	Ag3	Ag2	126.72(11)	C27	C28	C29	110.0(5)
N9	Ag3	Ag4	43.60(10)	C30	C29	C28	111.2(4)
Ag1	Ag4	Ag3	88.494(16)	N8	C30	C29	111.8(4)
N9	Ag4	Ag1	124.74(12)	N14	C46	C47	110.6(3)
N9	Ag4	Ag3	44.04(10)	C48	C47	C46	109.8(4)
N13	Ag4	Ag1	44.45(8)	C47	C48	C49	109.8(4)
N13	Ag4	Ag3	126.47(8)	C50	C49	C48	111.9(3)
N13	Ag4	N9	169.07(14)	N14	C50	C49	110.3(3)
N1	P1	N2	123.48(17)	N15	C51	C52	110.8(3)
N1	P1	N3	110.26(17)	C53	C52	C51	111.0(3)
N1	P1	N4	109.88(17)	C52	C53	C54	111.0(3)
N3	P1	N2	99.57(17)	C55	C54	C53	110.5(4)
N4	P1	N2	101.63(17)	N15	C55	C54	110.6(3)
N4	P1	N3	111.33(18)	N16	C56	C57	109.7(3)
N5	P2	N6	117.35(19)	C56	C57	C58	110.0(3)
N5	P2	N8	111.70(19)	C59	C58	C57	110.9(3)
N5	P2	N7A	116.3(5)	C60	C59	C58	110.5(3)

N5	P2	N7B	114.3(2)
N8	P2	N6	100.92(18)
N8	P2	N7A	99.2(7)
N8	P2	N7B	111.0(2)
N7A	P2	N6	108.8(6)
N7B	P2	N6	100.4(2)
N9	P3	N10A	112.5(6)
N9	P3	N11B	107.6(5)
N9	P3	N12A	108.3(14)
N9	P3	N10B	118.0(4)
N9	P3	N11A	120.2(3)
N9	P3	N12B	111.7(6)
N10A	P3	N12A	102.1(14)
N11B	P3	N10A	103.8(10)
N11B	P3	N12A	122.4(12)
N10B	P3	N11A	97.9(6)
N12B	P3	N10B	106.0(6)
N12B	P3	N11A	100.7(5)
N13	P4	N14	115.55(16)
N13	P4	N15	116.36(17)
N13	P4	N16	110.43(15)
N15	P4	N14	99.38(15)
N16	P4	N14	107.14(15)
N16	P4	N15	107.02(16)
Ag2	N1	Ag1	89.97(12)
P1	N1	Ag1	112.82(16)
P1	N1	Ag2	117.18(18)
C1	N2	P1	117.6(3)
C5	N2	P1	117.5(3)
C5	N2	C1	110.0(3)
C6	N3	P1	118.1(3)
C6	N3	C10	111.9(3)
C10	N3	P1	124.0(3)
C11	N4	P1	123.9(3)
C11	N4	C15	112.8(3)
C15	N4	P1	123.3(3)
Ag3	N5	Ag2	89.17(13)
P2	N5	Ag2	122.8(2)
P2	N5	Ag3	137.3(2)
C16	N6	P2	116.5(3)
C20	N6	P2	116.6(3)
C20	N6	C16	109.3(3)
C26	N8	P2	124.5(3)
C30	N8	P2	118.8(3)
C30	N8	C26	112.0(4)
Ag4	N9	Ag3	92.36(14)
P3	N9	Ag3	123.2(2)
P3	N9	Ag4	136.7(3)
Ag4	N13	Ag1	91.51(12)
P4	N13	Ag1	130.92(17)
P4	N13	Ag4	128.98(17)
C46	N14	P4	115.6(2)
C46	N14	C50	110.5(3)
C50	N14	P4	116.0(2)
C51	N15	P4	127.8(3)
C55	N15	P4	118.8(2)
N16	C60	C59	110.6(3)
C21A	N7A	P2	126.8(9)
C25A	N7A	P2	120.5(9)
C25A	N7A	C21A	111.5(5)
N7A	C21A	C22A	109.3(5)
C23A	C22A	C21A	112.0(6)
C22A	C23A	C24A	112.8(5)
C25A	C24A	C23A	115.1(7)
C24A	C25A	N7A	119.1(7)
C31A	N10A	P3	126.3(13)
C35A	N10A	P3	121.9(11)
C35A	N10A	C31A	111.6(6)
N10A	C31A	C32A	109.0(6)
C33A	C32A	C31A	111.9(7)
C32A	C33A	C34A	111.1(6)
C35A	C34A	C33A	110.2(6)
N10A	C35A	C34A	110.4(7)
C36B	N11B	P3	123.5(8)
C36B	N11B	C40B	112.2(7)
C40B	N11B	P3	116.4(8)
N11B	C36B	C37B	111.7(7)
C36B	C37B	C38B	110.6(9)
C37B	C38B	C39B	106.3(9)
C40B	C39B	C38B	110.1(10)
C39B	C40B	N11B	113.7(8)
C45A	N12A	P3	129(3)
C41A	N12A	P3	104.4(19)
C41A	N12A	C45A	120(3)
C44A	C45A	N12A	121(4)
C45A	C44A	C43A	119(3)
C42A	C43A	C44A	105(3)
C43A	C42A	C41A	113(3)
N12A	C41A	C42A	108(2)
C21B	N7B	P2	121.9(4)
C25B	N7B	P2	124.8(4)
C25B	N7B	C21B	111.5(4)
N7B	C21B	C22B	109.5(5)
C23B	C22B	C21B	111.8(5)
C22B	C23B	C24B	112.3(5)
C25B	C24B	C23B	114.4(6)
C24B	C25B	N7B	118.6(6)
C31B	N10B	P3	116.4(5)
C35B	N10B	P3	116.6(9)
C35B	N10B	C31B	111.7(5)
N10B	C31B	C32B	109.0(5)
C33B	C32B	C31B	111.8(6)
C32B	C33B	C34B	111.1(5)
C35B	C34B	C33B	110.2(6)
N10B	C35B	C34B	110.5(7)
C36A	N11A	P3	127.9(5)
C36A	N11A	C40A	112.4(7)
C40A	N11A	P3	114.1(5)
N11A	C36A	C37A	111.8(7)
C36A	C37A	C38A	110.5(9)
C37A	C38A	C39A	105.8(9)
C40A	C39A	C38A	110.0(10)

C55	N15	C51	112.1(3)	C39A	C40A	N11A	113.8(8)
C56	N16	P4	122.9(2)	C41B	N12B	P3	126.0(10)
C56	N16	C60	112.5(3)	C45B	N12B	P3	122.4(14)
C60	N16	P4	122.8(2)	C45B	N12B	C41B	104.6(12)
N2	C1	C2	110.2(4)	C42B	C41B	N12B	107.2(8)
C3	C2	C1	111.0(4)	C41B	C42B	C43B	109.8(9)
C2	C3	C4	110.2(4)	C44B	C43B	C42B	111.2(12)
C5	C4	C3	110.5(4)	C43B	C44B	C45B	108.1(9)
N2	C5	C4	110.3(4)	N12B	C45B	C44B	106.3(13)
N3	C6	C7	110.3(3)				

Table S10. Crystallographic Data and Structure Refinement for **1-Ce**

	2-Ce
Empirical Formula	$C_{45}H_{90}Ce_{16}N_{12}P_3$
Formula Weight	1032.31
Temperature (K)	99.99
Crystal System	Triclinic
Space Group	*P-1*
a/Å	13.827(2)
b/Å	14.5142(18)
c/Å	16.6474(19)
α/°	88.104(5)
β/°	70.874(7)
γ/°	62.002(6)
Volume/Å3	2757.7(7)
Z	2
Z'	2
ρ(g/cm3)	1.243
μ(mm-1)	0.953
F(000)	1094.0
Crystal Size/mm3	0.37 x 0.258 x 0.216
Radiation	MoKα (λ=0.71073)
2θ range for data collection(°)	4.428 to 56.644
Index Ranges	-18 ≤ h ≤ 18, -19 ≤ k ≤19, -21≤ 1 ≤ 22
Reflections Collected	56846
Independent Reflections	13672 [Rint = 0.0439, Rsigma = 0.0346]
Data/Restraints/Parameters	13672/12/569
Goodness-of-Fit on F2	1.052
Final R Indexes [I>=2σ (I)]	R1=0.0266, wR2=0.0637
Final R Indexes [all data]	R1=0.0288, wR2=0.0656
Largest Diff. Peak/Hole/ (e Å3)	1.45/-1.18
Flack Parameter	-
Completeness to 2θ	99

Table S11: Bond Lengths in Å for **1-Ce**.

Atom	Atom	Length/Å
Ce1	Ce11	3.8769(5)
Ce1	P0021	3.4067(5)
Ce1	N1	2.4178(14)
Ce1	N11	2.4956(15)
Ce1	N5	2.2731(15)
Ce1	N9	2.2752(15)
P002	N1	1.5446(14)
P002	N2	1.7119(15)
P002	N3	1.6762(15)
P002	N4	1.6611(15)
P003	N5	1.5270(15)
P003	N6	1.6944(15)
P003	N7	1.6858(15)
P003	N8	1.6875(16)
P004	N9	1.5298(15)
P004	N10	1.6799(18)
P004	N12	1.6998(15)
P004	N11A	1.723(3)
P004	N11B	1.649(6)
N2	C1	1.492(2)
N2	C5	1.470(2)
N3	C6	1.469(2)
N3	C10	1.472(2)
N4	C11	1.464(2)
N4	C15	1.460(2)
N6	C16	1.467(2)
N6	C20	1.463(2)
N7	C21	1.465(2)
N7	C25	1.467(2)
N8	C26	1.465(3)
N8	C30	1.465(2)
N10	C31	1.459(3)
N10	C35	1.458(2)
N12	C41	1.467(2)
N12	C45	1.467(2)
C1	C2	1.509(3)
C2	C3	1.530(3)
C3	C4	1.514(3)
C4	C5	1.499(3)
C6	C7	1.527(2)
C7	C8	1.524(3)
C8	C9	1.524(3)
C9	C10	1.520(3)
C11	C12	1.522(3)
C12	C13	1.523(3)
C13	C14	1.523(3)
C14	C15	1.526(3)
C16	C17	1.512(3)
C17	C18	1.528(3)
C18	C19	1.518(3)
C19	C20	1.518(3)
C21	C22	1.518(3)
C22	C23	1.528(3)
C23	C24	1.520(3)
C24	C25	1.524(3)
C26	C27	1.525(3)
C27	C28	1.526(4)
C28	C29	1.511(4)
C29	C30	1.524(3)
C31	C32	1.516(3)
C32	C33	1.525(3)
C33	C34	1.517(3)
C34	C35	1.519(3)
C41	C42	1.524(3)
C42	C43	1.522(3)
C43	C44	1.515(3)
C44	C45	1.522(3)
N11A	C36A	1.540(8)
N11A	C40A	1.532(8)
C36A	C37A	1.516(4)
C37A	C38A	1.527(4)
C38A	C39A	1.521(4)
C39A	C40A	1.517(4)
N11B	C36B	1.540(8)
N11B	C40B	1.533(8)
C36B	C37B	1.516(4)
C37B	C38B	1.527(4)
C38B	C39B	1.521(4)
C39B	C40B	1.518(4)

[1] 1-X,1-Y,1-Z

Table S12: Bond Angles in ° for **1-Ce**.

Atom	Atom	Atom	Angle/°
P0021	Ce1	Ce11	60.689(11)
N11	Ce1	Ce11	37.20(3)
N1	Ce1	Ce11	38.61(3)
C31	N10	P004	122.37(13)
C35	N10	P004	122.02(15)
C35	N10	C31	112.11(19)

N1	Ce1	P0021	98.79(4)	C41	N12	P004	113.99(12)
N11	Ce1	P0021	24.70(3)	C45	N12	P004	115.58(12)
N1	Ce1	N11	75.82(5)	C45	N12	C41	110.40(14)
N5	Ce1	Ce11	125.33(4)	N2	C1	C2	111.82(15)
N5	Ce1	P0021	122.60(4)	C1	C2	C3	112.19(16)
N5	Ce1	N1	110.94(5)	C4	C3	C2	108.89(16)
N5	Ce1	N11	123.51(5)	C5	C4	C3	110.57(18)
N5	Ce1	N9	105.89(6)	N2	C5	C4	111.09(18)
N9	Ce1	Ce11	125.52(4)	N3	C6	C7	109.51(15)
N9	Ce1	P0021	108.18(4)	C8	C7	C6	111.29(15)
N9	Ce1	N1	110.07(5)	C9	C8	C7	111.05(16)
N9	Ce1	N11	124.76(5)	C10	C9	C8	111.22(17)
N1	P002	Ce11	42.46(5)	N3	C10	C9	108.96(15)
N1	P002	N2	110.02(8)	N4	C11	C12	110.98(17)
N1	P002	N3	119.46(8)	C11	C12	C13	110.3(2)
N1	P002	N4	113.94(8)	C12	C13	C14	111.14(17)
N2	P002	Ce11	72.52(5)	C13	C14	C15	110.82(18)
N3	P002	Ce11	108.84(5)	N4	C15	C14	110.06(16)
N3	P002	N2	100.56(7)	N6	C16	C17	111.05(17)
N4	P002	Ce11	147.12(6)	C16	C17	C18	111.49(18)
N4	P002	N2	108.28(8)	C19	C18	C17	110.07(17)
N4	P002	N3	103.35(8)	C20	C19	C18	110.26(18)
N5	P003	N6	113.62(8)	N6	C20	C19	110.79(16)
N5	P003	N7	120.02(8)	N7	C21	C22	110.04(15)
N5	P003	N8	113.31(8)	C21	C22	C23	110.70(17)
N7	P003	N6	99.57(7)	C24	C23	C22	110.33(18)
N7	P003	N8	99.49(8)	C23	C24	C25	111.39(18)
N8	P003	N6	109.13(8)	N7	C25	C24	110.15(16)
N9	P004	N10	113.27(9)	N8	C26	C27	109.51(18)
N9	P004	N12	119.52(8)	C26	C27	C28	110.3(2)
N9	P004	N11A	115.6(4)	C29	C28	C27	110.65(18)
N9	P004	N11B	112.9(4)	C28	C29	C30	111.49(19)
N10	P004	N12	102.22(8)	N8	C30	C29	110.75(18)
N10	P004	N11A	102.2(8)	N10	C31	C32	110.86(17)
N12	P004	N11A	101.8(3)	C31	C32	C33	111.93(17)
N11B	P004	N10	110.4(7)	C34	C33	C32	110.08(17)
N11B	P004	N12	97.0(3)	C33	C34	C35	109.8(2)
Ce1	N1	Ce11	104.18(5)	N10	C35	C34	110.48(18)
P002	N1	Ce1	137.12(8)	N12	C41	C42	110.75(16)
P002	N1	Ce11	112.84(7)	C43	C42	C41	110.52(16)
C1	N2	P002	110.64(11)	C44	C43	C42	109.92(17)
C5	N2	P002	120.76(12)	C43	C44	C45	110.69(17)
C5	N2	C1	110.71(14)	N12	C45	C44	110.22(17)
C6	N3	P002	116.79(11)	C36A	N11A	P004	118.0(4)
C6	N3	C10	109.93(14)	C40A	N11A	P004	126.8(4)
C10	N3	P002	117.70(11)	C40A	N11A	C36A	105.0(8)
C11	N4	P002	124.22(13)	C37A	C36A	N11A	103.3(6)
C15	N4	P002	122.69(12)	C36A	C37A	C38A	110.9(3)
C15	N4	C11	112.48(15)	C39A	C38A	C37A	109.7(2)
P003	N5	Ce1	173.82(10)	C40A	C39A	C38A	111.3(3)
C16	N6	P003	116.92(13)	C39A	C40A	N11A	104.0(6)
C20	N6	P003	121.61(12)	C36B	N11B	P004	109.4(6)
C20	N6	C16	111.97(15)	C40B	N11B	P004	119.5(8)
C21	N7	P003	116.05(11)	C40B	N11B	C36B	104.6(7)
C21	N7	C25	110.51(15)	C37B	C36B	N11B	103.7(6)
C25	N7	P003	115.95(12)	C36B	C37B	C38B	111.3(3)

C26	N8	P003	122.49(13)	C39B	C38B	C37B	109.9(2)
C26	N8	C30	111.64(16)	C40B	C39B	C38B	111.2(2)
C30	N8	P003	116.33(13)	C39B	C40B	N11B	103.5(6)
P004	N9	Ce1	178.25(10)				

[1] 1-X,1-Y,1-Z

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