Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Incorporation of coinage metal-NHC complexes into heptaphosphide clusters

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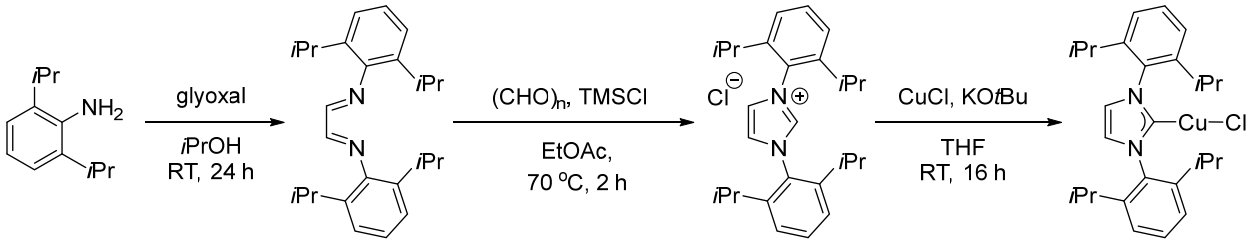
1. General Information

All reactions with phosphorus-containing species were performed under an argon atmosphere in a glovebox. Anhydrous 1,2-dimethoxyethane (DME) was purchased from Sigma-Aldrich. Anhydrous THF was obtained from a solvent purification system (Glass Contour). Sodium metal (cubes dispersed in mineral oil, Sigma-Aldrich) was handled in the glovebox after being washed with hexanes to remove oil. All organic reagents (Sigma-Aldrich), red phosphorus (Alfa Aeasar), and $NHC^{Dipp}AuCl$ (Sigma-Aldrich) were used as received. Chlorotrimethylsilane (TMSCl, Sigma-Aldrich) was purchased in a SureSeal® bottle. THF-d_8 and benzene-d_6 (Sigma-Aldrich) were purchased in ampoules and used as received, since the water content (< 0.0100 wt. %) was sufficiently low to work safely with the polyphosphide complexes.

2. Experimental Procedures

Preparation of $NHC^{Dipp}CuCl$



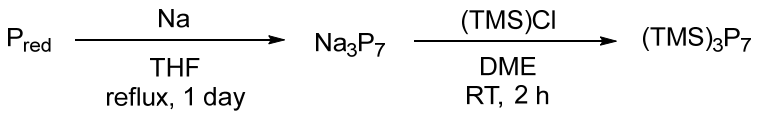
***N,N'*-1,4-Bis(2,6-diisopropylphenyl)-1,4-diazabutadiene** was prepared according to the previously reported procedure.[1] To a mixture of 2,6-diisopropylaniline (10 mL, 51. 4 mmol, 1 equiv) in isopropyl alcohol (30 mL) was added dropwise a dilute solution of glyoxal (40 wt.% in H_2O, 0.5 equiv) in a mixture of water (5 mL) and isopropyl alcohol (5 mL). A yellow precipitate appeared within a few minutes, and the reaction mixture was stirred at room temperature (RT) for 24 h. The resulting suspension was filtered by suction, and the solid product was rinsed with water and dried *in vacuo*. The resulting yellow powder is pure enough to proceed to the next synthetic step without further purification. Yield = 8.3 g (85%). ^{1}H NMR (600 MHz, $CDCl_3$), δ (ppm): 8.10 (s, 2H), 7.16–7.20 (m, 6 H), 2.92–2.97 (m, 4 H), 1.22 (d, 24 H). The observed NMR signals were consistent with the reported values.[1]

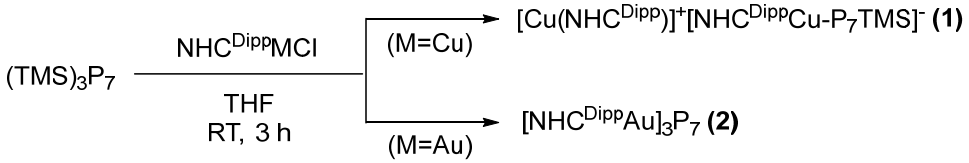
***N,N'*-1,3-Bis(2,6-diisopropylphenyl)imidazolium chloride** was prepared according to the previously reported procedure.[2] A solution of *N,N'*-1,4-Bis(2,6-diisopropylphenyl)-1,4-diazabutadiene (2.0 g, 5.34 mmol, 1 equiv) and paraformaldehyde (0.165 g, 5.5 mmol, 1.03 equiv)

in ethyl acetate (40 mL) was pre-heated to 70 °C. A solution of chlorotrimethylsilane (0.7 mL, 5.5 mmol, 1.03 equiv) in ethyl acetate (8 mL) was added dropwise with vigorous stirring. The mixture was further stirred at 70 °C for 2 h and then cooled down in an ice bath to precipitate a white solid product, which was filtered, washed with ethyl acetate and ether, and dried by suction. Yield = 1.97 g (87%). ^{1}H NMR (600 MHz, CD_3CN), δ (ppm): 9.55 (s, 1H), 7.87 (d, 2H), 7.65 (t, 2 H), 7.47 (d, 4H), 2.38–2.44 (m, 4H), 1.27 (d, 12H), 1.21 (d, 12H). The observed NMR signals were consistent with reported values.[2]

NHC^{Dipp}CuCl was prepared according to the previously reported procedure.[3] *N,N'*-1,3-Bis(2,6-diisopropylphenyl)imidazolium chloride (1.97 g, 4.64 mmol, 1 equiv) and CuCl (0.459 g, 4.64 mmol, 1 equiv) were suspended in dry THF (45 mL). Potassium *tert*-butoxide (1.0 M in THF, 5 mL, 1.05 equiv) was added, and the reaction mixture was stirred at r.t. for 16 h. The mixture was filtered through a plug of Celite and washed with DCM. The volatiles were removed under reduced pressure, and the solid product was dried *in vacuo*. The product was purified by column chromatography, using a hexanes/ethyl acetate mixture (7:3 v/v) as eluent (R_f = 0.32). Yield = 1.92 g (85%). ^{1}H NMR (600 MHz, $CDCl_3$), δ (ppm): 7.50 (t, 2H), 7.30 (d, 4H), 7.13 (s, 2H), 2.54–2.58 (m, 4 H), 1.31 (d, 12H), 1.23 (d, 12H). The observed NMR signals were consistent with reported values.[4]

Preparation of Polyphosphides





Scheme S1. Synthesis of complexes **1** and **2** starting from red phosphorus.

Na_3P_7 was prepared according to the previously reported procedure.[5] Red phosphorus (46.5 mg, 1.501 mmol, 1 equiv) and sodium metal (17.3 mg, 0.751 mmol, 0.5 equiv) were placed in a 7 mL vial and suspended in THF (3 mL). The mixture was heated at reflux for 1 day to afford a light-green solid, which was recovered by filtration, washed with THF (3×3 mL), and dried *in vacuo*. The crude material was used for the next reaction without purification.

$(TMS)_3P_7$ was prepared according to the previously reported procedure.[6] To a suspension of Na_3P_7 (60 mg, 0.21 mmol, 1 equiv) in 1,2-dimethoxyethane (DME) (0.7 mL, 0.3 M) in a 7 mL vial was added (TMS)Cl (0.13 mL, 1 mmol, 5 equiv). The resulting greenish slurry was stirred at r.t. for 2 h and then filtered through a microsyringe filter to remove insoluble substances. The yellow filtrate was concentrated under reduced pressure to afford a yellow polycrystalline product. Yield = 74.9 mg (81%). $^{31}P\{^1H\}$ NMR (243 MHz, C_6D_6), δ (ppm): 0 (m, 3P), –99.8 (m, 1P), –156.8 (m, 3P); ^1H NMR (600 MHz, C_6D_6), δ (ppm): 0.23 (s); ^{13}C NMR (151 MHz, C_6D_6), δ (ppm): 3.50. The observed NMR signals were consistent with reported values.[7-11]

$[NHC^{Dipp}\text{-}Cu\text{-}NHC^{Dipp}]^+$ $[NHC^{Dipp}\text{-}Cu(\eta^4\text{-}P_7)(TMS)]^-$ (1). A solution of $(TMS)_3P_7$ (50 mg, 0.12 mmol, 1 equiv) in THF (0.6 mL) was added to a suspension of $NHC^{Dipp}CuCl$ (167.6 mg, 0.36 mmol, 3 equiv) in THF (0.5 mL). The color immediately changed from light-yellow to dark-red. The reaction mixture was stirred at r.t. for 3 h and then filtered through a microsyringe filter to remove insoluble substances. The solvent was removed under reduced pressure to afford a dark-red solid product in 90% yield. X-ray quality crystals were grown by slow evaporation of THF solution of the compound. $^{31}P\{^1H\}$ NMR (243 MHz, THF-d_8), δ (ppm): 1.8 (t, 1P, $^1J_{PP}$ = 321.3 Hz), –89.4 (m, 2P), –98.7 (m, 2P), –141.7 (m, 2P). ^1H NMR (600 MHz, THF-d_8), δ (ppm): 7.18–7.52 (m, 24H), 2.62–2.83 (m, 12H), 1.27 (dd, 48H), 1.17 (dd, 24H), 0.07 (s, 6H), –0.36 (s, 3H). ^{13}C NMR (151 MHz, THF-d_8), δ (ppm): 181.7, 146.6, 146.4, 139.5, 135.8, 130.9, 129.0, 124.6, 124.4, 123.7, 122.3, 29.4, 29.0, 24.9, 23.8, 23.5, 1.8. ESI-MS (MeCN), *m/z*: 669.0359 $[(NHC^{Dipp}\text{-}Cu)P_7H]^-$, 218.8192 $[P_7H_2]^-$.

$(NHC^{Dipp}\text{-}Au)_3P_7$ (2). A solution of $(TMS)_3P_7$ (20 mg, 0.05 mmol, 1 equiv) in THF (0.2 mL) was added to a suspension of $NHC^{Dipp}AuCl$ (85.4 mg, 0.15 mmol, 3 equiv) in THF (0.3 mL). The reaction mixture was stirred at r.t. for 3 h to afford a yellow solution. The solvent was removed under reduced pressure to afford a yellow solid product in 91% yield. X-ray quality crystals were grown by slow evaporation of THF solution of the complex. $^{31}P\{^1H\}$ NMR (243 MHz, C_6D_6), δ (ppm) 8.9 (m, 3P), –79.5 (m, 1P), –183.5 (m, 3P). ^1H NMR (600 MHz, C_6D_6), δ (ppm): 7.07–7.27 (m, 6H), 6.25 (s, 2H), 2.51 (m, 4H), 1.57 (m, 12H), 1.12 (m, 12H). ^{13}C NMR (151 MHz, C_6D_6), δ (ppm) 145.8, 135.4, 130.5, 124.2, 121.9, 29.0, 25.3, 24.3. ESI-MS (MeCN), *m/z*: 1973.5733 $[M+H]^+$.

3. X-Ray Crystallography

Single-crystal X-ray diffraction was performed on a Bruker APEX-II diffractometer with a CCD detector or on a Rigaku-Oxford Diffraction Synergy-S diffractometer with a HyPix detector. A selected single crystal was suspended in Paratone-N oil (Hampton Research) and mounted on a cryoloop, which was cooled to the desired temperature in an N_2 cold stream. The data set was recorded as ω-scans at 0.3-0.5° step width and integrated with the Bruker SAINT[12] or CrysAlis[13] software package. A multi-scan adsorption correction was applied based on multiple equivalent measurements (SADABS).[14] The space group was determined with XPREP,[15] and the crystal structure solution and refinement were carried out using the SHELX software.[16] The final refinement was performed with anisotropic atomic displacement parameters for all non-hydrogen atoms. All H atoms were placed in calculated positions and refined in the riding model. Full details of the crystal structure refinement and the final structural parameters have been deposited with the Cambridge Crystallographic Data Centre (CCDC). The CCDC registry numbers and a brief summary of data collection and refinement are provided in the Table S1.

Table S1. Data collection and structure refinement parameters for **1** and **2**.

Formula	$Cu_2P_7SiN_6C_{84}H_{117}$ (**1**)	$Au_3P_7N_7C_{85}H_{116}$ (**2**·THF)
CCDC number	1978717	1978718
Formula weight	1582.79	2045.52
Space group	*Pbcn*	$P2_1/c$
a, Å	24.290(2)	18.4686(2)
b, Å	25.025(2)	17.4445(1)
c, Å	28.319(3)	34.2250(3)
β, deg	90	125.216(1)
V, Å^3	17214(3)	9008.4(2)
Z	8	4
Crystal color	red	light yellow
Crystal size, mm^3	0.50×0.40×0.30	0.20×0.20×0.10
d_{calc}, g/cm^3	1.221	1.508
μ, mm^{-1}	0.683	10.52
T, K	100(1)	150(1)
λ, Å	0.71073 (Mo-*K*α)	1.54184 (Cu-*K*α)
$2\theta_{max}$, deg	24.71	78.25
Total reflections	158052	331734
R_{int}	0.106	0.185
Unique reflections	14686	19133
Parameters refined	956	943
Restraints used	0	0
R_1, wR_2 [$I > 2\sigma(I)$][a]	0.088, 0.139	0.036, 0.038
R_1, wR_2 (all data)	0.210, 0.246	0.097, 0.099
Goodness of fit[b]	1.027	1.064
Diff. peak/hole, e/Å^3	1.85, –1.92	1.59, –1.81

[a] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{½}$

[b] Goodness-of-fit = $[\Sigma[w(F_o^2-F_c^2)^2]/(N_{obs}-N_{params})]^{½}$, based on all data

Disorder Modeling for Structure 1. The refinement of crystal structure **1** revealed that the $[NHC^{Dipp}Cu\text{-}P_7(TMS)]^-$ anion contains a $(TMS)P_7^{2-}$ cage disordered over two positions in a 3:2 ratio. In both orientations, an open face of the partially de-protected $(TMS)P_7^{2-}$ fragment is η^4-coordinated to the NHC^{Dipp}-capped Cu(I) center, which thus exhibits a square-pyramidal coordination (Fig. S1b).

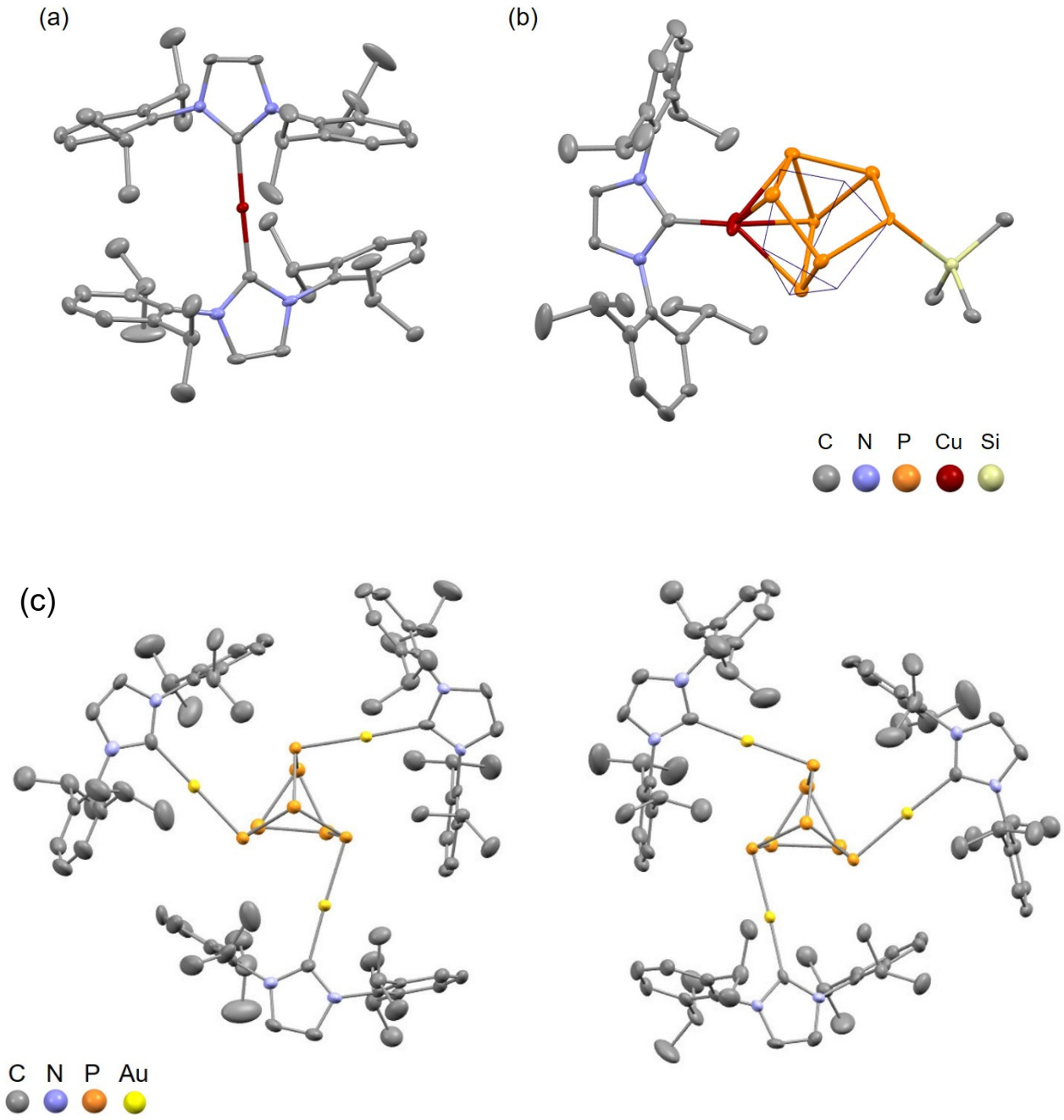


Figure S1. Cation (a) and anion (b) of complex **1**. The second orientation of the disordered P_7 cage is depicted by black solid lines. (c) Stereoisomers of complex **2**. The H atoms are omitted for clarity.

4. NMR spectra

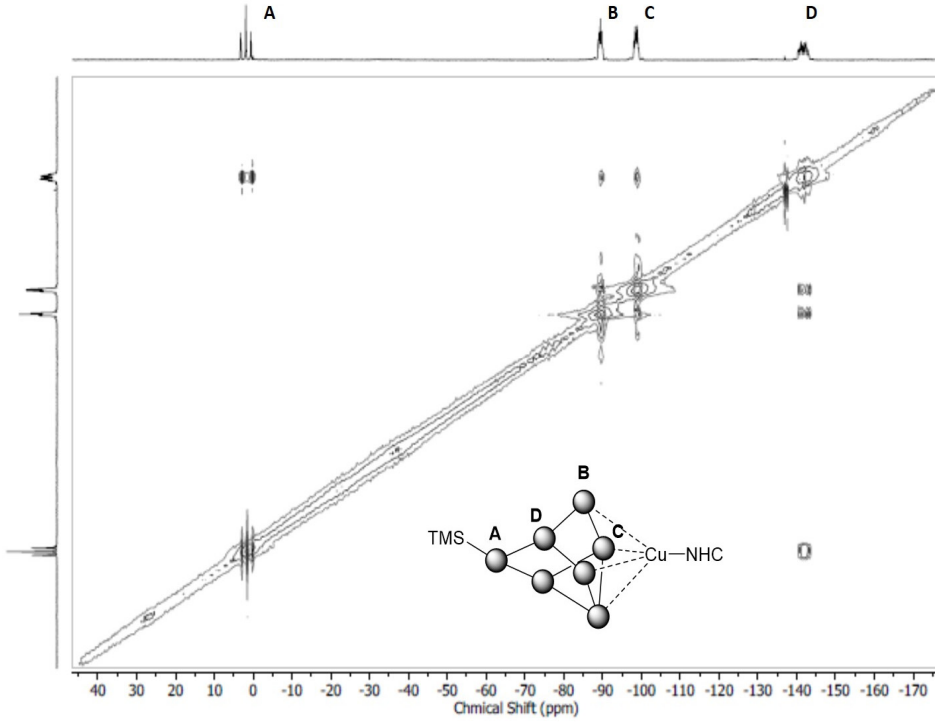


Figure S2. ^{31}P-^{31}P COSY NMR spectrum of complex **1** in THF.

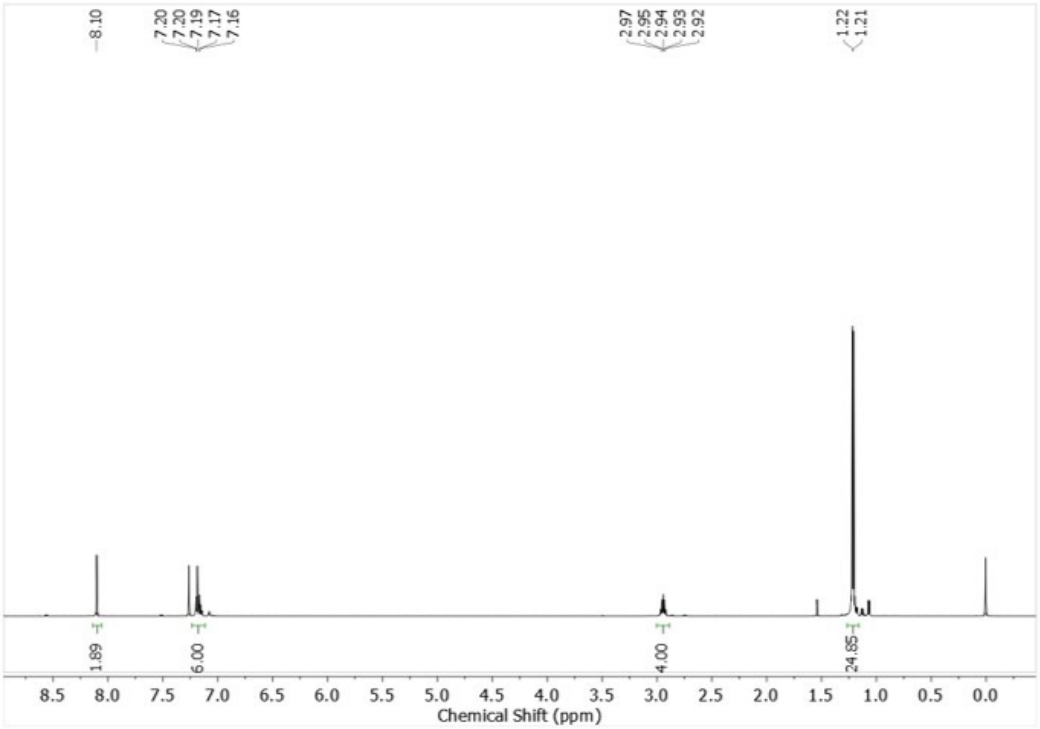


Figure S3. ^{1}H NMR spectrum of *N,N'*-1,4-Bis(2,6-diisopropylphenyl)-1,4-diazabutadiene.

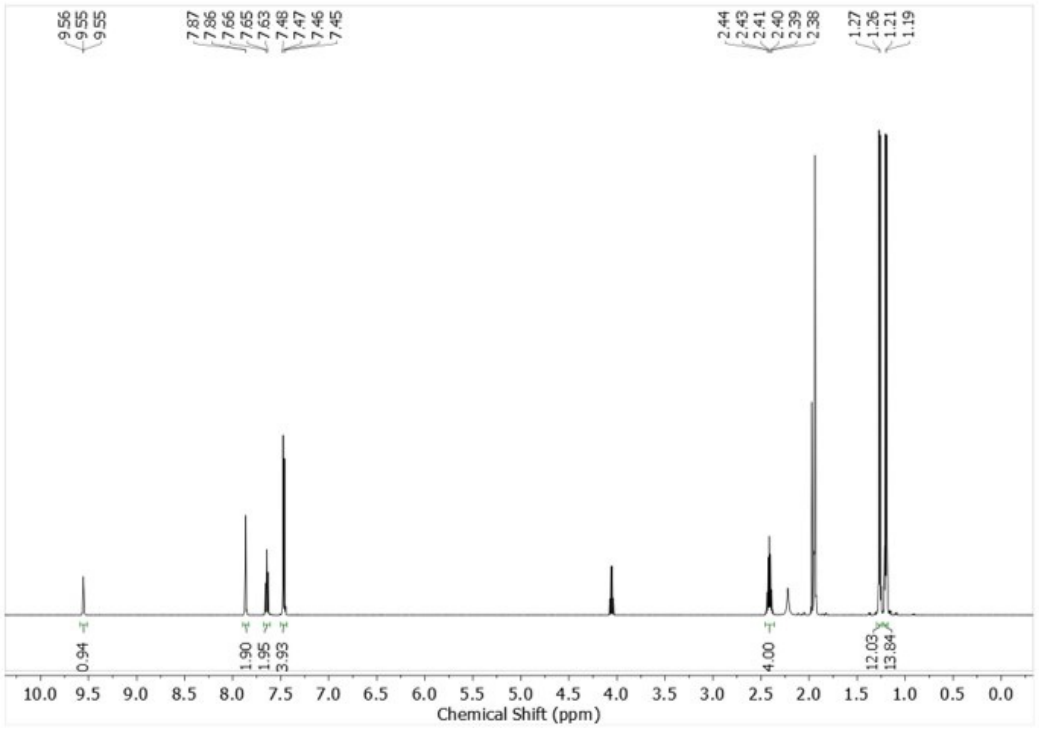


Figure S4. ^{1}H NMR spectrum of *N,N'*-1,3-Bis(2,6-diisopropylphenyl)imidazolium chloride.

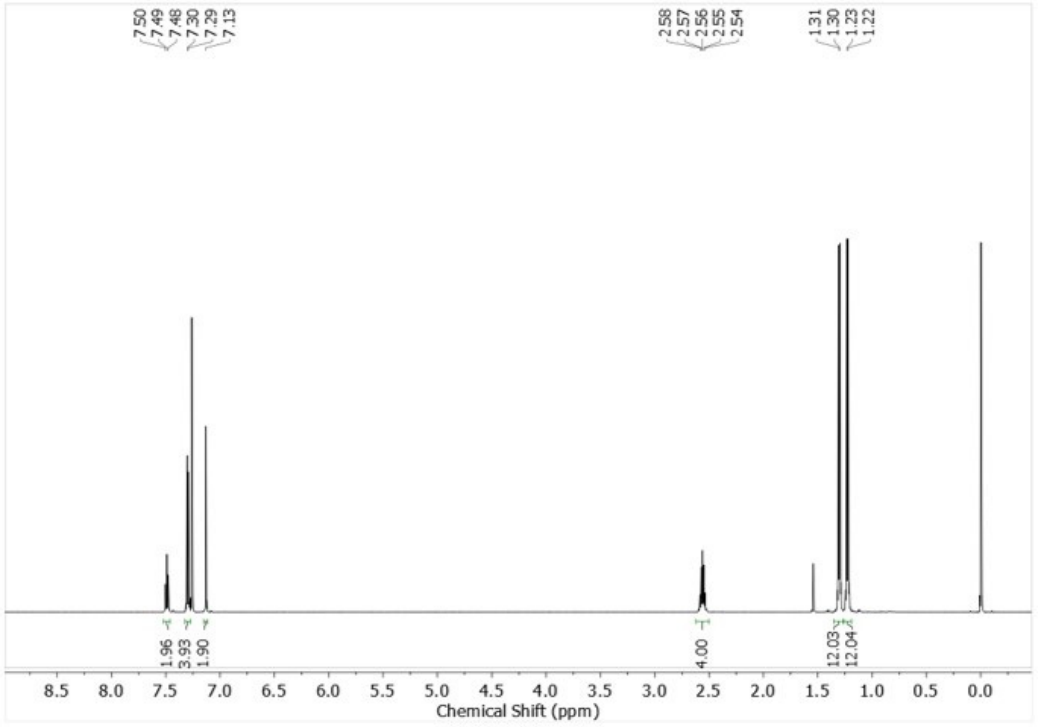


Figure S5. ^{1}H NMR spectrum of *N,N'*-1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene]copper(I) chloride.

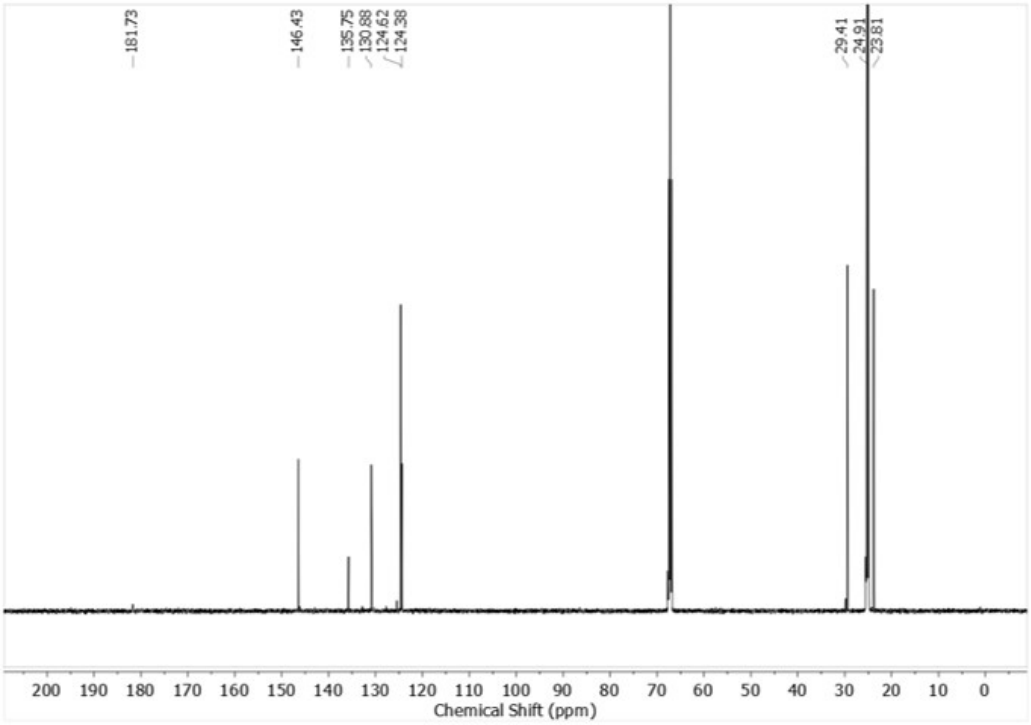


Figure S6. ^{13}C NMR spectrum of *N,N'*-1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene]copper(I) chloride.

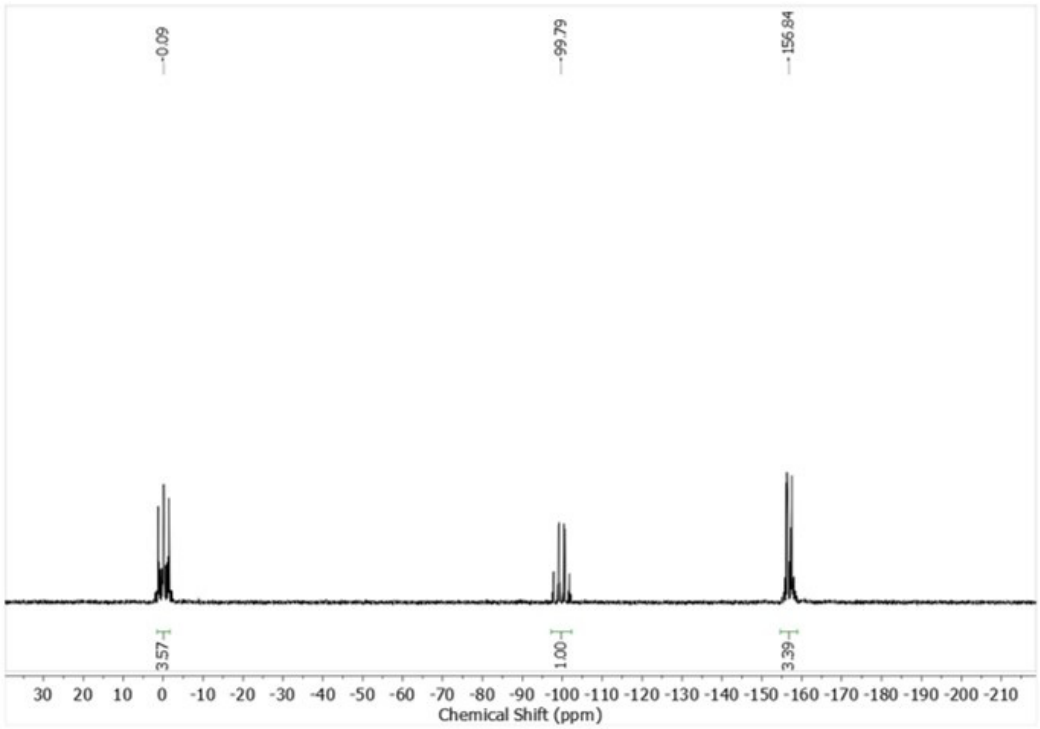


Figure S7. $^{31}P\{^{1}H\}$ NMR spectrum of $(TMS)_3P_7$.

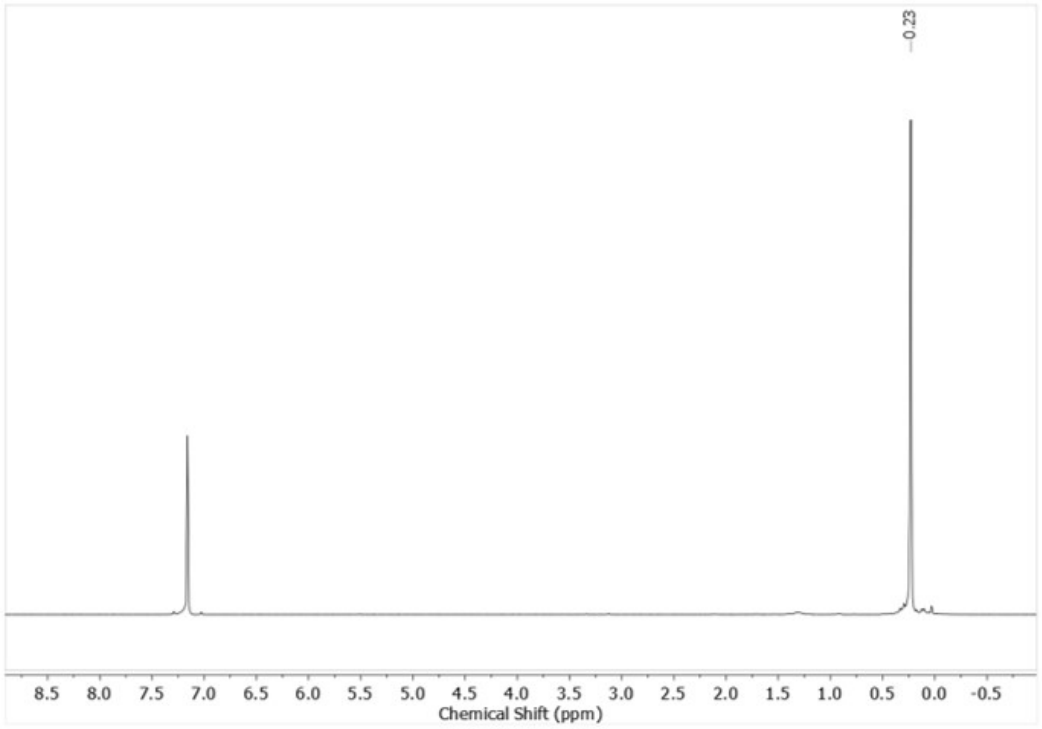


Figure S8. ^{1}H NMR spectrum of $(TMS)_3P_7$.

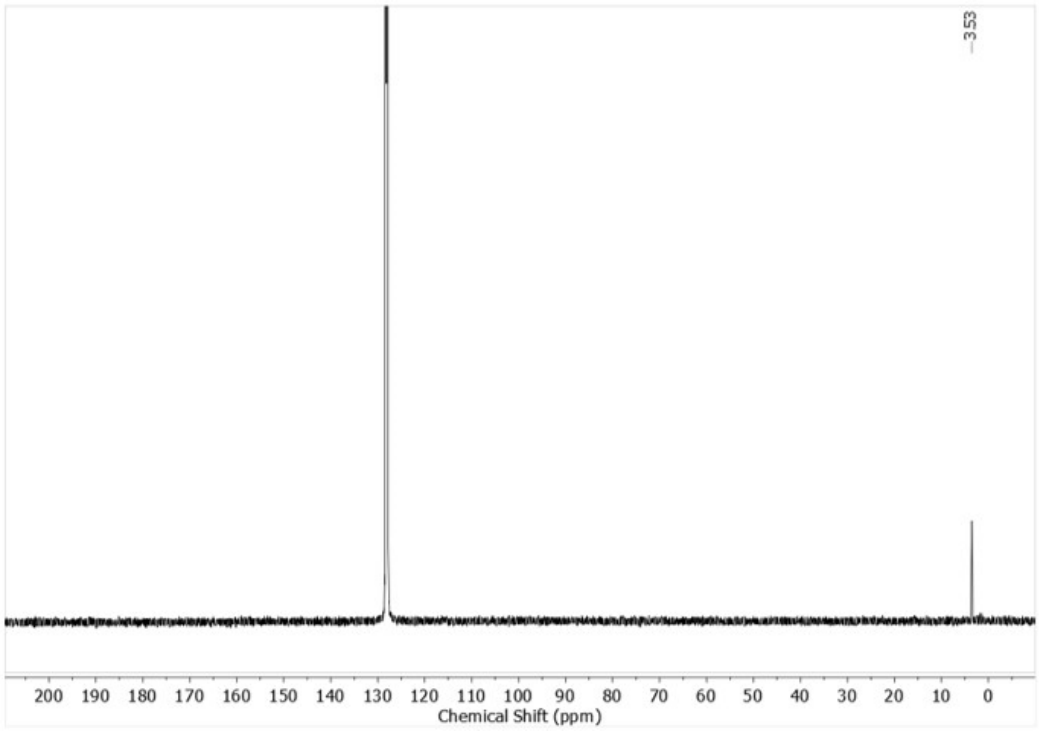


Figure S9. ^{13}C NMR spectrum of $(TMS)_3P_7$.

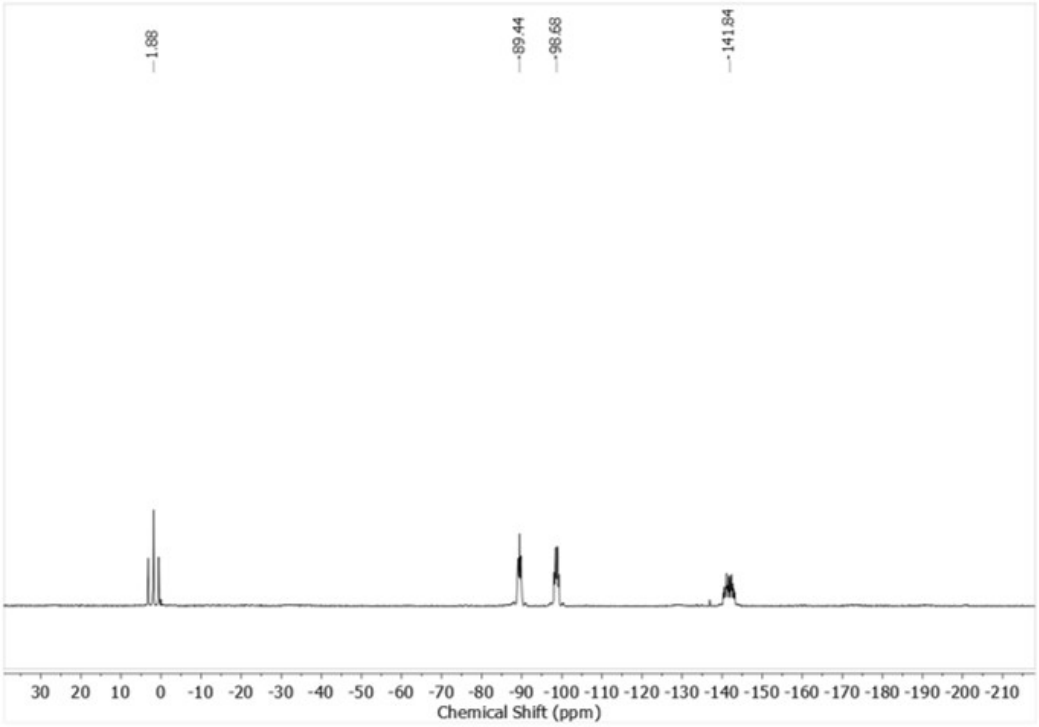


Figure S10. $^{31}P\{^{1}H\}$ NMR spectrum of [NHC^{Dipp}-Cu-NHC^{Dipp}][$NHC^{Dipp}Cu(\eta^4\text{-}P_7)(TMS)$].

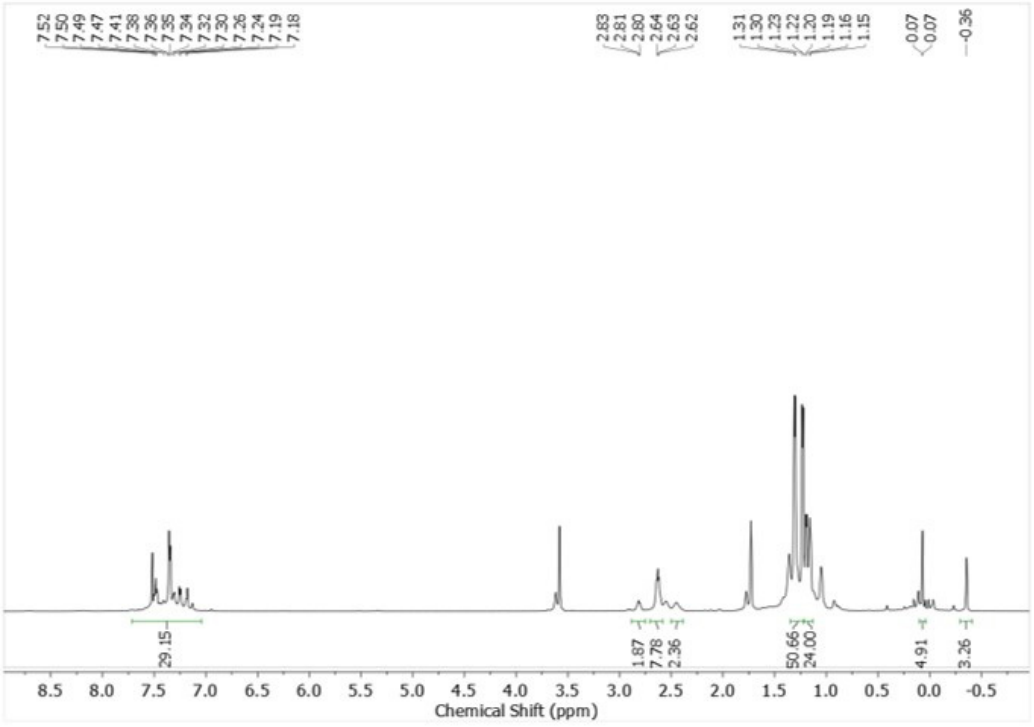


Figure S11. ^{1}H NMR spectrum of [NHC^{Dipp}-Cu-NHC^{Dipp}][$NHC^{Dipp}Cu(\eta^4\text{-}P_7)(TMS)$].

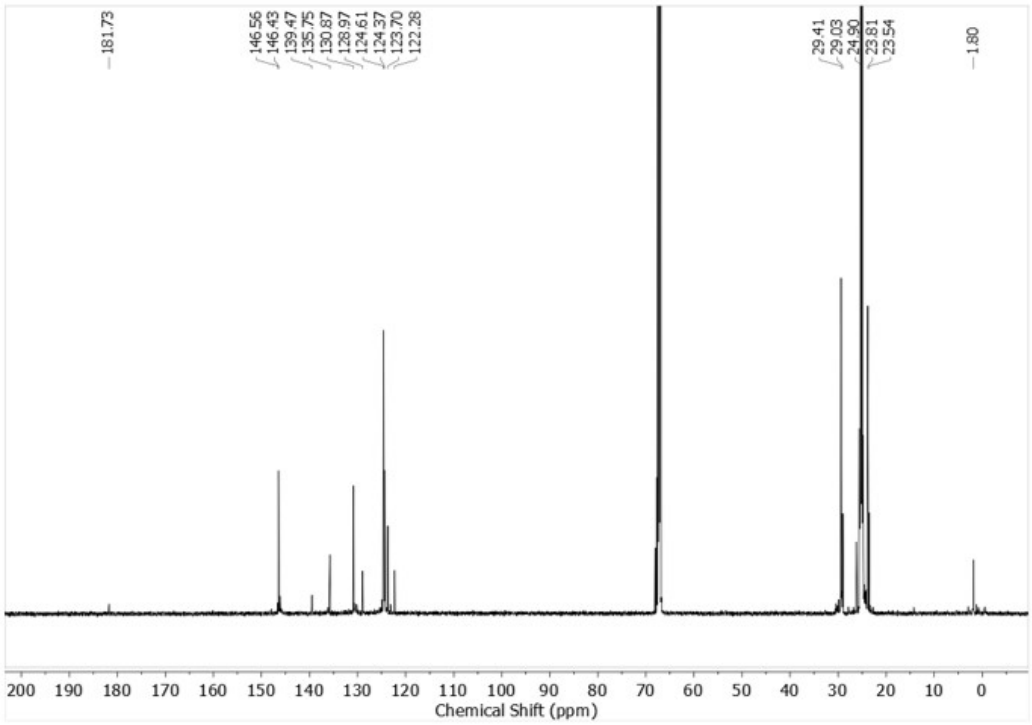


Figure S12. ^{13}C NMR spectrum of [NHC^{Dipp}-Cu-NHC^{Dipp}][NHC^{Dipp}Cu(η^4-P_7)(TMS)].

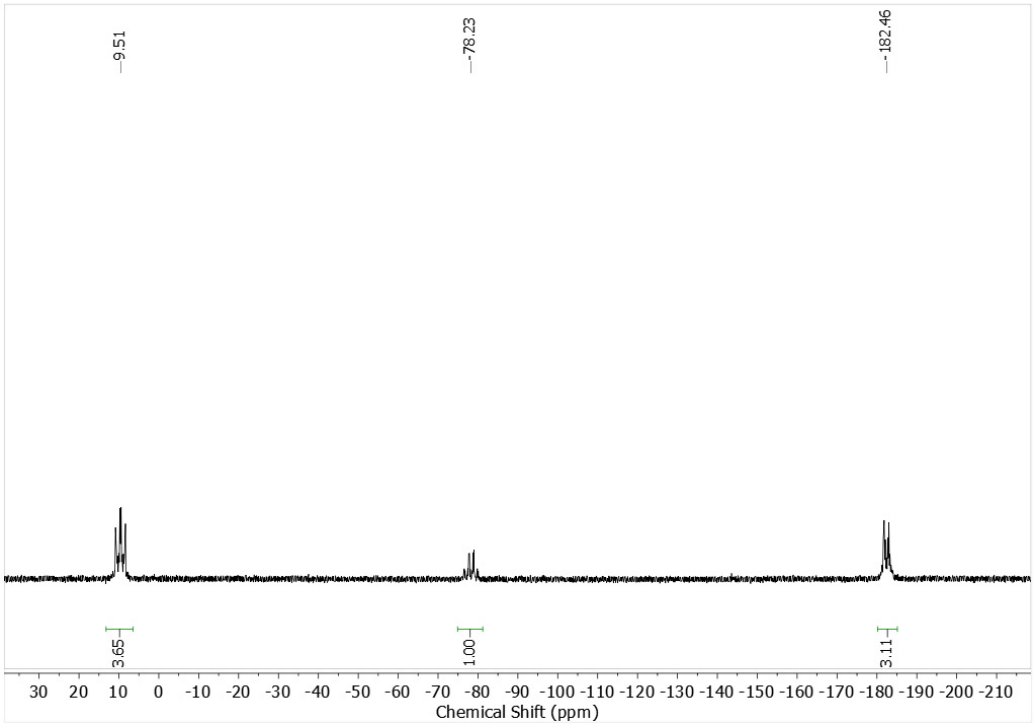


Figure S13. $^{31}P\{^1H\}$ NMR spectrum of (NHC^{Dipp}Au)$_3P_7$.

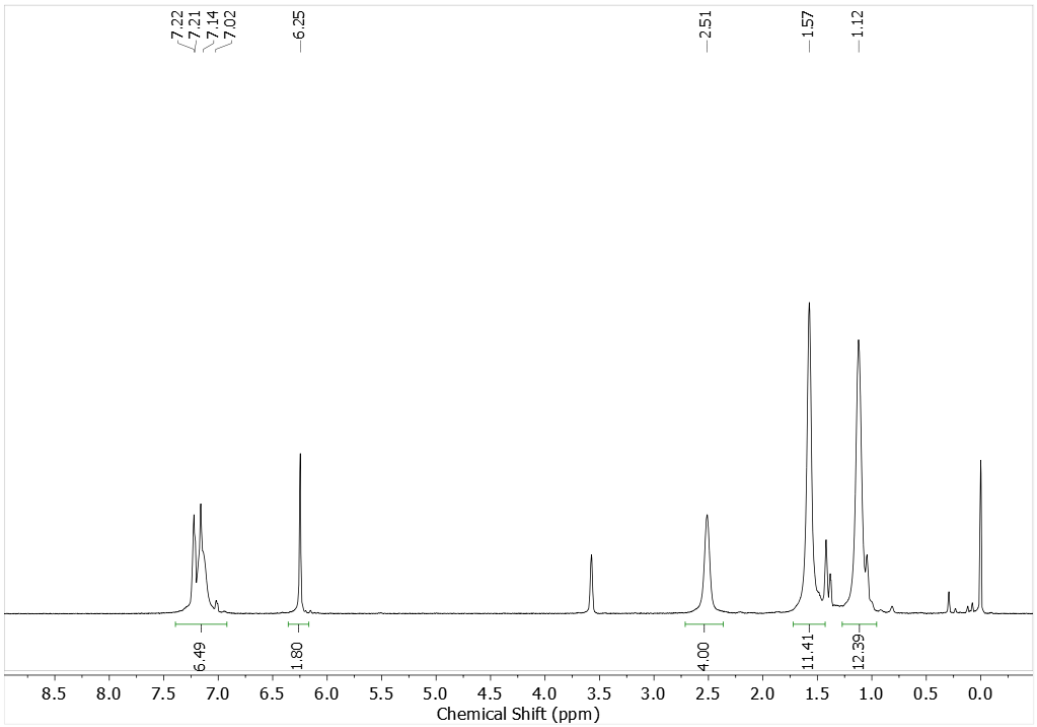


Figure S14. ^{1}H NMR spectrum of $(NHC^{Dipp}Au)_3P_7$.

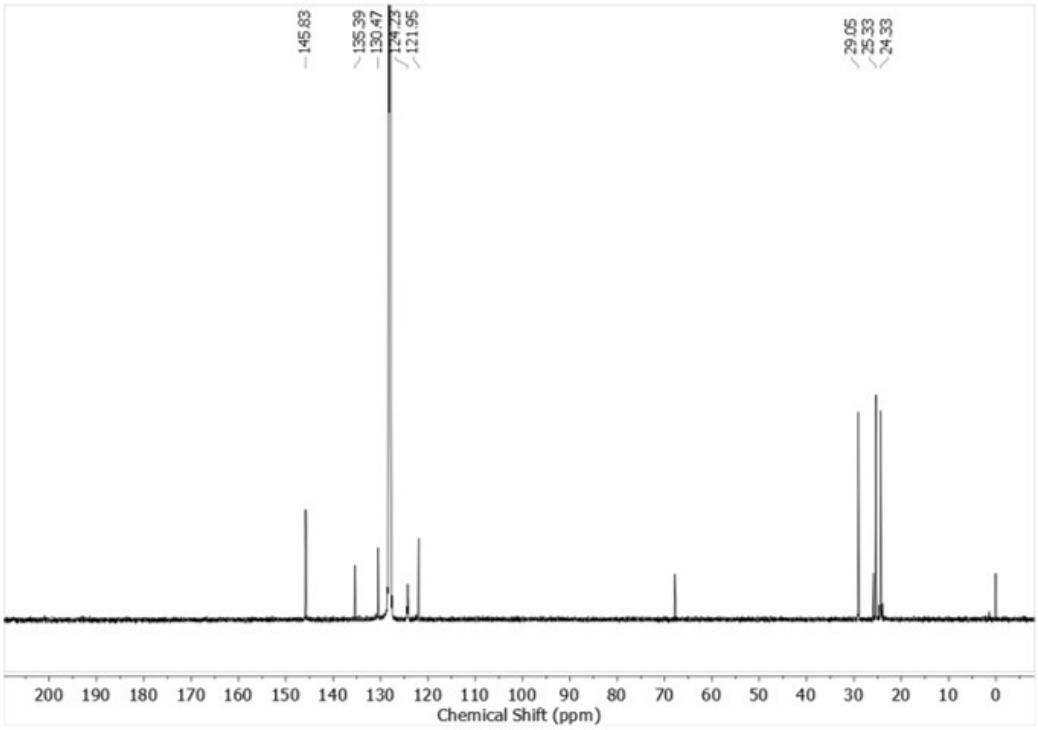


Figure S15. ^{13}C NMR spectrum of $(NHC^{Dipp}Au)_3P_7$.

5. Computational Details

Geometry optimization for $P_7(TMS)_3$, $(NHC^{Dipp}Cu)P_7(TMS)_2$ and $[(NHC^{Dipp}Cu)P_7(TMS)]^-$ anion complexes were optimized using hybrid correlation–exchange parameter-free functional of Perdew–Burke–Erzenhof (PBE0)[17] functional with triple-ζ quality Def2-TZVP basis sets. Optimization of hydrogen atoms positions in the crystal structure geometry of $[(NHC^{Dipp}Cu)P_7(TMS)]^-$ anion was performed with help of `optimizehydrogen` procedure as it implemented in the ORCA program suite, keeping positions of other atoms frozen. $(NHC^{Dipp}Au)_3P_7$ was optimized at PBEh-3c level of theory.[18] For PBEh-3c calculations, basis set superposition errors (BSSE) and London dispersion effects were counted with help of geometrical counterpart (gCP)[19] and dispersion correction (D3).[20, 21] Calculations were accelerated by applying the resolution of identity (RI)[22] approximation RIJCOSX (RI for Coulomb integral and COSX numerical integration for HF-exchange) together with the Def2/J auxiliary basis sets.[23] All these calculations were carried out using ORCA 4.0.0 program package.[24]

The natural bond orbital (NBO) analysis[25, 26] was performed at PBE0/Def2-TZVP level of theory using the NBO 6.0 program.[27] The total bonding energy and energy decomposition analysis (EDA)[28-30] were calculated using the PBE0 functional. All atoms were described by uncontracted Slater-type orbitals (STOs) with TZ2P quality as basis functions.[31] An auxiliary set of s, p, d, and f STOs was used to fit the molecular densities and to represent the Coulomb and exchange potentials accurately in each SCF cycle. Scalar relativistic effects have been taken into account by zero-order regular approximation (ZORA). The total bonding energy was calculated as $\Delta E_{bonding} = \Delta E_{int} + \Delta E_{prep}$, where ΔE_{int} is the total interaction energy and ΔE_{prep} represents preparation energy. The total interaction energy was evaluated as $\Delta E_{int} = \Delta E_{orb} + \Delta E_{elest} + \Delta E_{Pauli}$, where ΔE_{orb} is orbital or covalent component, ΔE_{elest} is electrostatic or ionic term, and ΔE_{Pauli} described Pauli repulsion. ^{31}P-NMR chemical shifts were evaluated at the same level of theory. The EDA and NMR calculations were performed using ADF2018 program package.[32, 33] On the basis of converged wave functions generated by ORCA 4.0.0 suite of program, the topology analysis on the electronic structure of the crystal structure of $[(NHC^{Dipp}Cu)P_7(TMS)]^-$ anion was carried out using Quantum Theory of Atom In Molecule (QTAIM).[34, 35] These calculations were accomplished by AIMALL program.[27]

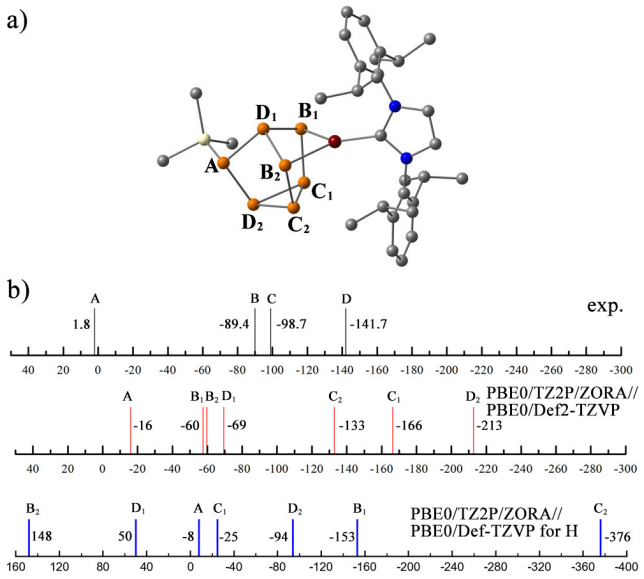


Figure S16. (*a*) The DFT optimized structure of complex **1**. Hydrogen atoms are omitted for clarity. (*b*) Experimental ^{31}P-NMR chemical shifts observed at 1:3 ratio of the reactants (*top*), calculated chemical shifts for fully optimized complex **1** (*middle*), and for X-ray based model (*bottom*) (PBE0/TZ2P/ZORA).

Table S2. The results of EDA and NBO analyses of complex **1**.[a]

Parameters	Energy (kcal mol^{-1})
EDA	
$\Delta E_{bonding}$	-88.83
ΔE_{prep}	61.20
ΔE_{int}	-150.03
ΔE_{orb}	-57.61
ΔE_{elest}	-262.78
ΔE_{Pauli}	170.35
NBO	
σ(P3–P4) → 4s(Cu)	12.96
σ(P1–P3) → 4s(Cu)	32.07
σ(P1–P6) → 4s(Cu)	10.84
3s(P4) → 4s(Cu)	13.85
3p(P4) → 4s(Cu)	51.56
3s(P6) → 4s(Cu)	16.09
3p(P6) → 4s(Cu)	64.41
$3d_{yz}$(Cu) → σ*(P1–P6)	5.23
$3d_{xy}$(Cu) → σ*(P1–P6)	1.43

[a] EDA was performed at PBE0/TZ2P/ZORA level of theory. NBO was performed at PBE0/Def2-TZVP level.

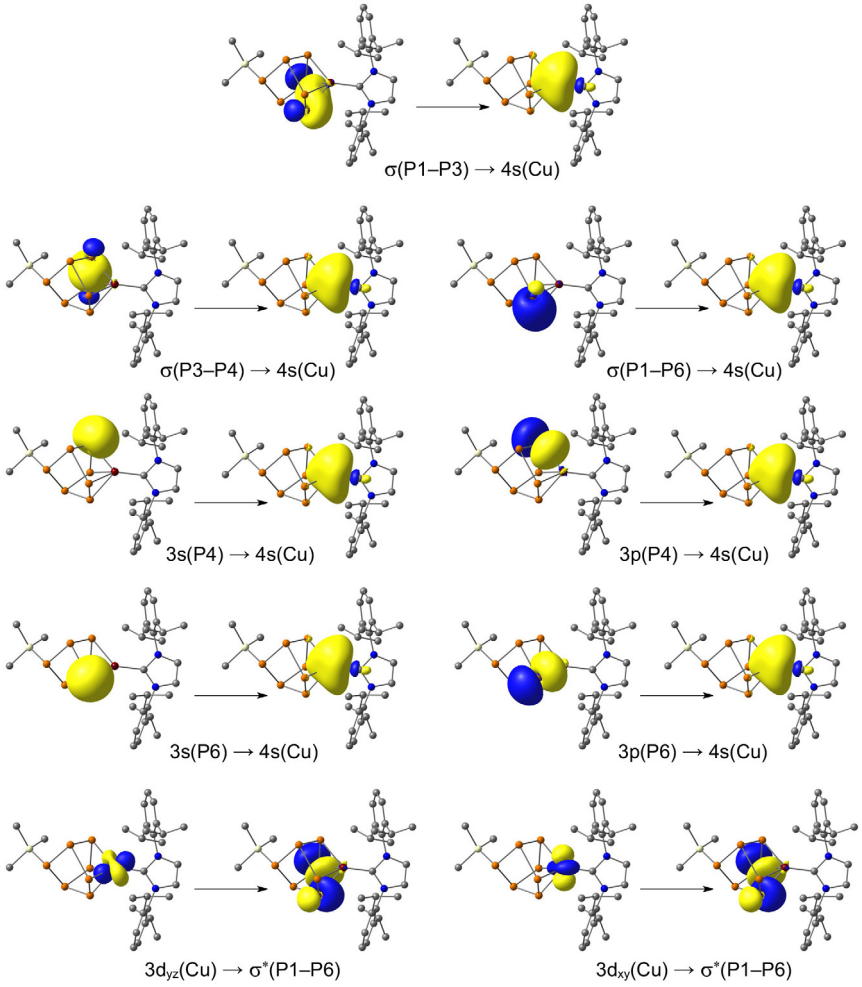


Figure S17. NBOs describing donor-acceptor interactions in complex **1** (PBE0/Def2-TZVP).

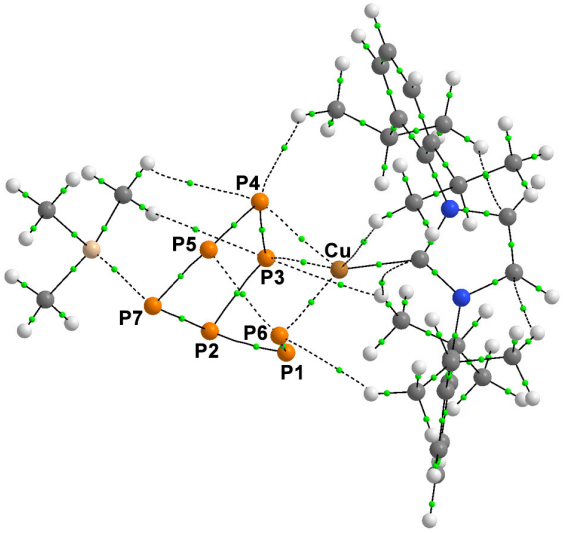


Figure S18. Bond critical points and bond paths for complex **1** (PBE0/Def2-TZVP).

Table S3. Selected topological parameters for bond critical points (BCPs) in the crystal structure of complex **1** (PBE0/Def2-TZVP).[a]

Parameters	BCP(P3-Cu)	BCP(P4-Cu)	BCP(P6-Cu)
$\boldsymbol{\rho_b}$	0.053	0.056	0.066
$\boldsymbol{\nabla^2\rho_b}$	0.109	0.113	0.131
λ_1	-0.037	-0.044	-0.055
λ_2	-0.016	-0.027	-0.030
λ_3	0.162	0.184	0.216
ε	1.374	0.601	0.836
$\lvert\lambda_1\rvert/\lambda_3$	0.230	0.230	0.250
$G(r_b)$	0.038	0.041	0.051
$V(r_b)$	-0.049	-0.054	-0.069
$h(r_b)$	-0.011	-0.013	-0.018
$G(r_b)/\boldsymbol{\rho_b}$	0.710	0.730	0.770
$V(r_b)/G(r_b)$	1.280	1.310	1.350
$I(r_b)= h(r_b)/\boldsymbol{\rho_b}$	-0.200	-0.230	-0.270

[a] $\boldsymbol{\rho_b}$ is electron density [e Bhor^{-3}]; $\boldsymbol{\nabla^2\rho_b}$ is the Laplacian of electron density [e Bhor^{-5}]; λ_1, λ_2, and λ_3 are the eigenvalues of $\boldsymbol{\nabla^2\rho_b}$ along the axis of cartesian coordinates; ε is the bond ellipticity, $\varepsilon=(\lambda_1-\lambda_2)/\lambda_1$; $G(r_b)$, $V(r_b)$, and $H(r_b)$ are the kinetic, potential and total energy densities [Hartree Bhor^{-3}]. $G(r_b)/\boldsymbol{\rho_b}$ is the kinetic energy density per electron [Hartree e^{-1}]; $V(r_b)/G(r_b)$ is the ratio between kinetic and potential energu densities; $I(r_b)$ is the total energy density per electron.

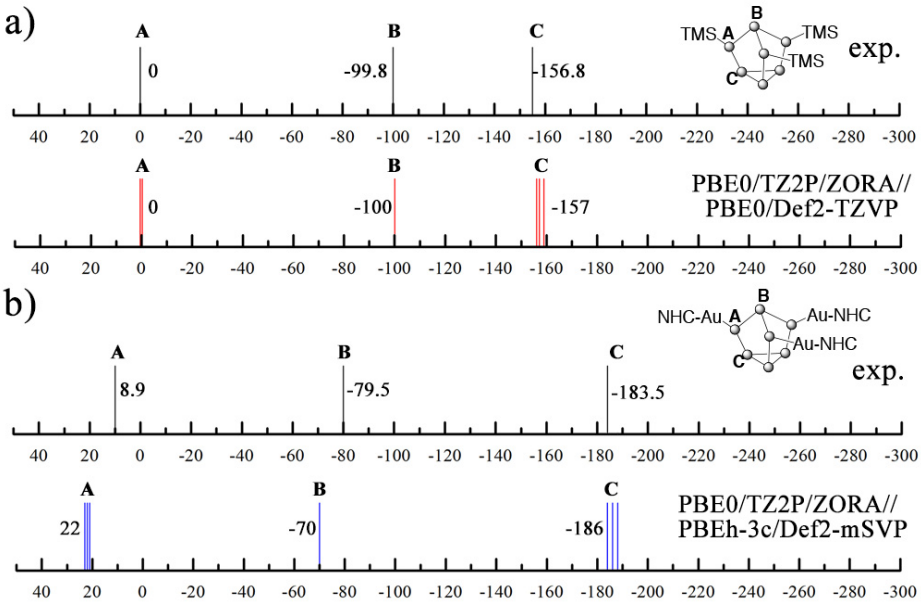


Figure S19. The experimental and DFT calculated $^{31}P\{^1H\}$ NMR chemical shifts of $(TMS)_3P_7$ (a) and complex **2** (b).

Table S4. Cartesian coordinates for the fully optimized geometry of complex **1** at PBE0/Def2-TZVP.

Si	0.3488290030	0.2196093028	6.5317466706
C	-0.4644656417	0.2691712329	8.2357105232
H	0.2294050846	0.6593354158	8.9882546886
H	-0.7872816938	-0.7280211400	8.5459077576
H	-1.3468144410	0.9146238097	8.2193852821
C	1.8151297715	-0.9598854885	6.6085149293
H	2.3328548554	-0.9791771225	5.6465813263
H	1.4899978015	-1.9785350511	6.8342202067
H	2.5254964050	-0.6454298769	7.3806830283
C	0.9682394480	1.9474480790	6.1431892345
H	0.1487598439	2.6697922072	6.1632476524
H	1.4159692107	1.9755393374	5.1470809630
H	1.7173904510	2.2504839355	6.8834730783
P	-0.9639187200	1.9042946237	2.7252129883
P	0.7753252293	0.6227227644	2.5668963724
P	-0.0672924411	-1.2434805323	3.3070721379
P	-2.1818839340	1.1452843709	4.4347746608
P	-1.1823714610	-0.6678122279	5.1211238519
P	-2.7213974389	0.5411336193	2.3652843604
P	-1.8263647057	-1.4206313611	2.0408241892
Cu	-0.3034502783	-0.2293885251	0.5997393277
C	0.0512158965	4.2355381894	-0.5389721483
C	0.1896059459	-3.5834286641	-1.7086368620
C	0.2593880440	-4.5128205201	-2.9195166799
C	0.6723750668	-0.5020471617	-3.4215892807
C	1.5488996999	-2.9979050219	-1.3957884825
C	1.8365937314	-1.6381205919	-1.5556921192
C	2.5685055125	-3.8229867402	-0.9323917502
C	3.0877173199	-1.0947546820	-1.2436531561
C	3.3935430743	0.3796401164	-1.3903212137
C	3.8193607478	-3.3144396548	-0.6340628001
C	4.4172889123	0.6204438618	-2.4991463885
C	4.0722524052	-1.9630589326	-0.7847953444
C	3.8535350000	0.9942261476	-0.0709365913
C	-0.0888581074	-0.1120273425	-1.3128483404
C	-0.3613010726	0.3571960526	-3.5215947135
C	-0.4102189358	-4.2943625676	-0.4988937167
C	-0.2610804927	3.3811463148	-1.7634382489
C	-0.0416699271	4.1701678522	-3.0539146110
C	-1.6584599956	2.8032460695	-1.7162766192
C	-1.9103034523	1.4437213507	-1.9244684730
C	-2.7489557739	3.6307544490	-1.4708115487
C	-3.1977838389	0.8982511347	-1.8604323114
C	-3.4535286071	-0.5779476344	-2.0725727737
C	-3.8982186209	-0.8484723030	-3.5106846269
C	-4.4573274088	-1.1501794351	-1.0778923616
C	-4.0331533807	3.1214289381	-1.4248557754
C	-4.2523884077	1.7684578992	-1.6111031059

N	0.8245831997	-0.7749991015	-2.0774679902
N	-0.8124323562	0.5816645955	-2.2364632968
H	0.9793333855	4.5602622218	-3.0957006101
H	-0.1200796889	3.6815309367	0.3862607647
H	0.6483053205	-3.9969119683	-3.8013938695
H	1.0981685995	4.5506390539	-0.5618820786
H	0.9096780199	-5.3696712341	-2.7206952694
H	1.3069623745	-0.9389016992	-4.1736119699
H	2.3733175659	-4.8803586290	-0.7919235178
H	2.4689727620	0.8862925778	-1.6746106303
H	4.0732700008	0.2260512972	-3.4590073246
H	3.1048402698	0.8534128512	0.7119817889
H	4.6037177554	1.6913962479	-2.6181224364
H	4.0160439225	2.0687086733	-0.1960769601
H	4.5985089507	-3.9739466226	-0.2673097166
H	5.3717648336	0.1403014834	-2.2643885899
H	5.0496045888	-1.5687585968	-0.5298810152
H	4.7959672450	0.5546588560	0.2687933286
H	0.1953158091	-5.1536180310	-0.1963799103
H	0.4420076383	2.5454573297	-1.7579521404
H	-0.4795214589	-2.7578211201	-1.9590896131
H	-0.5625862166	5.1403094044	-0.5100073568
H	-0.7349943547	-4.8980788627	-3.1612812328
H	-0.8129680925	0.8235436450	-4.3803967971
H	-0.5005397087	-3.6155579250	0.3513054701
H	-0.2041456369	3.5491588614	-3.9385394099
H	-0.7282821306	5.0198924181	-3.1125727022
H	-1.4116799121	-4.6620545719	-0.7383501964
H	-2.5092148350	-1.1000181590	-1.9029898202
H	-3.1588215255	-0.5011469058	-4.2365428534
H	-4.0497256617	-1.9201102859	-3.6689999544
H	-2.5848653191	4.6875034398	-1.2937918958
H	-4.5130846240	-2.2356401979	-1.1932259632
H	-4.8427809441	-0.3394333608	-3.7255611822
H	-4.1609974550	-0.9364630334	-0.0494253003
H	-5.4635112631	-0.7524746270	-1.2398268563
H	-4.8692719344	3.7803227637	-1.2178665363
H	-5.2596888259	1.3760838085	-1.5403195520

Table S5. Cartesian coordinates for the crystal structure of complex **1** with optimization of only H atoms at PBE0/Def2-TZVP.

Si	0.4932585176	0.4197577359	6.3946259421
C	-0.1127026659	1.8067446093	7.4886228004
H	0.6215733205	2.0713656918	8.2573195619
H	-1.0425841520	1.5255646703	7.9908578866
H	-0.3169280325	2.6947751349	6.8853659964
C	0.8132160482	-1.0906940198	7.4229283752
H	1.2043844898	-1.9005006678	6.8010174954
H	-0.0876470236	-1.4593621472	7.9208358230

H	1.5585617577	-0.8703001109	8.1946013334
C	2.1158383716	0.8962951561	5.6322824598
H	2.0215813107	1.7441319827	4.9506141686
H	2.5280794302	0.0672370327	5.0538070572
H	2.8249926881	1.1672841469	6.4244330575
P	0.6102904529	1.2980713192	2.3303401221
P	1.0645296230	-0.8106000327	2.4589189011
P	-0.5223730702	-1.5996641360	3.6737136767
P	-1.0586817383	1.6899734735	3.6735867605
P	-1.2069542426	-0.0402965069	4.9956132335
P	-1.8230661610	1.3202525040	1.9060837126
P	-2.2737236878	-0.5494920998	2.0614838654
Cu	-0.4253600174	-0.1867927082	0.6394092229
C	0.0460557152	3.6200786249	-0.7932881547
C	0.1888509400	-3.3537793428	-2.1639460455
C	0.3570377505	-4.1526499369	-3.4507272674
C	0.8153688840	-0.2722342823	-3.3021235698
C	1.5071958362	-2.8876261437	-1.5537975100
C	1.8460775283	-1.5560694579	-1.4124513138
C	2.4500260622	-3.8401218867	-1.1183578721
C	2.9928748491	-1.1055812048	-0.8057713810
C	3.2333599872	0.3758974603	-0.5812516909
C	3.6082312094	-3.4418532681	-0.5717015168
C	3.8315674507	0.9987842644	-1.8562734332
C	3.9094076855	-2.0778013306	-0.4059534105
C	4.1045046797	0.6680686650	0.6354696322
C	-0.1286766604	-0.0465506100	-1.2443679088
C	-0.2348253576	0.5445928392	-3.4307023930
C	-0.6113839849	-4.1357359089	-1.1198935952
C	-0.6775175648	3.5272259655	-2.0588744380
C	-0.8365046720	4.9178755596	-2.6600750969
C	-1.9901825689	2.7572691340	-1.8810944944
C	-2.0248719032	1.3797244141	-1.9319636857
C	-3.1962108382	3.4325980706	-1.6584809075
C	-3.1946079833	0.6667466532	-1.7865050071
C	-3.2004569210	-0.8834082316	-1.9177638579
C	-3.2644088412	-1.2882414465	-3.3492916523
C	-4.2517147522	-1.5412804316	-1.0978301924
C	-4.3596130481	2.7416007284	-1.5292204988
C	-4.3651325542	1.3775320286	-1.5966488447
N	0.8955018548	-0.5928758010	-1.9622211200
N	-0.8085855287	0.6488967270	-2.1925127135
H	0.1489274323	5.3256505362	-2.8980963042
H	0.2357942539	2.6484443841	-0.3331559619
H	0.8737685370	-3.5711873053	-4.2186144482
H	1.0121905097	4.1199807971	-0.9229707427
H	0.9354492388	-5.0661496359	-3.2814373468
H	1.5294646984	-0.6317280977	-4.0231794147
H	2.2146053282	-4.8953035942	-1.2069195089
H	2.2573748745	0.8317524581	-0.3928097781
H	3.1648167866	0.8774180593	-2.7118827574

H	3.7168331912	0.1595491704	1.5205227944
H	4.0084583781	2.0688611228	-1.7153242674
H	4.0943681799	1.7405617387	0.8420315739
H	4.3292537586	-4.1752374927	-0.2237427105
H	4.7878848117	0.5245091042	-2.0962513680
H	4.8247331347	-1.7884361495	0.0928303299
H	5.1444336181	0.3658945728	0.4756645999
H	-0.0802924876	-5.0404442663	-0.8105988007
H	-0.0700493797	2.9505643266	-2.7649212293
H	-0.3924679514	-2.4663443512	-2.4161587298
H	-0.5214012673	4.1940926407	-0.0534294111
H	-0.6209378364	-4.4443274242	-3.8424936951
H	-0.6521970913	1.0264015729	-4.2986971558
H	-0.7892699119	-3.5276049879	-0.2305503247
H	-1.4324816929	4.9149603357	-3.5768011401
H	-1.3093572036	5.6072466622	-1.9548986098
H	-1.5785969034	-4.4403726568	-1.5287273370
H	-2.2449950957	-1.2073717768	-1.4973573310
H	-2.4634395966	-0.8450019691	-3.9447906343
H	-3.1844412248	-2.3761993259	-3.4527530883
H	-3.1917216015	4.5148933824	-1.6031456449
H	-4.1504778375	-2.6289814895	-1.1675087815
H	-4.2154474751	-0.9858629726	-3.8030503258
H	-4.1597098173	-1.2691559204	-0.0437213590
H	-5.2640360813	-1.2981073651	-1.4432263396
H	-5.2888023137	3.2763602094	-1.3590707034
H	-5.2955264358	0.8358128278	-1.4732855604

Table S5. Cartesian coordinates for the optimized geometry of the proposed intermediates to complex **1** with at PBE0/Def2-TZVP.

Si	0.4996263780	0.7126825450	6.5491547360
C	-0.1475084690	0.6414127000	8.3103269310
H	0.5376447180	1.1600529460	8.9882134040
H	-0.2498914870	-0.3912048880	8.6519462960
H	-1.1265585310	1.1204455320	8.3906929170
C	2.1251071680	-0.2145483340	6.4268060440
H	2.5383845590	-0.1478678860	5.4180697170
H	2.0048612160	-1.2714171600	6.6753022240
H	2.8516383280	0.2172656080	7.1223042940
C	0.7261750020	2.4990952680	6.0411634240
H	-0.2035479200	3.0636002390	6.1419529710
H	1.0599539730	2.5714275570	5.0042711510
H	1.4791755900	2.9675693060	6.6836792270
P	-1.4860247840	1.9490514930	2.7648082630
P	0.4449668540	0.9445447170	2.5516528940
P	0.0044855820	-0.9778455070	3.4654448810
P	-2.3589484890	1.1545818330	4.6451194240
P	-1.0353759020	-0.4464269600	5.3149328040
P	-3.0520953810	0.3730159580	2.6941543320

P	-1.7655850140	-1.3470045030	2.2507445800
Cu	0.0196545010	0.2287251630	0.4487640280
C	0.5706660820	4.0595894670	-0.5605119860
C	0.1907552320	-3.5144931660	-1.9757136280
C	0.3287074310	-4.5390925600	-3.1005723830
C	0.6875556880	-0.4870742380	-3.5792915020
C	1.5390443150	-2.9569848330	-1.5746059660
C	1.8668045860	-1.6032064630	-1.7010131590
C	2.5100963060	-3.8061789130	-1.0548390290
C	3.1172657590	-1.0904097400	-1.3388719390
C	3.4874851800	0.3671611030	-1.5051960850
C	3.7518727890	-3.3266967740	-0.6800298420
C	4.5753903340	0.5333389330	-2.5656386530
C	4.0500832190	-1.9840026890	-0.8235514310
C	3.9080259040	1.0006521220	-0.1815508200
C	0.0425478930	0.0380995280	-1.4788694520
C	-0.3066429470	0.4211036030	-3.6772772450
C	-0.5448630490	-4.1077896040	-0.7764387820
C	0.0867721050	3.4868662480	-1.8900111010
C	0.2467341380	4.5046813140	-3.0185074570
C	-1.3424312140	2.9980082360	-1.8018464160
C	-1.7101501630	1.6721219830	-2.0524837000
C	-2.3557718080	3.8912264620	-1.4713286730
C	-3.0367930400	1.2306914740	-1.9970795190
C	-3.4317192750	-0.1963457290	-2.3082498070
C	-4.1043463260	-0.2830422260	-3.6783045560
C	-4.3208060590	-0.8015285980	-1.2264713610
C	-3.6742443950	3.4823720110	-1.4006647630
C	-4.0096373360	2.1668641780	-1.6655536670
N	0.8837180030	-0.7071874050	-2.2340233970
N	-0.6857129890	0.7268927840	-2.3892163150
H	1.2904224740	4.8181405470	-3.1027096360
H	0.4817472430	3.3269776480	0.2442707660
H	0.8334323960	-4.1144653870	-3.9717143750
H	1.6196730460	4.3570167050	-0.6375934830
H	0.9041849340	-5.4099062440	-2.7762380920
H	1.2670838840	-0.9902855360	-4.3342710990
H	2.2865125030	-4.8603939460	-0.9368095010
H	2.6025515460	0.9043835090	-1.8533571980
H	4.2677308090	0.1149474680	-3.5270609280
H	3.1212498670	0.9113739950	0.5703621650
H	4.8047216570	1.5917292240	-2.7129662920
H	4.1215379550	2.0630599310	-0.3243232150
H	4.4924525710	-4.0044922780	-0.2708445910
H	5.4987699230	0.0313898160	-2.2648295730
H	5.0266915550	-1.6186086580	-0.5277068750
H	4.8129608280	0.5340793780	0.2163091460
H	0.0084652320	-4.9465858910	-0.3461094690
H	0.7243718810	2.6322353310	-2.1271397470
H	-0.4195683110	-2.6914637330	-2.3544155820
H	-0.0037982240	4.9439654920	-0.2735975030

H	-0.6560925900	-4.8920777890	-3.4167453430
H	-0.7699689580	0.8745094210	-4.5366825830
H	-0.6921629420	-3.3596884780	0.0054779260
H	-0.0631264550	4.0891366430	-3.9804317920
H	-0.3545260470	5.3984380530	-2.8330400570
H	-1.5264706220	-4.4795783250	-1.0822390370
H	-2.5195565020	-0.7964416010	-2.3473086550
H	-3.4603881840	0.1069039960	-4.4701713220
H	-4.3482034460	-1.3208028590	-3.9197341370
H	-2.1039373330	4.9235524430	-1.2578433110
H	-4.5123327880	-1.8549960430	-1.4452510880
H	-5.0335982560	0.2927951880	-3.6935942680
H	-3.8494285410	-0.7371186750	-0.2442547780
H	-5.2892374040	-0.2986084810	-1.1692307910
H	-4.4468594120	4.1931800680	-1.1309485640
H	-5.0464708320	1.8580766110	-1.6034422210
Si	-2.9558904260	-3.0842195340	3.1492093930
C	-1.7150011260	-4.4332897260	3.5469205060
H	-1.0527866550	-4.1265713430	4.3597627460
H	-2.2381458380	-5.3432492830	3.8576106410
H	-1.0950309460	-4.6760519470	2.6806684740
C	-3.9813591170	-2.6782377070	4.6618549680
H	-4.6933313460	-1.8754110310	4.4573354730
H	-4.5468904190	-3.5667393820	4.9623854640
H	-3.3513248000	-2.3686987360	5.4972786220
C	-4.1019255740	-3.6526605620	1.7721804030
H	-3.5393707480	-3.9334420480	0.8788492730
H	-4.6808603410	-4.5221705210	2.0989778490
H	-4.8075970300	-2.8654718350	1.4952915960

Table S5. Cartesian coordinates for the optimized geometry of complex **2** with at PBEh-3c/Def2-mSVP.

P	-1.8018069022	1.7952266365	2.9389541394
P	0.3048036790	1.1790805179	3.1301375166
P	0.0861557393	-1.0004791162	3.2075601079
P	-2.8909176863	0.2959469147	4.1745336035
P	-1.3660055693	-1.1504219679	4.8406575474
P	-2.8627871602	0.1090049098	1.9596497449
P	-1.2343124406	-1.2987831970	1.4874774513
Au	0.7592297778	1.3712855987	0.8287596114
C	-1.6278235659	4.7159659187	0.1910645538
C	3.2853895221	-1.0166037857	-1.3142051411
C	4.0670498332	-1.7897484345	-2.3771581193
C	2.1467808708	1.8701126191	-3.1543872487
C	4.0332618789	0.2317852890	-0.8963807345
C	3.5518779580	1.5219855427	-1.1274830677
C	5.2516066512	0.1151217312	-0.2367643175
C	4.2234003349	2.6711035335	-0.7060821544
C	3.6453116438	4.0599604530	-0.8691832727

C	5.9514632067	1.2349318465	0.1740520930
C	4.6277665885	5.0173085274	-1.5412295558
C	5.4398438525	2.4997877767	-0.0559852436
C	3.1786158585	4.5976907566	0.4853753577
C	1.1152226752	1.5859617626	-1.1768452177
C	0.8173252976	1.9172335601	-3.3785169120
C	2.9583682827	-1.9006173470	-0.1108559763
C	-1.1624685422	4.0594536105	-1.1062618121
C	-1.3346089897	5.0078160502	-2.2946641583
C	-1.8639458310	2.7462469354	-1.3829959787
C	-1.2035736121	1.6448473642	-1.9331621930
C	-3.2226701147	2.6109879169	-1.1268042337
C	-1.8474988318	0.4407683866	-2.2324557491
C	-1.1249103572	-0.7376282783	-2.8512726555
C	-1.3285692437	-0.7473329155	-4.3690236947
C	-1.5435324326	-2.0776731033	-2.2518776954
C	-3.8867000898	1.4317052493	-1.4090373225
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N	0.2057300971	1.7332019600	-2.1583483771
H	-0.8291455302	5.9569722625	-2.1065962313
H	-1.5973368020	4.0144472046	1.0253798562
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H	5.6524968390	-0.8689638593	-0.0298366890
H	2.7647165909	4.0057871852	-1.5132977895
H	4.9501297687	4.6420772397	-2.5130497998
H	2.4473348670	3.9295472165	0.9425765211
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H	6.8964631439	1.1207172903	0.6888974561
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H	5.9893155772	3.3675438563	0.2880055354
H	4.0126007468	4.7041426069	1.1830227764
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H	-0.0943378839	3.8693477535	-0.9857829800
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H	-0.7639385444	-1.5612529914	-4.8270448762
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H	-0.9306965858	-2.8780014578	-2.6706157216

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Au	-2.4571037299	-3.1654228420	2.2298103786
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C	-5.5367084064	-5.7674619718	3.5072467829
C	-6.0461180676	-2.5744928836	2.3196375227
C	-5.5725317829	-3.2704048492	3.4336321581
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C	-5.6228487145	-2.7555028488	4.7325035842
C	-5.1372040549	-3.5307116346	5.9394006601
C	-6.6493814235	-0.7765633037	3.8118553474
C	-6.3277782734	-4.1200836013	6.7009135280
C	-6.1774234477	-1.4931025655	4.8957195244
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C	-5.5165920402	-2.1492230298	-0.1168896766
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C	-1.2527749885	-6.7328195262	3.5241994552
C	-2.2192186407	-6.6151538844	2.5228628037
C	-0.0511974012	-7.3421125768	3.1806729084
C	-2.0116946571	-7.0399529870	1.2100010811
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H	-0.6155931396	-4.7010760028	6.2420986022
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H	-6.5545951057	-5.8657890563	3.8406292485
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H	-6.9615591188	-4.7340805540	6.0590059461
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H	-4.6126439679	-7.7710102549	3.3535019882
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C	0.5431835800	1.6631578349	7.6428251960
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H	5.1640592064	-0.2607015078	9.3406723283

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H	-1.6503760460	-1.5103882595	11.3269364246

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