Supporting Information:

Phosphinoamido Ligand Supported Heterobimetallic Rare-Earth Metal-Palldium Complexes: Versatile Structures and Redox Reactivities

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1. NMR Spectroscopic Data

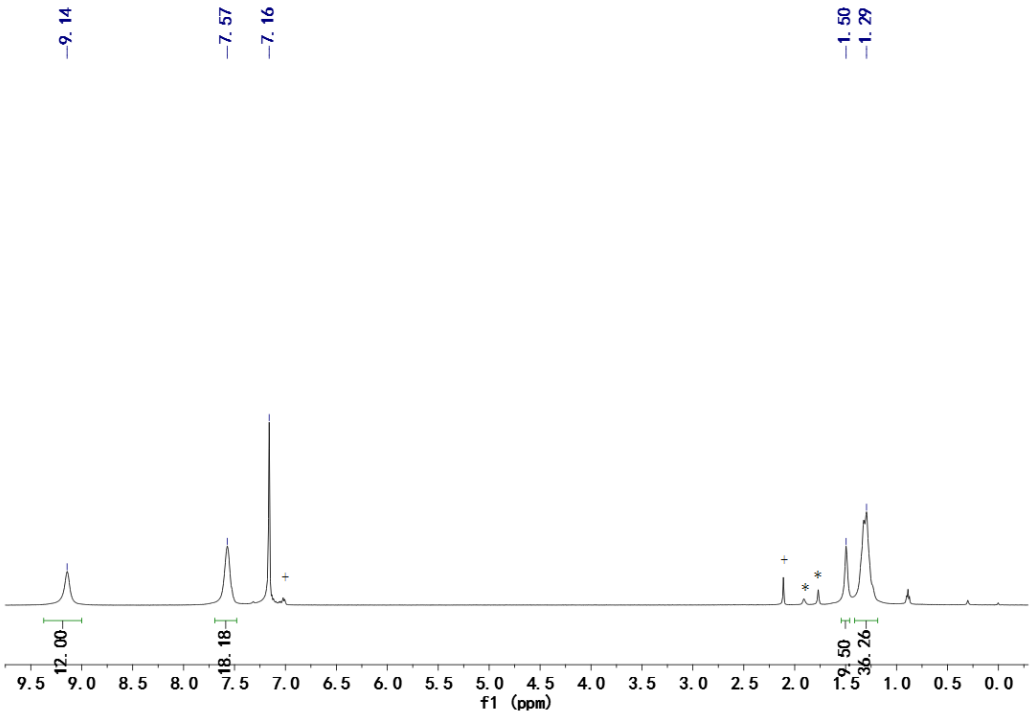

Figure S1. ^{1}H NMR spectrum of **4** in C_6D_6 at 25 °C. (* denotes small amount of free ligand and small amount of toluene)

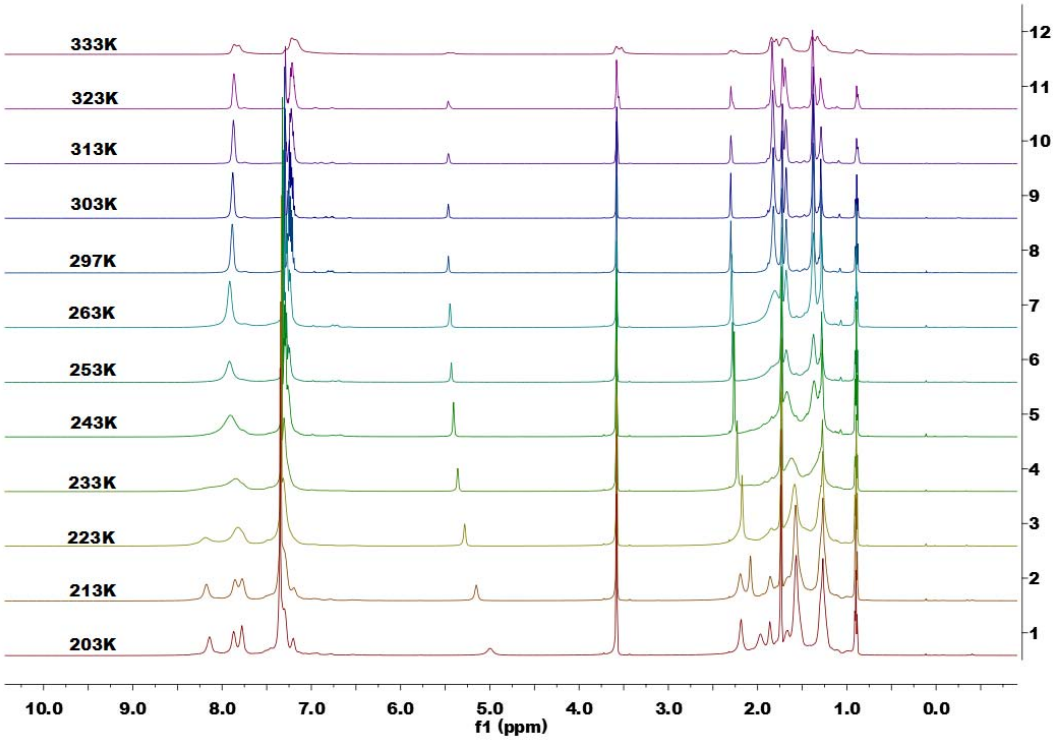

Figure S2. VT-^{1}H NMR spectra of **7** in THF-d_8 at various temperature.

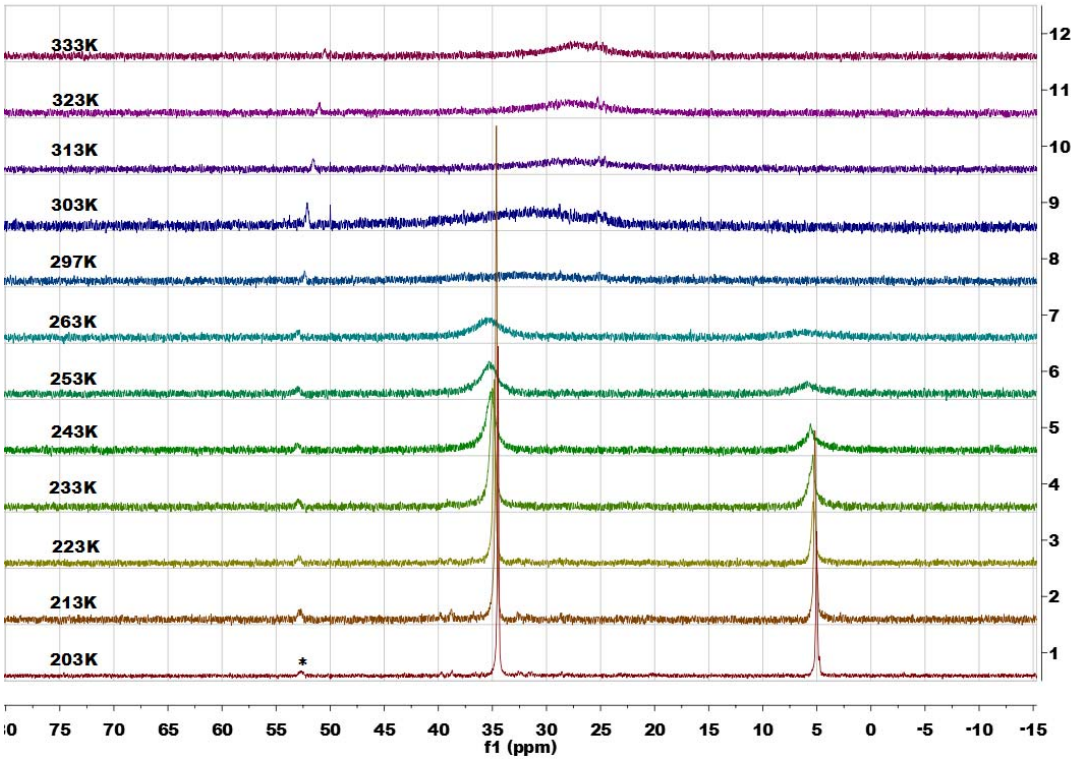

Figure S3. VT-$^{31}P\{^{1}H\}$ NMR spectra of **7** in THF-d_8 at various temperature. (* denotes small amount of impurities)

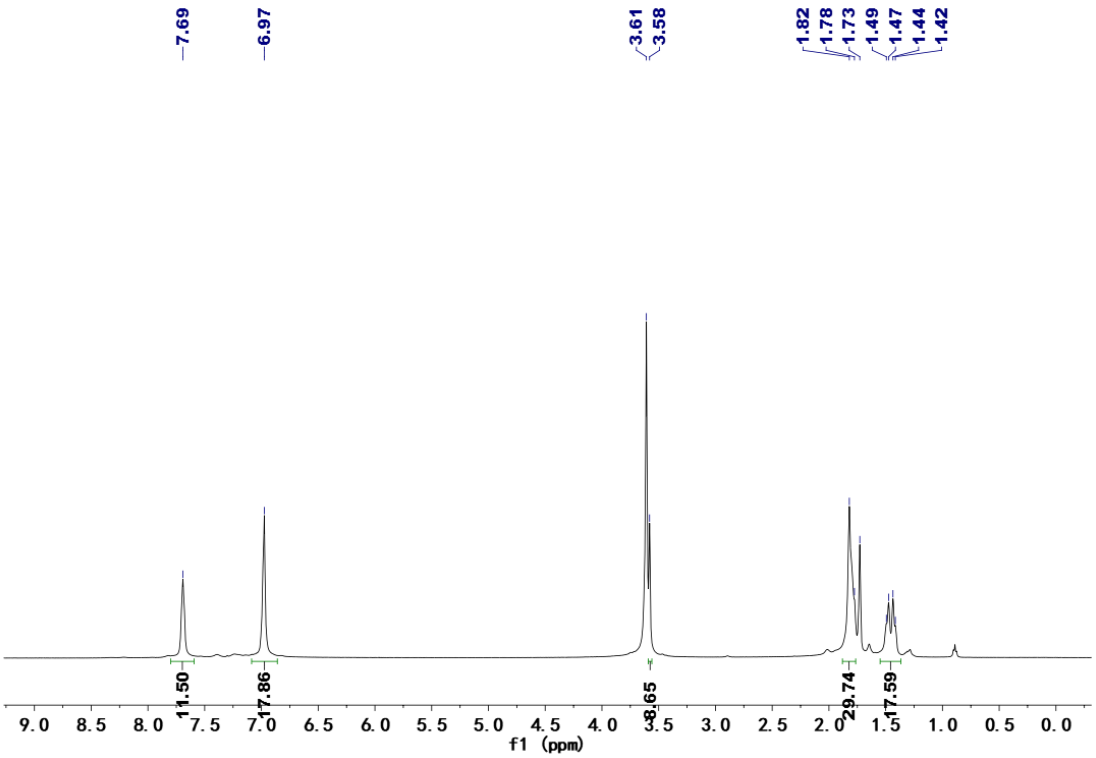

Figure S4. ^{1}H NMR spectrum of **11** in THF-d_8 at 25 °C.

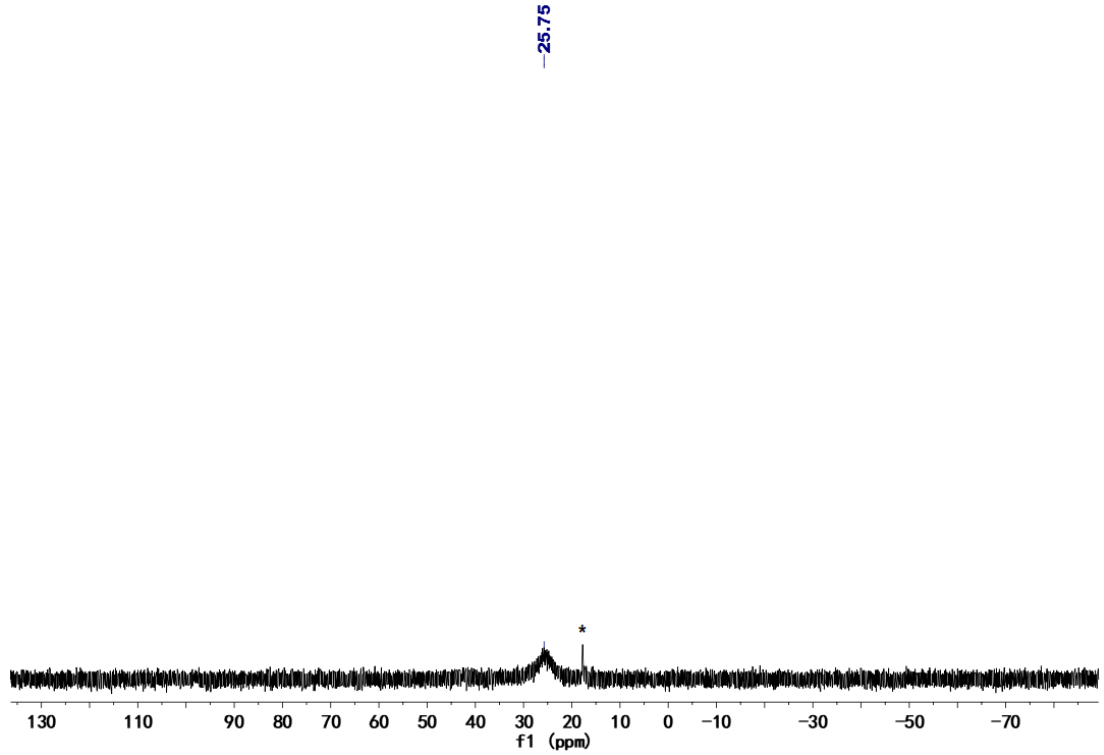

Figure S5. $^{31}P\{^{1}H\}$ NMR spectrum of **11** in THF-d_8 at 25 °C.(* denotes small amount of free ligand)

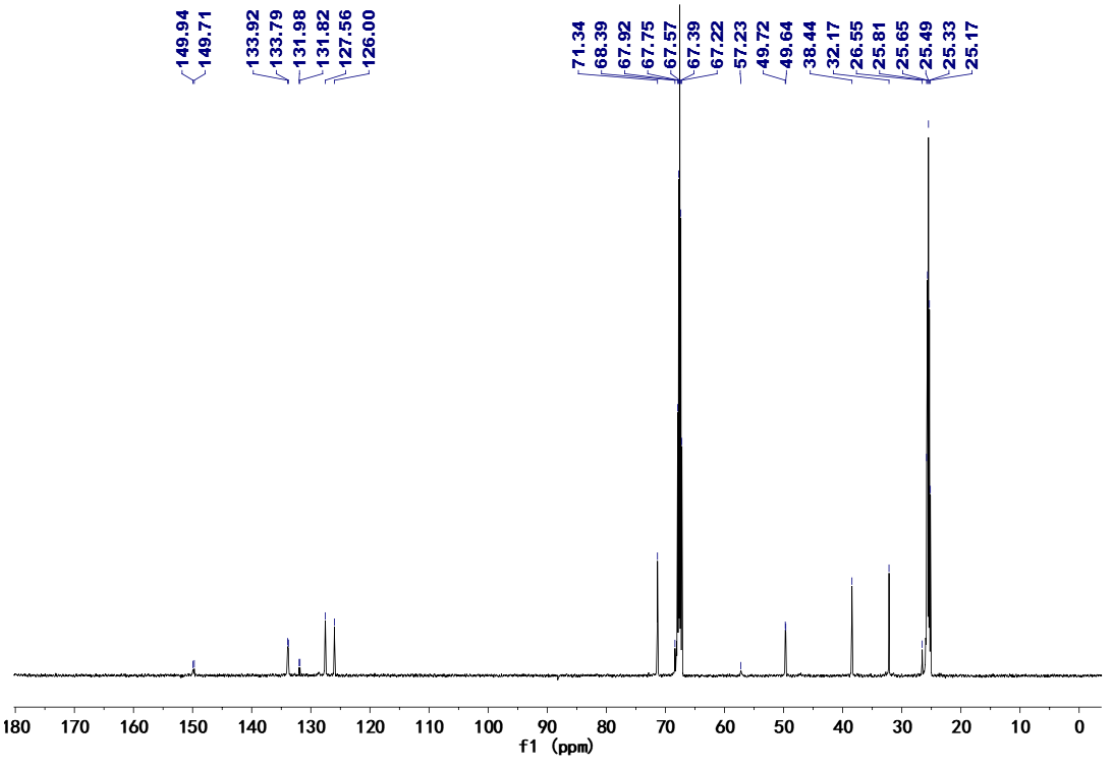

Figure S6. $^{13}C\{^{1}H\}$ NMR spectrum of **11** in THF-d_8 at 25 °C.

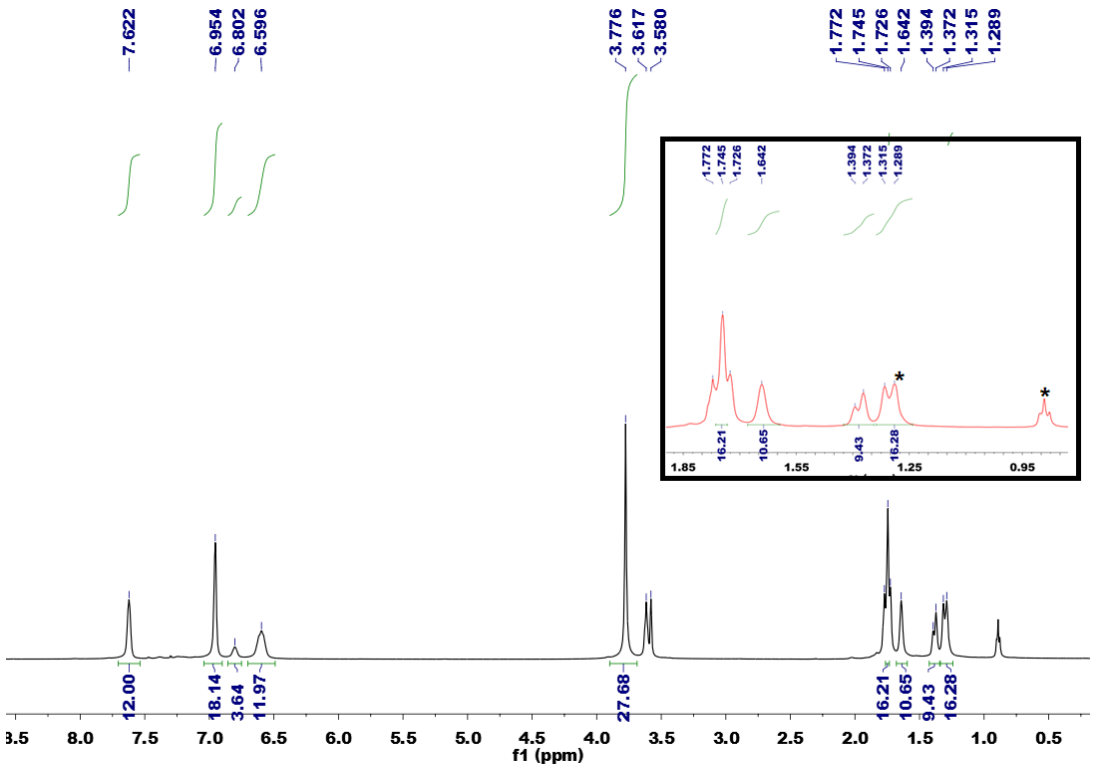

Figure S7. ^{1}H NMR spectrum of **12** in THF-d_8 at 25 °C. (*denotes small amount of *n*-hexane)

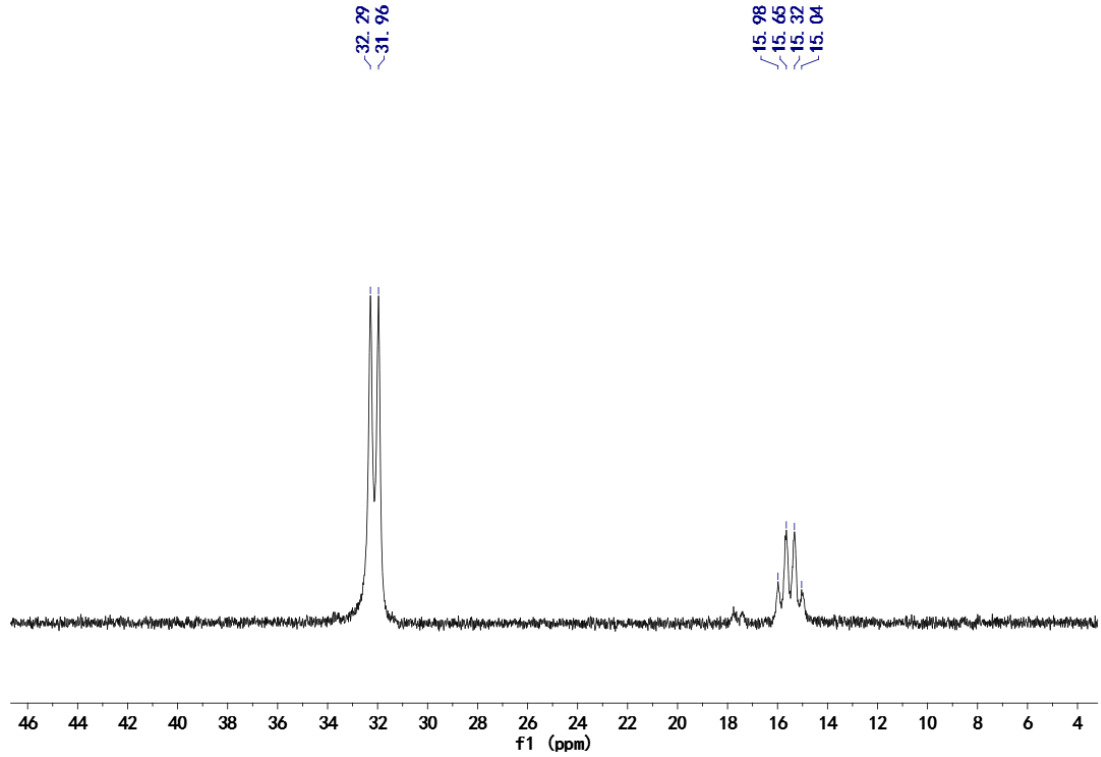

Figure S8. ^{31}P{^{1}H} NMR spectrum of **12** in THF-d_8 at 25 °C.

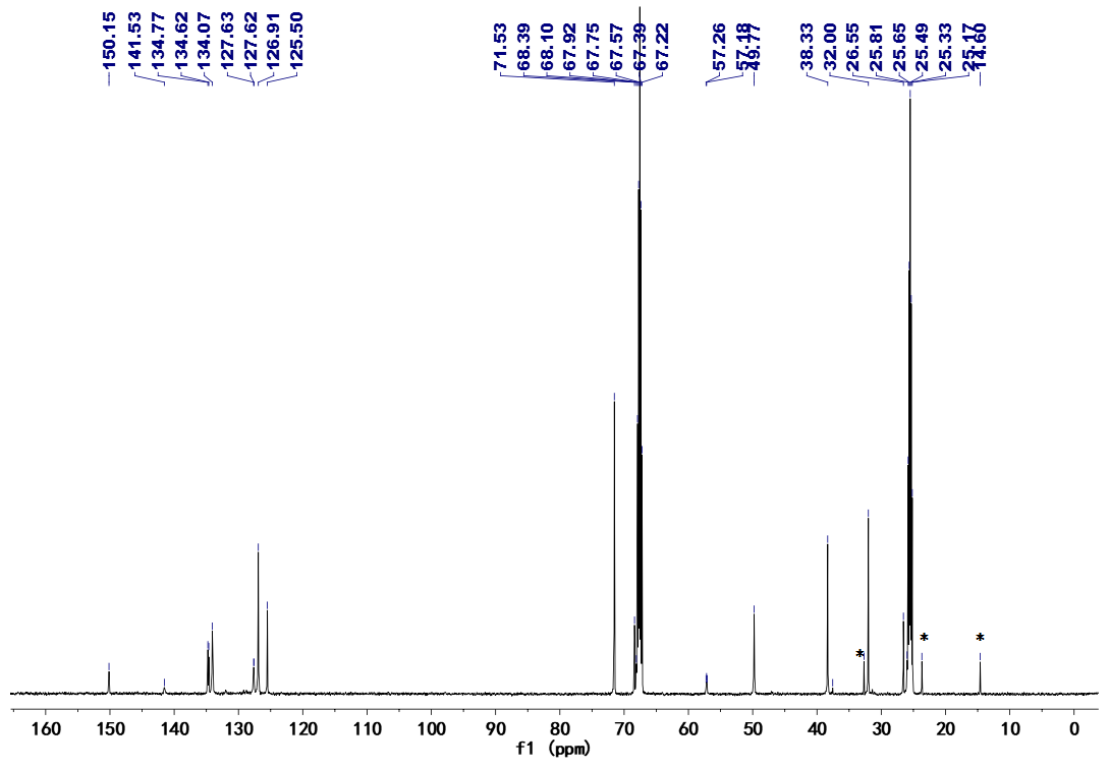

Figure S9. $^{13}C\{^{1}H\}$ NMR spectrum of **12** in THF-d_8 at 25 °C. (*denotes small amount of *n*-hexane)

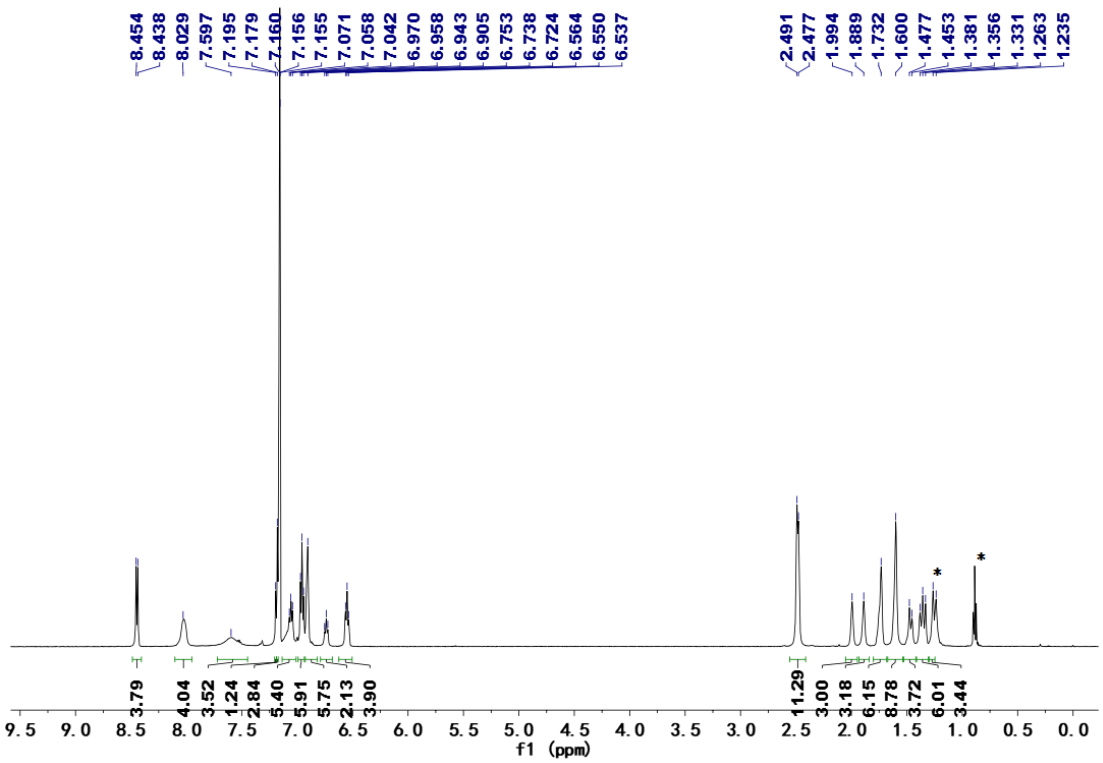

Figure S10. ^{1}H NMR spectrum of **14** in C_6D_6 at 25 °C. (*denotes small amount of *n*-hexane)

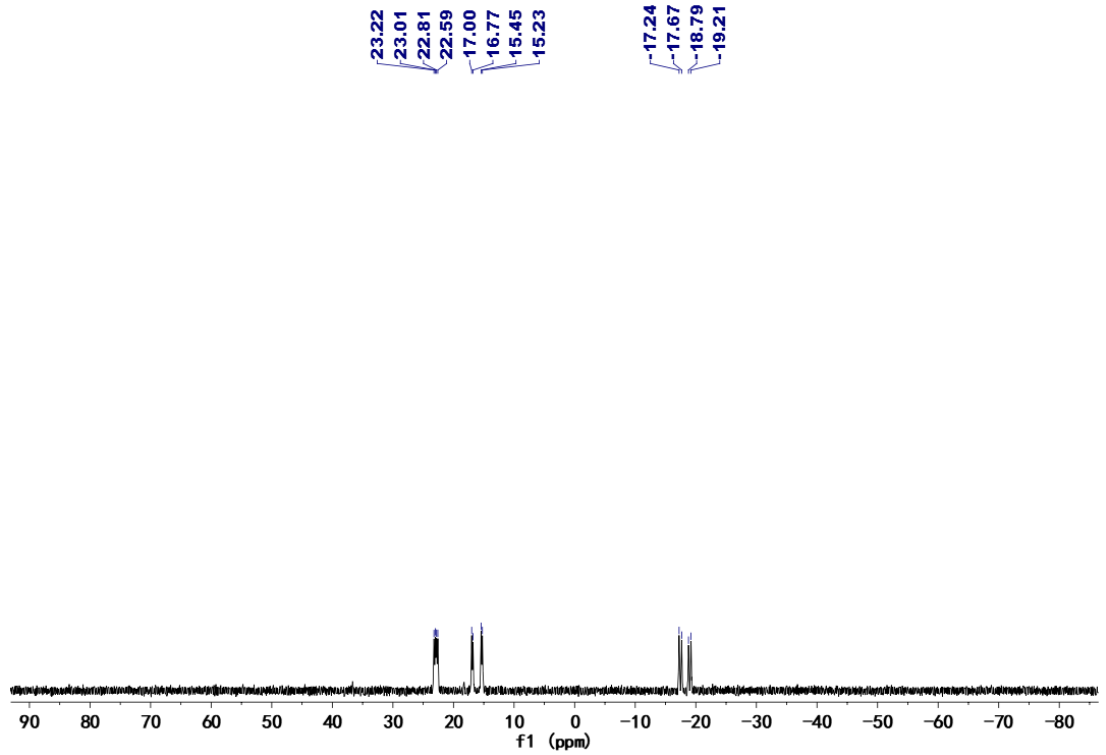

Figure S11. $^{31}P\{^{1}H\}$ NMR spectrum of **14** in C_6D_6 at 25 °C.

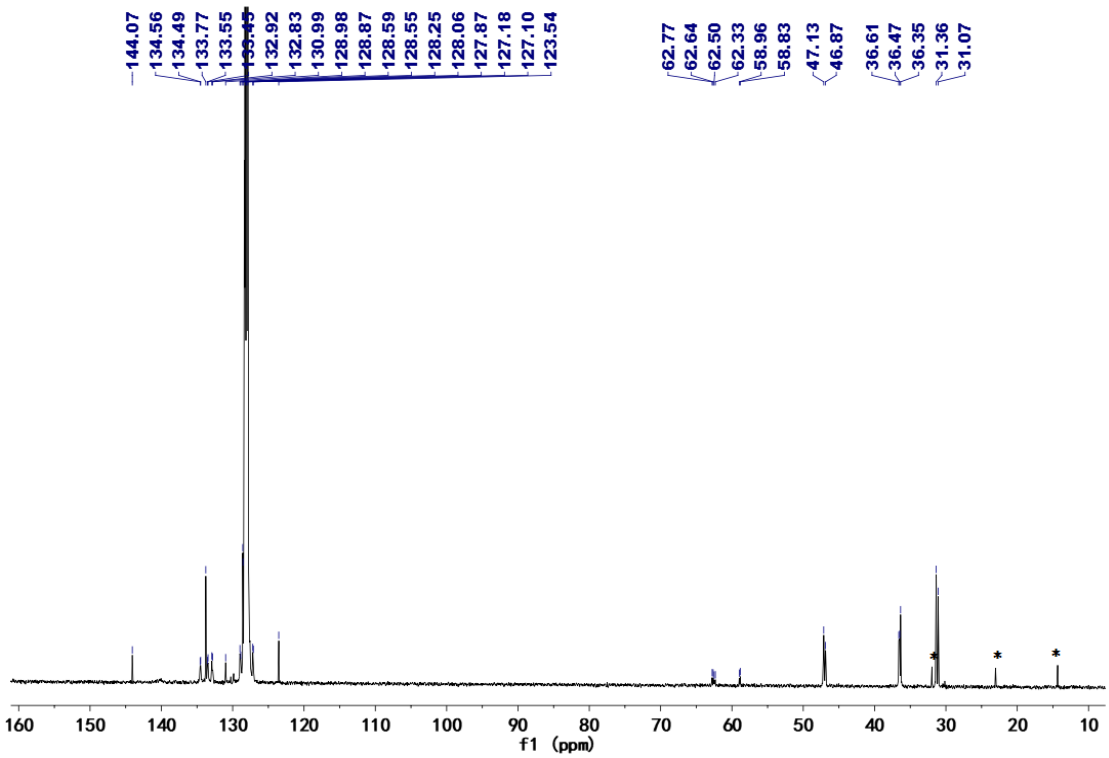

Figure S12. $^{13}C\{^{1}H\}$ NMR spectrum of **14** in C_6D_6 at 25 °C. (*denotes small amount of *n*-hexane)

2. X-ray Crystallography

X-ray Crystallography. Data were collected on a Bruker CCD area-detector diffractometer with Mo Kα radiation (graphite monochromator, λ = 0.71073 Å) using ω scans. The SMART program package was used for the data collection and unit cell determination; processing of the raw frame data was performed using SAINT; absorption corrections were applied with SADABS. The structures were solved by direct methods and refined against F^2 using all reflections with the SHELXL-97 software as implemented in the program WinGX. Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were placed in calculated positions. Crystal parameters and refinement results are given in **Table S1-S2**.

Table S1. Crystallographic and Refinement Data [a,b] for **5-9.**

	5	**6**	**7**	**8**	**9**
formula	$C_{66}H_{75}GdN_3P_3{\cdot}C_6H_6$	$C_{66}H_{75}N_3P_3PdSc$	$C_{140}H_{162}N_6P_6Pd_2Y_2$	$C_{140}H_{162}N_6P_6Pd_2Sm_2$	$C_{140}H_{162}Gd_2N_6P_6Pd_2$
Fw, g·mol^{-1}	1238.55	1154.57	2505.19	2628.07	2641.87
cryst size, mm	0.22 x 0.21 x 0.2	0.22 x 0.21 x 0.2	0.18 x 0.16 x 0.15	0.21 x 0.18 x 0.16	0.15 x 0.13 x 0.12
cryst. syst.	Monoclinic	cubic	triclinic	triclinic	triclinic
space group	P 1 21/n 1	P a -3	P -1	P -1	P -1
T, K	273.15	293.15	300.00	300.00	300.00
a, Å	13.570(3)	23.4731(4)	13.8280(5)	13.8708(10)	13.8494(7)
b, Å	38.373(8)	23.4731(4)	13.9082(6)	13.9163(10)	13.9163(8)
c, Å	13.783(3)	23.4731(4)	21.5268(9)	21.5197(16)	21.5292(12)
α, °	90	90	76.694(2)	76.465(2)	76.576(2)
β, °	97.79(3)	90	76.480(2)	76.104(2)	76.284(2)
γ, °	90	90	61.7760(10)	61.998(2)	61.892(2)
V, Å^3	7111(3)	12933.4(7)	3512.0(3)	3524.5(4)	3520.3(3)
Z	4	8	1	1	1
D_{calcd}, Kg·m^{-3}	1.157	1.186	1.184	1.238	1.246
F(000)	2572	4832	1304	1350	1354
μ, mm^{-1}	1.039	0.496	1.185	1.186	1.296
θ range /°	2.901 - 27.531	1.503-24.995	2.943- 27.806	2.847-27.636	2.941-27.544
refns collected	182238	90202	257948	77213	87034
indep reflns (R_{int})	16291 (0.0688)	3813 (0.1761)	16278 (0.0413)	16114 (0.0571)	16136 (0.0435)
reflns obsd [$I > 2\sigma(I)$]	12879	2155	14002	13022	13858
data/restrnts/params	16291 / 1674 / 700	3813 / 2420 / 393	16278/1704/703	16114/1698/703	16136/1698/703
*R*1, *wR*2 ($I > 2\sigma(I)$)	0.0494, 0.1196	0.0635, 0.1594	0.0420, 0.0979	0.0610, 0.1562	0.0519, 0.1160
*R*1, *wR*2 (all data)	0.0652,0.1263	0.1192, 0.2000	0.0538, 0.1093	0.0759, 0.1654	0.0632, 0.1218
GOF on F2	1.020	1.056	1.062	1.039	1.129
$\Delta\rho_{max, min}$, e·Å^{-3}	0.688, -1.006	0.485, -0.354	1.044, -0.826	1.284, -1.002	1.697, -1.369

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = \{\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2\}^{1/2}$.

Table S2. Crystallographic and Refinement Data [a,b] for **10, 11, 12, 14** and **15.**

	10	**11**	**12**	**14**	**15**
formula	$C_{140}H_{162}N_6P_6Pd_2Yb_2 \cdot C_6H_6$	$C_{86}H_{115}KN_3O_8P_3Yb$	$2(C_{84}H_{90}N_3P_4PdYb) \cdot 4(C_{10}H_{20}K_{0.5}O_4)$	$C_{78}H_{85}N_3P_3PdS_2Sc$	$C_{78}H_{85}N_3P_3PdS_2Yb \cdot 0.5(C_7H_8)$
Fw, g·mol^{-1}	2751.55	1623.85	3985.04	1372.88	1500.96
cryst size, mm	0.22 x 0.21 x 0.20	0.12 x 0.11 x 0.1	0.22 x 0.21 x 0.2	0.22 x 0.21 x 0.2	0.12 x 0.11 x 0.1
cryst. syst.	triclinic	Monoclinic	triclinic	Monoclinic	Monoclinic
space group	P -1	P 1 21/c 1	P -1	P 1 21/c 1	P 1 21/c 1
T, K	300.00	300.00	293.00	300.00	293.15
a, Å	16.16(10)	13.595(4)	15.94(3)	14.5833(14)	14.5010(8)
b, Å	19.85(10)	26.411(7)	25.30(5)	20.841(2)	20.8293(11)
c, Å	23.51(11)	26.469(7)	28.99(5)	24.931(3)	24.8710(14)
α, °	102.38(8)	90	95.28(8)	90	90
β, °	97.83(8)	100.664(4)	105.02(11)	94.704(4)	95.3790(10)
γ, °	90.57(19)	90	91.01(9)	90	90
V, Å^3	7288(67)	9340(4)	11233(34)	7551.8(14)	7479.1(7)
Z	2	4	2	4	4
D_{calcd}, Kg·m^{-3}	1.254	1.155	1.178	1.208	1.333
F(000)	2816	3400	4136	2872	3068
μ, mm^{-1}	1.627	1.146	1.130	0.489	1.645
θ range /°	2.795-27.318	1.524-25.000	2.844-28.681	2.845-27.567	1.410-27.488
refns collected	144945	64432	259815	167852	65130
indep reflns (R_{int})	32258 (0.0836)	16409(0.0963)	55260(0.0772)	17369(0.1044)	17061(0.0670)
reflns obsd [$I > 2\sigma(I)$]	19922	11113	32754	12607	11277
data/restrnts/params	32258/3487/1435	16409 /917/1104	55260/8291/2424	17369/1854/793	17061/793/0
*R*1, *wR*2 ($I > 2\sigma(I)$)	0.0973, 0.2588	0.1104, 0.2723	0.0723, 0.1715	0.0749, 0.1842	0.0385, 0.0708
*R*1, *wR*2 (all data)	0.1450, 0.3018	0.1499, 0.2993	0.1337, 0.2151	0.1027, 0.2043	0.0776, 0.0811
GOF on F2	1.040	1.177	1.021	1.034	1.016
$\Delta\rho_{max, min}$, e·Å^{-3}	8.687, -2.462	3.378, -1.744	3.626, -1.842	0.921, -0.646	1.002, -1.034

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = \{\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2\}^{1/2}$.

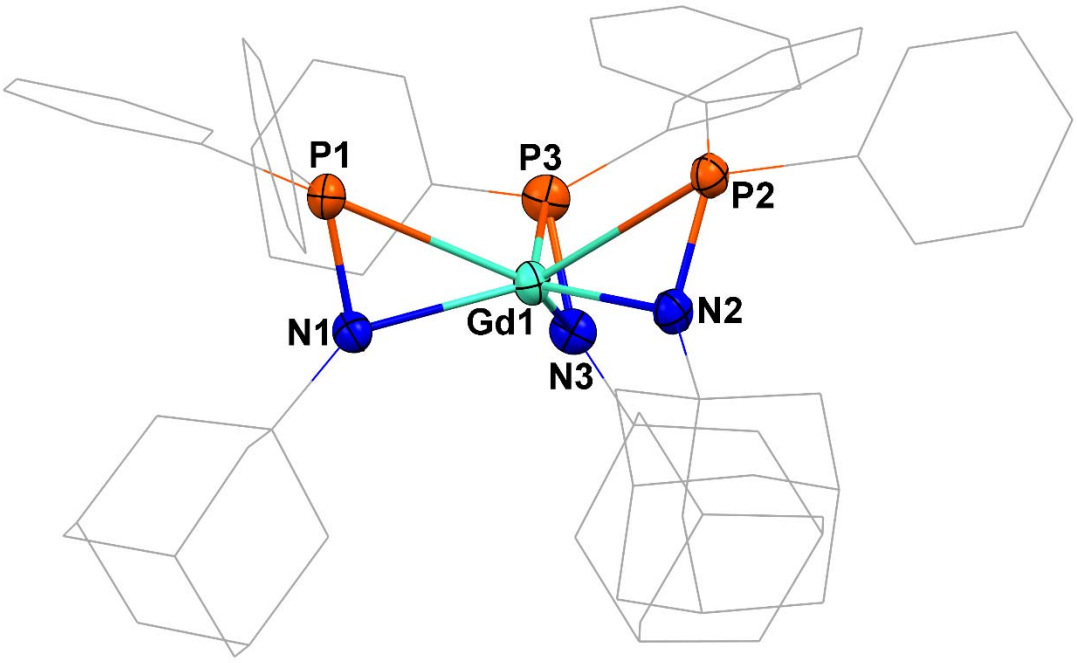

Fig. S13. Molecular structure of **5**. Hydrogen atoms and co-crystallized solvent molecule was omitted for clarity.

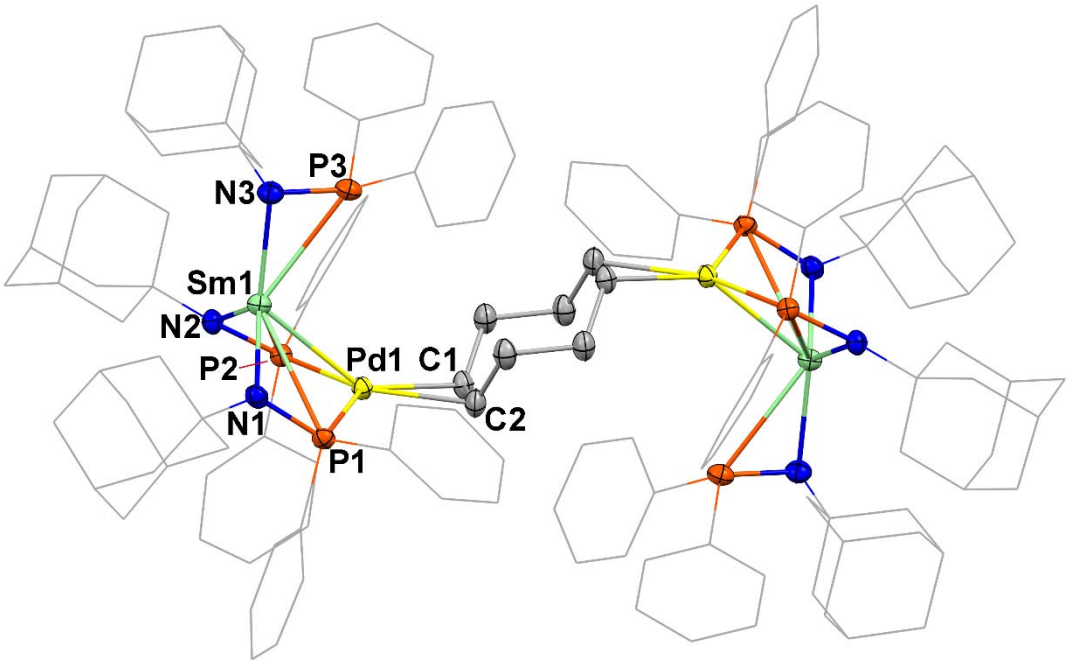

Fig. S14. Molecular structure of **8**. Hydrogen atoms were omitted for clarity.

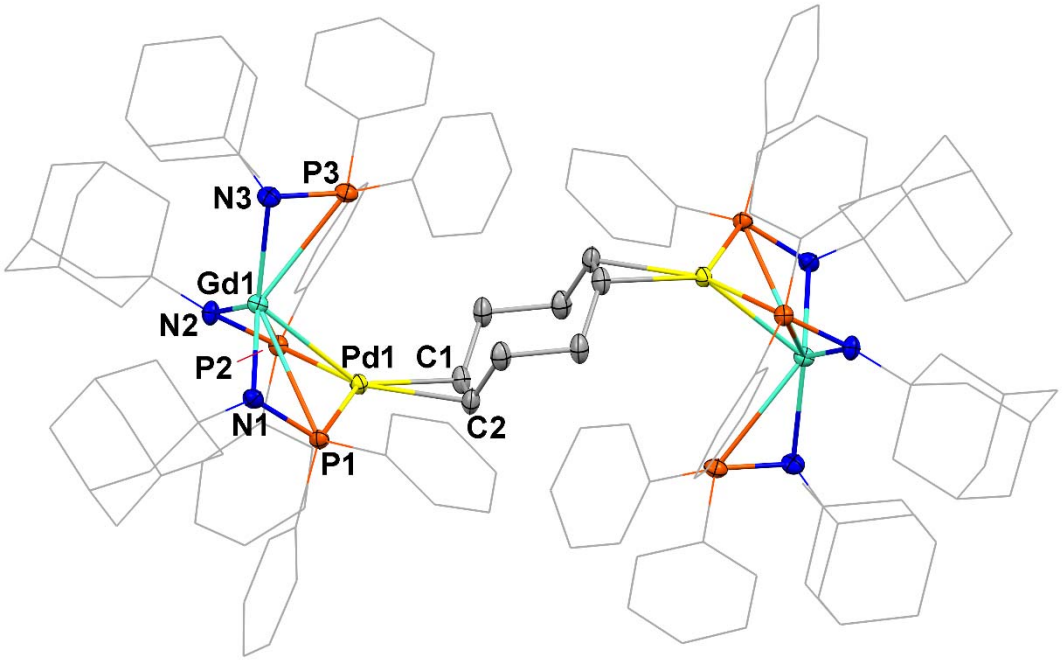

Fig. S15. Molecular structure of **9**. Hydrogen atoms were omitted for clarity.

3. Computational Results

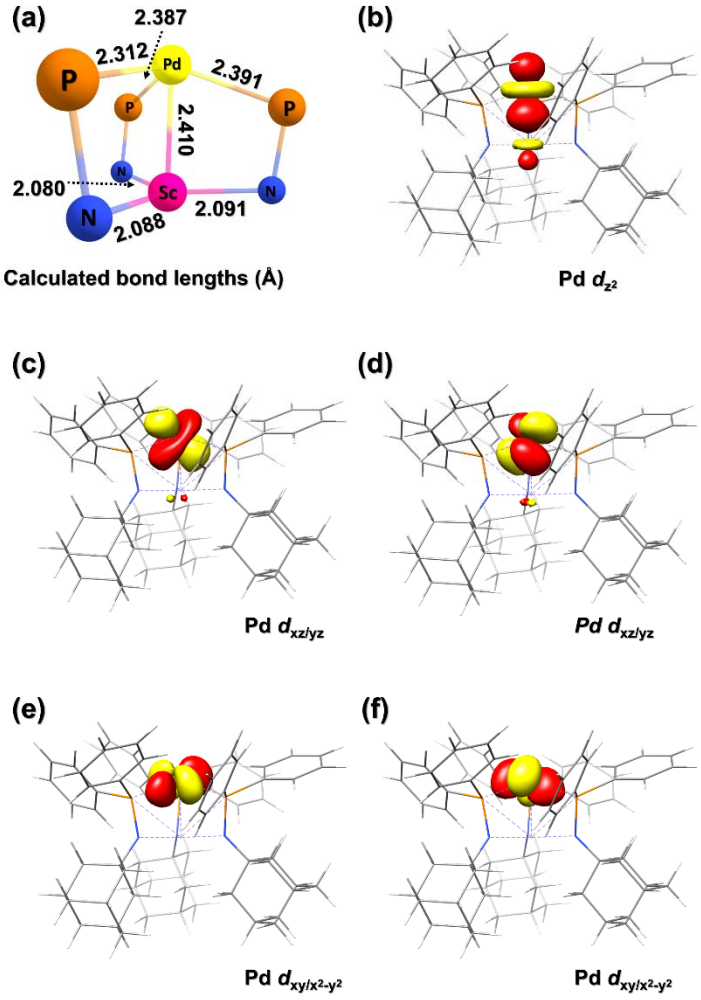

Fig. S16. Calculated bond lengths in the primary coordination sphere in **6** (a) and the localized *d* orbitals of Pd(0) centre (b-f).