

Supporting Information

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S1: Synthetic Details

General: All manipulations were performed under an inert atmosphere of dry nitrogen, using standard Schlenk techniques. Dry, oxygen-free solvents were employed unless otherwise mentioned. The compound **1** was prepared following reported procedure,^[1] while all other starting materials were purchased from commercial sources. NMR spectra were recorded on Bruker Avance 400 MHz spectrometers (¹H, 400.1 MHz; ¹³C, 100.5 MHz; ³¹P, 161.9 MHz). All spectra were obtained in the solvent indicated at 25 °C. The chemical shifts (δ) were measured according to IUPAC and expressed in ppm relative to SiMe₄ (¹H, ¹³C), and 85% H₃PO₄ (³¹P). Coupling constants *J* are reported in Hertz [Hz] as absolute values. The elemental analyses were acquired on Vario EL cube elemental analyzer. UV/vis spectra were measured on Shimadzu UV/vis/NIR UV-3600-spectrometer. Melting point (M. P.) were measured on Buchi M-560 apparatus.

Preparation of 4: KC₈ (1.0 equivalent) was added in small portions to a stirred solution of **1** (390.0 mg, 0.5 mmol) in THF (4 mL). After 5 minutes, the reaction mixture was

filtered, followed by removing of the solvent under reduced pressure. The remaining solid was washed with acetonitrile. Drying the residue *in vacuo* afforded a brown powder (156.8 mg). Brown crystals of **4** were obtained from a saturated solution of hexane and stored at $-30\text{ }^{\circ}\text{C}$. M. P. = $193\text{ }^{\circ}\text{C}$. UV/Vis (THF, λ (nm) ϵ ($\text{M}^{-1}\text{cm}^{-1}$)): 295.7 (2403), 323.5 (2114).

Preparation of 6: TEMPO (46.9 mg, 0.15 mmol) in THF (2 mL) was added dropwise to a stirred solution of freshly isolated **4** (53.5 mg, 0.05 mmol) in THF (3 mL). After stirring for 1 hour, the solvent was removed under reduced pressure. The remaining solid was washed with hexane and dried *in vacuo* to afford a blue powder **6** (21.5 mg, 0.03 mmol, 57.7 % yield). M. P. $> 250\text{ }^{\circ}\text{C}$. ^1H NMR (CD_3CN , 400 MHz): δ = 7.40 (m, 2 H, $\text{C}_{\text{ar}}\text{H}$), 7.21 (m, 4 H, $\text{C}_{\text{ar}}\text{H}$), 2.85 (m, 4 H, CHMe_2), 2.42 (m, 4 H, CH_2Me), 2.16 (s, 4 H, CH_2), 2.07 (m, 4 H, CH_2Me), 1.35 (s, 12 H, CH_3), 1.17 (d, 12 H, CH_3), 0.92 (m, 24 H, CH_3); $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_3CN , 100.5 MHz): δ = 178.5 (m, PCC), 153.8 (dd, $^1J_{\text{PC}}$ = 78.9 Hz, PCC, $^2J_{\text{PC}}$ = 53.4 Hz, PCC), 132.4 (C_{ar}), 130.7 (C_{ar}), 127.4 (C_{ar}), 126.4 (C_{ar}), 71.7, 65.3, 54.9, 42.5, 31.4, 29.6, 29.4, 28.6, 26.7, 24.2, 8.8; $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_3CN , 161.9 MHz) δ = 420.4 (d, $^2J_{\text{PP}}$ = 16.5 Hz, PCPO), 21.0 (d, $^2J_{\text{PP}}$ = 16.5 Hz, PCPO). Elemental analysis (%): calcd for $\text{C}_{46}\text{H}_{70}\text{N}_2\text{O}_2\text{P}_2$; C 74.16, H 9.47, N 3.76; found: C 73.25, H 8.358, N 3.04. UV/Vis (THF, λ (nm) ϵ ($\text{M}^{-1}\text{cm}^{-1}$)): 348.5 (2403).

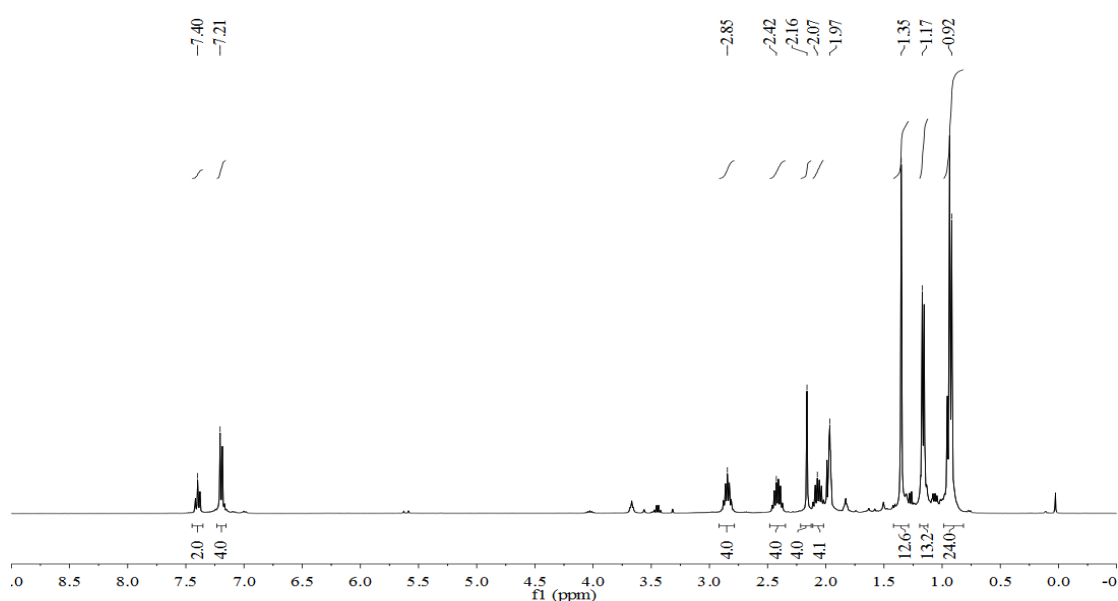


Figure S1. ^1H NMR spectrum of **6** in CD_3CN .

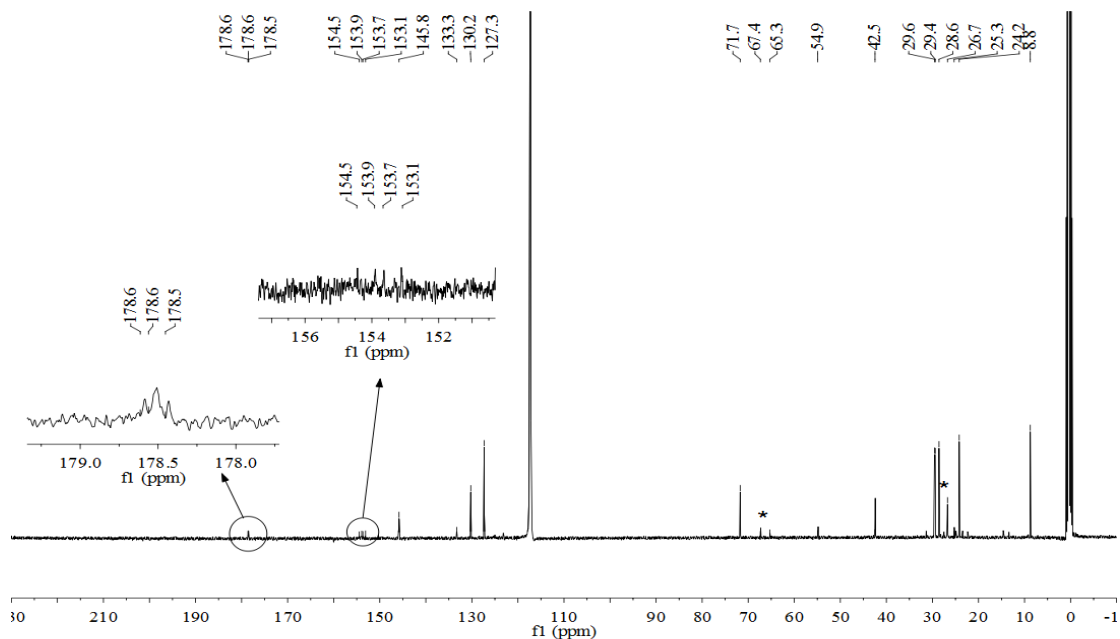


Figure S2. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **6** in CD_3CN . *THF.

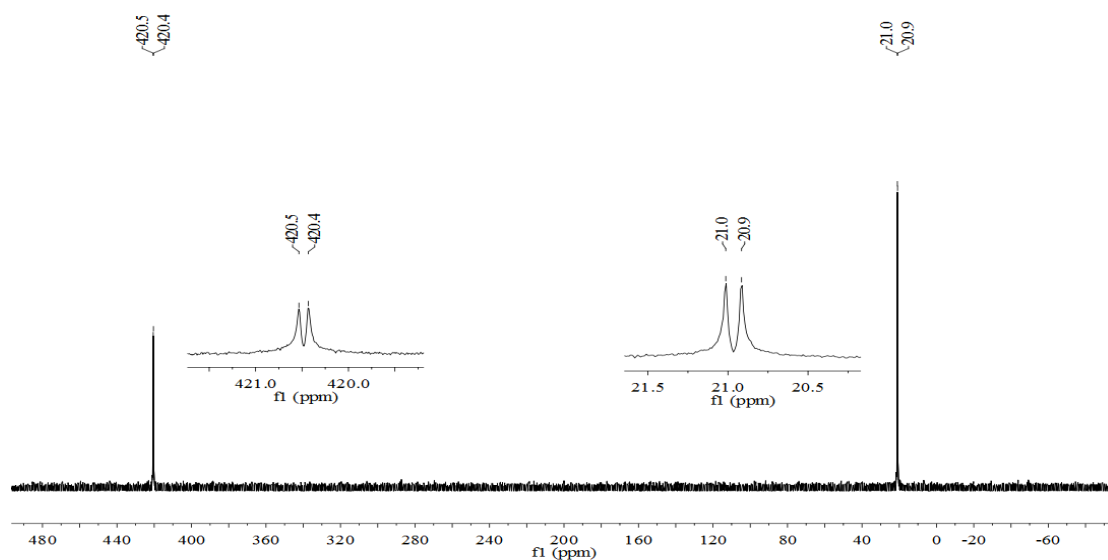


Figure S3. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **6** in CD_3CN .

Preparation of 7: $\text{ClAu}(\text{SMe}_2)$ (29.6 mg, 0.10 mmol) in THF (2 mL) was added dropwise to a stirred solution of freshly isolated **4** (53.5 mg, 0.05 mmol) in THF (3 mL). After stirring for 1 hour, the solvent was removed under reduced pressure. The remaining solid was washed with diethyl ether and dried *in vacuo* to afford a red powder

7 (35.8 mg, 0.03 mmol, 60.8 % yield). M. P. = 231 °C (Decomposition). ^1H NMR (CD_2Cl_2 , 400 MHz): δ = 7.37 (m, 2 H, $\text{C}_{\text{ar}}\text{H}$), 7.19 (d, 4 H, $\text{C}_{\text{ar}}\text{H}$), 2.77 (m, 8 H, CHMe_2), 2.34 (m, 4 H, CH_2Me), 2.19 (s, 4 H, CH_2), 1.37 (s, 12 H, CH_3), 1.24 (d, 12 H, CH_3), 1.11 (t, 24 H, CH_3), 1.06 (d, 12H, CH_3); $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 100.5 MHz): δ = 180.4 (m, PCC), 145.4 (C_{ar}), 144.4 (C_{ar}), 134.1 (dd, $^1J_{\text{PC}}$ = 54.0 Hz, PCC, $^2J_{\text{PC}}$ = 31.5 Hz, PCC), 132.2 (C_{ar}), 127.3 (C_{ar}), 73.5, 57.7, 43.4, 34.5, 29.6, 29.0, 27.6, 24.5 10.1; $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 161.9 MHz) δ = 437.6 (d, $^2J_{\text{PP}}$ = 21.0 Hz, PCPAu), 62.5 (d, $^2J_{\text{PP}}$ = 21.0 Hz, PCPAu). Elemental analysis (%): calcd for $\text{C}_{46}\text{H}_{70}\text{N}_2\text{P}_2\text{Au}_2\text{Cl}_2$; C 46.91, H 5.99, N 2.38; found: C 45.52, H 6.83, N 2.06. UV/Vis (THF, λ (nm) ϵ ($\text{M}^{-1}\text{cm}^{-1}$)): 546.0 (1350).

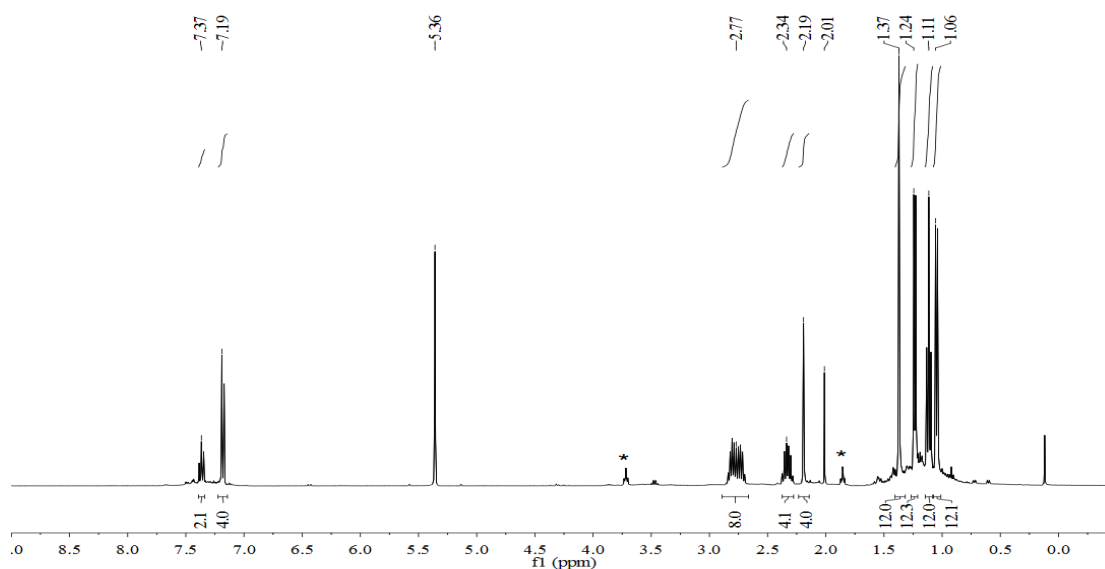


Figure S4. ^1H NMR spectrum of **7** in CD_2Cl_2 . *THF.

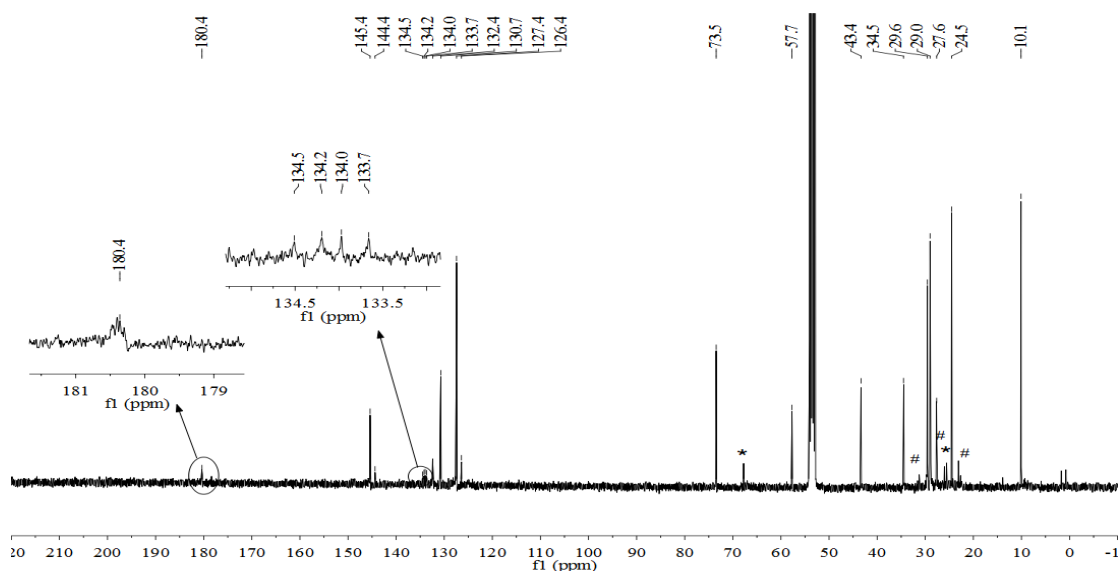


Figure S5. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **7** in CD_2Cl_2 . *THF, #Hexane.

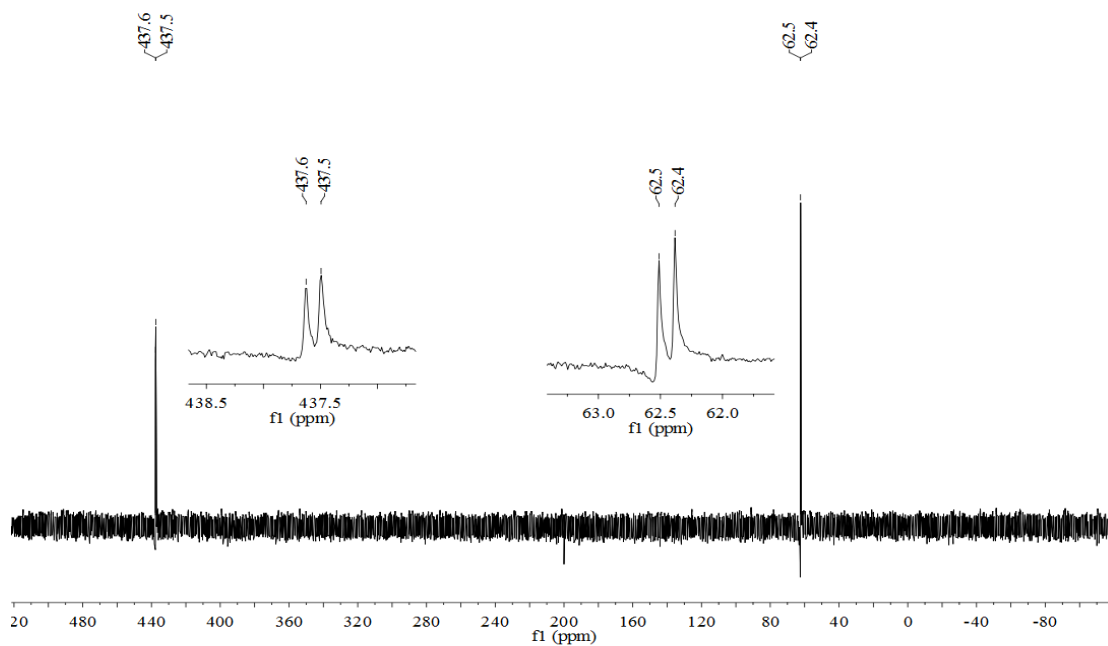


Figure S6. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **7** in CD_2Cl_2 .

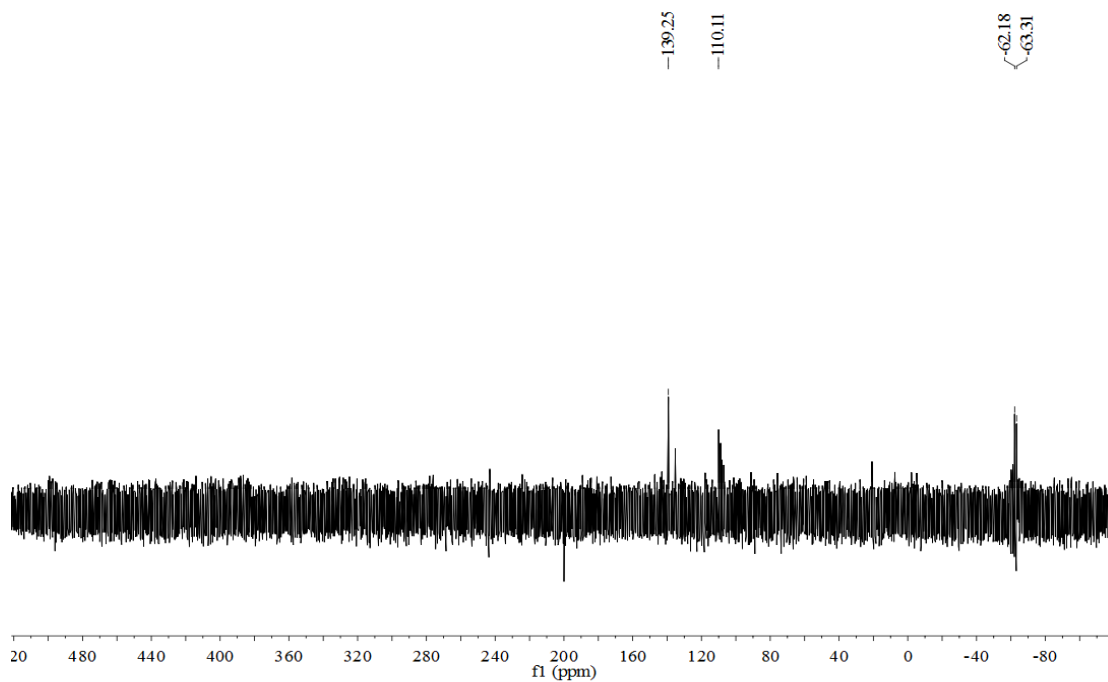


Figure S7. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of reaction mixture between **5** and TEMPO in toluene.

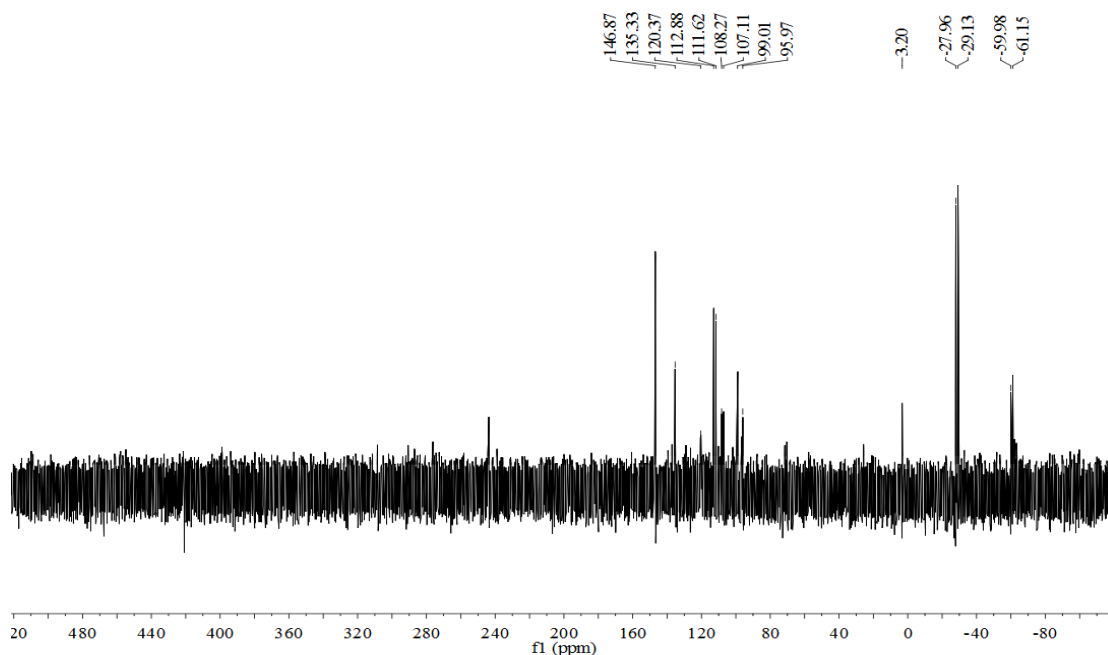


Figure S8. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of reaction mixture between **5** and $\text{ClAu}(\text{Me}_2\text{S})$ in toluene.

S2. X-Ray Diffraction Studies

These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/cgi-bin/catreq.cgi>, or by emailing data_request@ccdc.cam.ac.uk. The CCDC reference numbers are 1867485–1867487

Table S1. Crystal data and structure refinement for **4** (1867485)

Empirical formula	$\text{C}_{69}\text{H}_{105}\text{N}_3\text{P}_3$
Formula weight	1069.46
Temperature/K	150.00(10)
Crystal system	monoclinic
Space group	$\text{P}2_1/\text{c}$
$a/\text{\AA}$	9.5093(2)
$b/\text{\AA}$	27.8801(5)
$c/\text{\AA}$	24.3205(5)
$\alpha/^\circ$	90
$\beta/^\circ$	97.661(2)
$\gamma/^\circ$	90
Volume/ \AA^3	6390.3(2)
Z	4

$\rho_{\text{calc}}/\text{cm}^3$	1.112
μ/mm^{-1}	1.154
F(000)	2340.0
Crystal size/ mm^3	$0.1 \times 0.08 \times 0.07$
Radiation	CuK α ($\lambda = 1.54184$)
2 Θ range for data collection/ $^\circ$	7.326 to 146.914
Index ranges	$-7 \leq h \leq 11, -18 \leq k \leq 34, -30 \leq l \leq 28$
Reflections collected	22489
Independent reflections	12246 [$R_{\text{int}} = 0.0483, R_{\text{sigma}} = 0.0643$]
Data/restraints/parameters	12246/0/700
Goodness-of-fit on F^2	1.106
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.1137, wR_2 = 0.3140$
Final R indexes [all data]	$R_1 = 0.1257, wR_2 = 0.3215$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	1.70/-0.44

Table S2. Crystal data and structure refinement for **6** (1867486)

Empirical formula	$\text{C}_{58}\text{H}_{70}\text{N}_2\text{O}_2\text{P}_2\text{D}_{12}$
Formula weight	913.27
Temperature/K	150.00(10)
Crystal system	monoclinic
Space group	C2/c
a/ \AA	29.4871(13)
b/ \AA	10.2236(2)
c/ \AA	22.3739(10)
$\alpha/^\circ$	90
$\beta/^\circ$	131.533(7)
$\gamma/^\circ$	90
Volume/ \AA^3	5049.1(5)
Z	4
$\rho_{\text{calc}}/\text{cm}^3$	1.201
μ/mm^{-1}	1.108
F(000)	1960.0
Crystal size/ mm^3	$0.09 \times 0.08 \times 0.05$
Radiation	CuK α ($\lambda = 1.54184$)
2 Θ range for data collection/ $^\circ$	7.968 to 148.246
Index ranges	$-36 \leq h \leq 24, -12 \leq k \leq 12, -16 \leq l \leq 27$
Reflections collected	13877
Independent reflections	5019 [$R_{\text{int}} = 0.0212, R_{\text{sigma}} = 0.0187$]
Data/restraints/parameters	5019/0/298

Goodness-of-fit on F^2	1.052
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0378$, $wR_2 = 0.0995$
Final R indexes [all data]	$R_1 = 0.0412$, $wR_2 = 0.1027$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	0.33/-0.38

Table S3. Crystal data and structure refinement for **7** (1867487)

Empirical formula	$C_{52}H_{71}Au_2Cl_2FN_2P_2$
Formula weight	1269.88
Temperature/K	150.00(10)
Crystal system	monoclinic
Space group	C2
$a/\text{\AA}$	30.0735(15)
$b/\text{\AA}$	10.7348(3)
$c/\text{\AA}$	23.2145(12)
$\alpha/^\circ$	90
$\beta/^\circ$	130.949(9)
$\gamma/^\circ$	90
Volume/ \AA^3	5660.5(7)
Z	4
$\rho_{\text{calc}}/\text{cm}^3$	1.490
μ/mm^{-1}	11.279
F(000)	2512.0
Crystal size/ mm^3	$0.03 \times 0.02 \times 0.02$
Radiation	$\text{CuK}\alpha$ ($\lambda = 1.54184$)
2θ range for data collection/ $^\circ$	7.784 to 146.948
Index ranges	$-36 \leq h \leq 36$, $-13 \leq k \leq 12$, $-20 \leq l \leq 28$
Reflections collected	17955
Independent reflections	10747 [$R_{\text{int}} = 0.0722$, $R_{\text{sigma}} = 0.0866$]
Data/restraints/parameters	10747/1/550
Goodness-of-fit on F^2	1.003
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0546$, $wR_2 = 0.1378$
Final R indexes [all data]	$R_1 = 0.0592$, $wR_2 = 0.1445$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	1.59/-1.33
Flack parameter	-0.035(12)

S3: EPR analysis

Density functional theory calculations to compute the EPR parameters (Table S4) were performed using ORCA 3.0.3 [2], [3] on a machine running the OpenSUSE 13.1 x86_64 operating system with 8 processor cores. The g- and hyperfine tensors were calculated using a spin-unrestricted Kohn-Sham self-consistent field calculation method with a ZORA scalar relativistic Hamiltonian and the B3LYP functional, using the QZVPP basis set for P and the TZVPP basis set for all other nuclei, [4] and tighter convergence constraints. The spin-orbit coupling was calculated using the SOMF(1X) option in ORCA, which entails mean-field/effective potential treatment, the inclusion of 1-electron terms, semi-numeric Coulomb term computation, calculation of exchange terms via one-centre exact integrals including the spin-other orbit interaction, and inclusion of the local DFT correlation terms.

Table S4. EPR spin Hamiltonian parameters for compound **4**. DFT values are given in parentheses. Hyperfine couplings are in MHz.

quantity	principal values	isotropic	$\rho_s^{(b)}$	$\rho_p^{(b)}$	ρ^{tot}	R ^(a)
g values	2.0031, 2.0057, 2.0107 (2.0024, 2.0034, 2.0117)	2.0065 (2.0058)	-	-	-	0.6453868, 0.7231367, 0.2460673 0.1625257, -0.1847633, 0.9692512 0.7463654, -0.6655342, -0.0017155
P2 hyperfine	(-5, -15, 500) (-72, -94, 458)	160 (97)	0.06 (0.038)	0.51 (0.5384)	0.57 (0.576)	0.2552225, 0.9001007, -0.3531009 0.9668810, -0.2369948, 0.0947339 0.0015869, -0.3655848, -0.9307767
N3 hyperfine	- , - , ≈ 14 (1.61, 1.78, 17.15)	- (6.8)	- (0.01)	- (0.084)	- (0.090)	0.9043288, 0.1466711, 0.4008453 -0.1021958, 0.9861945, -0.1302938 -0.4144218, 0.0768637, 0.9068333
N4 hyperfine	- , - , ≈ 14 (1.62, 1.79, 17.24)	- (6.8)	- (0.01)	- (0.084)	- (0.090)	0.8404868, 0.3567306, 0.4078299 -0.3552111, 0.9311446, -0.0824301 -0.4091539, -0.0755843, 0.9093295

- a) Rotation matrix **R** from DFT where $\mathbf{A}^{mol} = \mathbf{R}\mathbf{A}^{eig}\mathbf{R}^T$ is the interaction in the molecular frame of the coordinate system given in section S4.
- b) The s-type orbital spin population contribution is given as a_{iso} / s_0 , and the p-type contribution as T / p_0 . Note that $A = a_{iso} + (-T, -T, 2T)$. The coupling constant for an s-type orbital is $s_0 = 2582$ MHz, and for a p-type orbital is $p_0 = 335$ MHz. These values were obtained from the DFT results using the computed spin populations and the corresponding hyperfine couplings.

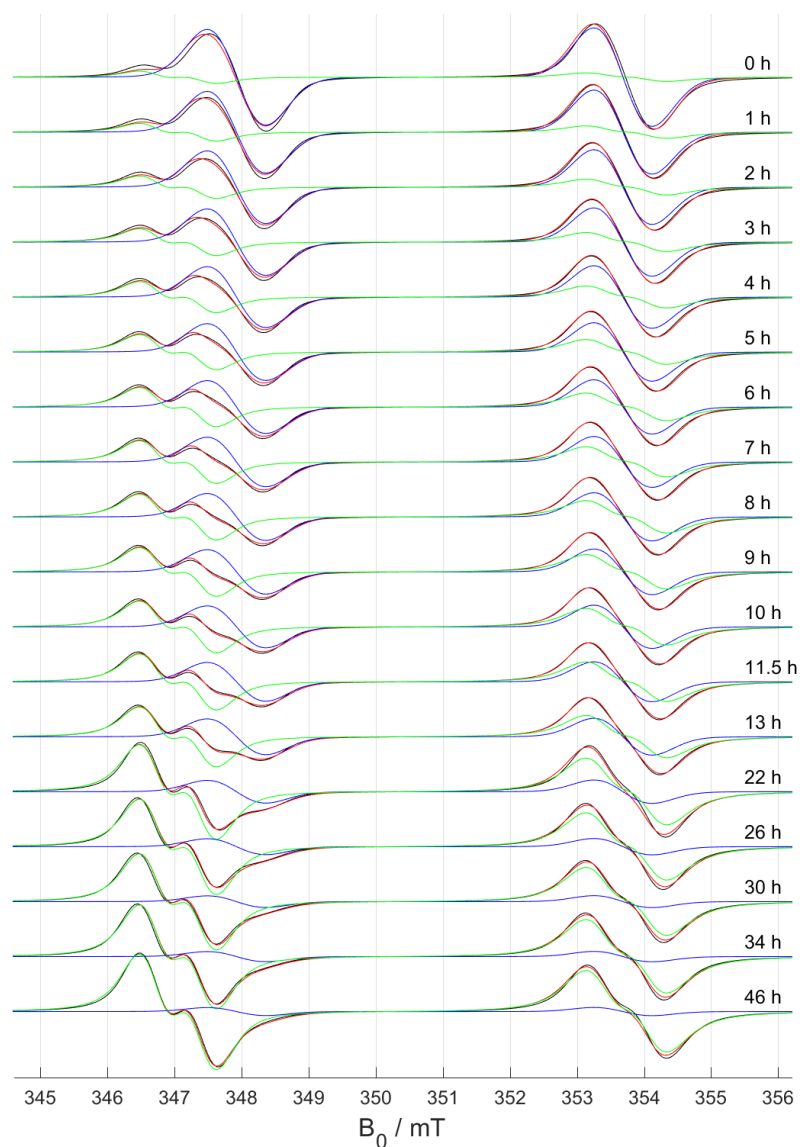


Figure S9. X-band (9.8553 GHz) CW EPR spectra of isolated product in hexane measured at room temperature as a function of time. Top: CW EPR spectra: experimental ‘—’ black, and simulations for **4+5** – blue, **4** – red and **5** – green. The simulation included and isotropic g-value and isotropic ^{31}P hyperfine coupling (see Table S4). Bottom: Signal intensities of component **4** and **5** as a function of time. **4** decays with a time constant of ca. 14 hrs.

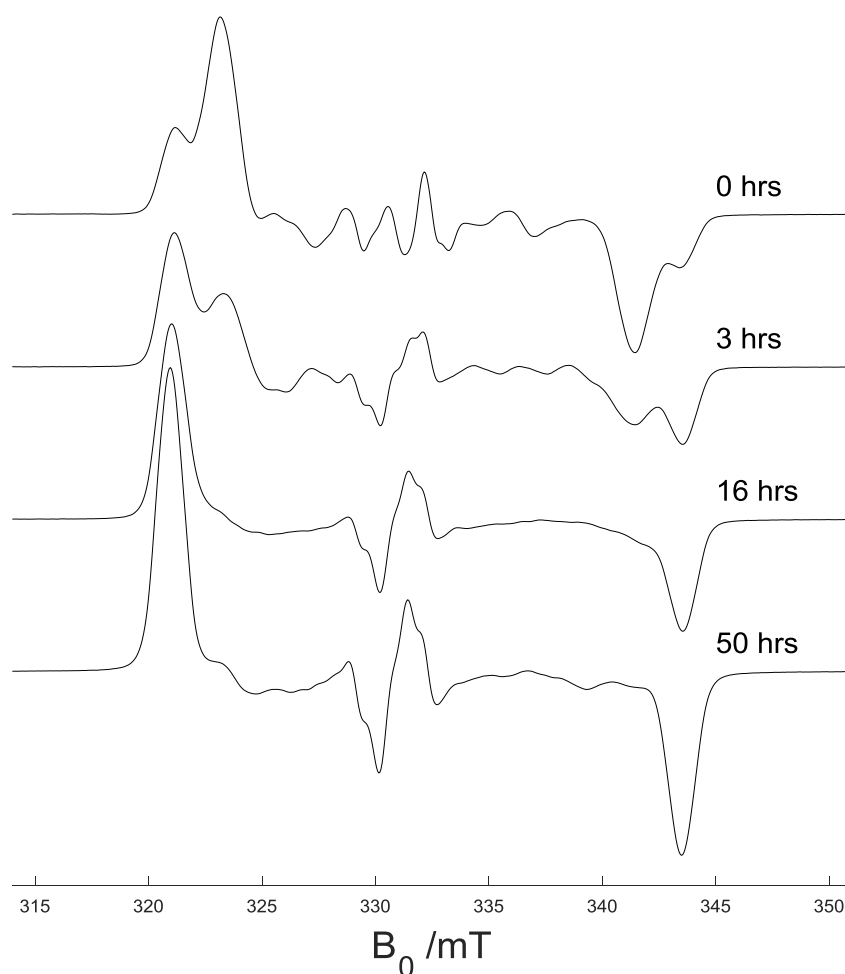


Figure S10. X-band (9.3162 GHz) CW EPR spectra of isolated product in hexane measured at 100K as a function of time. At $t = 0$ hrs the spectrum is a mixture of two components, **4** and **5**, and at 50 hrs it is one component, species **5**.

S4: Theoretical Details

Geometry optimizations were performed using the Gaussian09 optimizer.^[5] All geometry optimizations were computed using the functional BP86^[6] functional in combination with the def2-SVPP basis set.^[7] At each of the optimized structures vibrational analysis was performed to ensure that the geometry corresponds to an energy minimum.

4^M, $E = -1890.8515241$

P	-0.45980900	0.03099400	-0.78773500
P	-2.89228600	0.66798300	0.28130500
P	0.77539200	-0.26033500	1.13552700
N	-1.63047400	3.96363100	0.03337700
N	-3.40948600	-2.82194800	0.02492800
N	4.33495600	-1.62402000	-0.02910500
C	-1.38151600	1.51552500	-0.21733800
C	0.46019700	3.22417300	-0.72273700
C	-1.99130700	-0.80977200	-0.22069000
C	3.61655900	-0.47323000	0.30684400
C	5.77318300	-1.38097900	0.06376600
C	-0.93429300	2.81343300	-0.28400900
C	-2.23786400	-2.15982200	-0.28788300
C	0.35390400	4.74719200	-0.93534100
H	1.29126100	5.28061000	-0.73245900
H	0.05273300	4.96675100	-1.96979400
C	-1.22129900	-3.20274900	-0.71977500
C	-0.77295800	5.14838700	0.02573300
C	-3.24284100	-4.27470300	0.01848800
C	2.31882600	-0.40487700	0.61513500
C	4.58728900	0.70510500	0.28999700
C	-2.06005300	-4.47755200	-0.93776200
H	-1.50584700	-5.40248200	-0.73372100
H	-2.42563700	-4.51944300	-1.97388000
C	5.88271800	0.10589200	-0.29802900
H	5.89296800	0.21926300	-1.39123200
H	6.79082800	0.57345200	0.10363900
H	-3.01395800	-4.65537600	1.03533200
H	-4.16964200	-4.76408500	-0.31880600
H	-0.48476400	-3.34945700	0.08869000
H	6.15668000	-1.57493400	1.08820900
H	6.31772300	-2.04140900	-0.62814200
H	4.74315800	1.05633000	1.32221300
H	-0.38327600	5.36564100	1.04169400
H	-1.34231000	6.02985900	-0.30750700
H	1.17941700	2.98434900	0.07897400
C	3.80467800	-2.94030300	0.25008900
H	3.85592000	-3.19970900	1.32611700
H	2.75091200	-2.97617200	-0.05674600
H	4.36719900	-3.69273600	-0.32027400
C	-4.51771500	-2.22462000	0.73788300
H	-4.34380800	-2.18995900	1.82991300
H	-4.68331700	-1.19685200	0.38704800
H	-5.42984800	-2.80877700	0.54846000

C	-2.88459600	3.98432000	0.75464900
H	-3.53506900	3.17048300	0.40622400
H	-2.74263200	3.86623700	1.84547900
H	-3.39449100	4.94102300	0.57087000
H	4.19761000	1.55205000	-0.28843400
H	-0.66043500	-2.88548700	-1.60996900
H	0.78674000	2.67503700	-1.61688600

6^M, E = -1411.17369086

P	-0.00001400	1.35069600	-0.00081500
P	-0.00011400	-1.35011600	0.00068300
O	0.02378800	2.06578400	-1.32414700
N	3.47801100	-1.02819700	0.01046900
C	2.59085800	-0.00635900	0.01254800
C	1.20604400	-0.07192900	0.01108700
C	3.35134100	1.29992900	0.05254900
C	4.87332400	-0.58215200	0.14714700
C	4.80716100	0.89871400	-0.26046300
H	5.00088300	0.99499000	-1.33789900
H	5.54773200	1.50801400	0.27114100
O	-0.02387900	2.06681700	1.32197600
N	-3.47791300	-1.02819400	-0.01111300
C	-2.59095800	-0.00626700	-0.01260100
C	-1.20612200	-0.07187400	-0.01149800
C	-3.35157700	1.29994700	-0.05149000
C	-4.87347400	-0.58229200	-0.14583500
C	-4.80704000	0.89832700	0.26268300
H	-4.99969100	0.99389800	1.34035200
H	-5.54825900	1.50786300	-0.26776800
H	-3.23596400	1.73824100	-1.05657200
H	-2.91736200	2.02215600	0.65279800
H	-5.21032400	-0.71402900	-1.19046300
H	-5.52721600	-1.18841100	0.49824600
H	3.23483900	1.73776800	1.05773800
H	2.91765300	2.02238200	-0.65179200
H	5.20899000	-0.71446800	1.19209400
H	5.52787800	-1.18782600	-0.49653000
C	-3.10355300	-2.42481200	-0.07424100
H	-2.60704000	-2.66438500	-1.03045300
H	-2.39511800	-2.66433800	0.73448000
H	-3.99928500	-3.04759400	0.03414800
C	3.10411300	-2.42492800	0.07296800
H	2.61417000	-2.66714100	1.03192300
H	2.39028400	-2.66230000	-0.73158600

S5: References

- [1] Z. Li, Y. Hou, Y. Li, A. Hinz, J. R. Harmer, C.-Y. Su, G. Bertrand, H. Grützmacher, *Angew. Chem. Int. Ed.*, 2018, **57**, 198–202; *Angew. Chem.*, 2018, **130**, 204–208.
- [2] F. Neese, *WIREs. Comput. Mol. Sci.* **2012**, *2*, 73–78.
- [3] a) A. Schafer, H. Horn, R. Ahlrichs, *J. Chem. Phys.* **1992**, *97*, 2571–2577; b) F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297–3305.
- [4] a) D. A. Pantazis, X.-Y. Chen, C. R. Landis, F. Neese, *J. Chem. Theory. Comput.* **2008**, *4*, 908–919; b) D. A. Pantazis, F. Neese, *J. Chem. Theory. Comput.* **2009**, *5*, 2229–2238; c) D. A. Pantazis, F. Neese, *J. Chem. Theory. Comput.* **2011**, *7*, 677–684. d) D. A. Pantazis, F. Neese, *Theor. Chem. Acc.* **2012**, *131*, 1292.
- [5] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian 09, Revision C.01. Gaussian, Inc., Wallingford CT, **2009**.
- [6] (a) A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098–3100; (b) J. P. Perdew, *Phys. Rev. B* **1986**, *33*, 8822–8824.

- [7] (a) A. Schäfer, H. Horn, R. Ahlrichs, *J. Chem. Phys.* **1992**, 97, 2571–2577; (b) F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, 7, 3297–3305.