Transition metal-induced dehydrogenative coupling of zinc hydrides

Min Chen[1,†], Shengjie Jiang[1,†], Laurent Maron[2,*] and Xin Xu[1,*]

[1]*Key Laboratory of Organic Synthesis of Jiangsu Province, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, P. R. China;* [2] *LPCNO, CNRS & INSA, Université Paul Sabatier, 135 Avenue de Rangueil, 31077 Toulouse, France*

* laurent.maron@irsamc.ups-tlse.fr (L.M.); xinxu@suda.edu.cn (X.X.)

† These authors contributed equally to this work.

Supporting Information

General Procedures: All experiments were carried out under a dry Argon atmosphere using standard Schlenk techniques or in a glovebox. Solvents (including deuterated solvents used for NMR) were dried with Na and distilled under a dry nitrogen atmosphere prior to use. NMR spectra were recorded on a Bruker 400 MHz spectrometer. Chemical shifts were reported as δ units with reference to the residual solvent resonance or an external standard. The assignments of NMR data were supported by 1D and 2D NMR experiments. Elemental analysis data was recorded on a Carlo-Erba EA-1110 instrument. High resolution mass spectrometry were measured with a BRUKER micrOTF-Q III. Detection of H_2 using gas chromatography was recorded on an Agilent 7890B. Fourier transform infrared spectroscopy were measured with a Bruker VERTEX70. 2,6-Diisopropylphenol, $Ni(COD)_2$, and $Pd(PPh_3)_4$ were purchased from Strem. $ZnEt_2$ and $PhSiH_3$ were purchased from Adamas. Ligand precursors **HL** [**L** = $CH_3C(2,6\text{-}^iPr_2C_6H_3N)CHC(CH_3)NCH_2(CH_2)_nPPh_2$, **L^a**: n = 1; **L^b**: n = 2) were synthesized using a modified literature procedure.[1]

Computational details: Electronic structure calculations of the reaction mechanism proposed were carried out using Density Functional Theory (DFT). The calculations were carried out with the Gaussian09 software[2] at the DFT level using the hybrid functional B3PW91.[3] The zinc, palladium and nickel atom were treated with the small core pseudopotential from Stuttgart's Institute for Theoretical Chemistry,[4] while the sulfur, oxygen, nitrogen, carbon and hydrogen atoms were treated with the all electron 6-31G** Pople basis set.[5] The geometry optimizations (both from the minima and the transition states) were performed without any symmetry constraints. The GD3BJ,[6] scheme that includes dispersion effects according to the Grimme's D3 approach using the Becke_Johnson scheme was used. Natural population analysis (NPA) was performed using Weinhold's methodology.[7] Finally, Chemcraft is used for the visualization of the molecular orbitals.[8] Analytical calculations of the vibrational frequencies of the optimized geometry were done to confirm the minima and transition states obtained. Intrinsic reaction coordinate calculations were carried out to confirm that the transition states correspond to the ones that connect the intermediates obtained.

References

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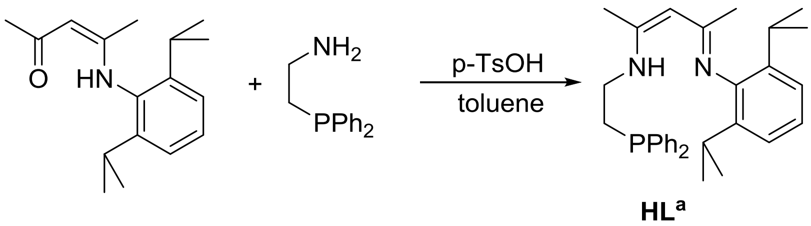
[8] www.chemcraftprog.com

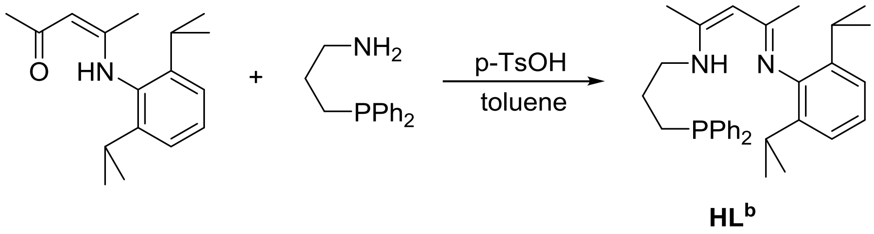
Preparation of HL[a]:



Scheme S1.

2-((2,6-Diisopropylphenyl)imido)-2-penten-4-one (7.78 g, 30.0 mmol), 2-(diphenylphosphino)ethanamine (6.87 g, 30.0 mmol) and a catalytic amount of *p*-toluenesulfonic acid (0.52 g, 3.0 mmol) were mixed in toluene (90 mL) and heated at reflux for 48 h. The water produced during the reaction was removed using a Dean-Stark trap. After the reaction was complete, the volatiles were removed under vacuum and the residue was recrystallized in methanol at -25 ^{o}C to afford **HL[a]** as a yellow crystalline solid (9.18 g, 65%).

Preparation of HL^b:



Scheme S2.

Following the procedure described for **HL^a**, reaction of 2-((2,6-diisopropylphenyl)imido)-2-penten-4-one (2.13 g, 8.2 mmol), 3-(diphenylphosphino)propylamine (1.99 g, 8.2 mmol) and a catalytic amount of *p*-toluenesulfonic acid (0.14 g, 0.8 mmol) gave **HL^b** as a pale yellow solid (2.38 g, 60%).

HRMS (ESI) m/z calcd. for $C_{32}H_{42}N_2P$ $[M + H]^+$: 485.3080; found: 485.3085.

^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 11.14 (br s, 1H, N*H*), 7.36 (m, 4H, *o-Ph*$_2$P), 7.21 (m, 2H, *m*-N*Ar*), 7.13 (m, 1H, *p*-N*Ar*), 7.04 (m, 6H, *m, p-Ph*$_2$P), 4.69 (s, 1H, MeC(N)C*H*), 3.14 (sp, $^3J_{HH}$ = 6.9 Hz, 2H, ArC*H*Me$_2$), 2.92 (m, 2H, NC*H*$_2$), 2.00 (m, 2H, PC*H*$_2$), 1.67 (s, 3H, *Me*C), 1.61 (s, 3H, *Me*C), 1.58 (m, 2H, NCH$_2$C*H*$_2$), 1.21 (d, $^3J_{HH}$ = 6.9 Hz, 6H, ArCH*Me*$_2$), 1.16 (d, $^3J_{HH}$ = 6.9 Hz, 6H, ArCH*Me*$_2$).

^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 298 K): δ = 166.7 (Me*C*), 155.6 (Me*C*), 147.6 (*i*-N*Ar*), 139.2 (d, $^1J_{PC}$ = 14.3 Hz, *i-Ph*$_2$P), 138.4 (*o*-N*Ar*), 133.1 (d, $^2J_{PC}$ = 18.6 Hz, *o-Ph*$_2$P), 128.8 (d, $^3J_{PC}$ = 6.5 Hz, *m-Ph*$_2$P), 128.7 (*p-Ph*$_2$P), 123.4 (*p*-N*Ar*), 123.3 (*m*-N*Ar*), 93.9 (MeC(N)*C*H), 44.0 (d, $^3J_{PC}$ = 13.9 Hz, NH*C*H$_2$), 28.6 (Ar*C*HMe$_2$), 27.5 (d, $^2J_{PC}$ = 16.8 Hz, NCH$_2$*C*H$_2$), 25.8 (d, $^1J_{PC}$ = 13.2 Hz, P*C*H$_2$), 24.3 (ArCH*Me*$_2$), 23.1 (ArCH*Me*$_2$), 21.8 (*Me*C), 19.2 (*Me*C).

^{31}P{^{1}H} NMR (162 MHz, C_6D_6, 298 K): δ = -16.6.

^{1}H, ^{1}H GCOSY (400 MHz / 400 MHz, C_6D_6, 298 K) [selected traces]: δ ^{1}H / δ ^{1}H = 11.14 / 2.92 (N*H* / NHC*H*$_2$), 7.36 / 7.04 (*o-Ph*$_2$P / *m-Ph*$_2$P), 7.21 / 7.13 (*m*-N*Ar* / *p*-N*Ar*), 3.14 / 1.16, 1.20 (ArC*H*Me$_2$ / ArCH*Me*$_2$, ArCH*Me*$_2$), 2.92 / 1.58 (NC*H*$_2$ / NCH$_2$C*H*$_2$), 2.00 / 1.58 (PC*H*$_2$ / NCH$_2$C*H*$_2$).

^{1}H, ^{13}C GHSQC (400 MHz / 101 MHz, C_6D_6, 298 K): δ ^{1}H / δ ^{13}C = 7.36 / 133.1 (*o-Ph*$_2$P), 7.21 / 123.3 (*m*-N*Ar*), 7.13 / 123.4 (*p*-N*Ar*), 7.04 / 128.8, 128.7 (*m-Ph*$_2$P, *p*-*Ph*$_2$P), 4.69 / 93.9 (MeC(N)*CH*), 3.14 / 28.6 (Ar*CH*Me$_2$), 2.92 / 44.0 (N*CH*$_2$), 2.00 / 25.8 (P*CH*$_2$), 1.67 / 21.8 (*Me*C), 1.61 / 19.2 (*Me*C), 1.58 / 27.5 (NCH$_2$*CH*$_2$), 1.21 / 23.1 (ArCH*Me*$_2$), 1.16 / 24.3 (ArCH*Me*$_2$).

^{1}H, ^{13}C GHMBC (400 MHz / 101 MHz, C_6D_6, 298 K) [selected traces]: δ ^{1}H / δ ^{13}C = 7.36 / 128.7 (*o*-*Ph*$_2$P / *p*-*Ph*$_2$P), 7.21 / 147.6 (*m*-N*Ar* / *i*-N*Ar*), 7.13 / 138.4 (*p*-N*Ar* / *o*-N*Ar*), 2.92 / 155.6 (NC*H*$_2$ / Me*C*(NCH$_2$), 2.00 / 139.2 (PC*H*$_2$ / *i*-*Ph*$_2$P).

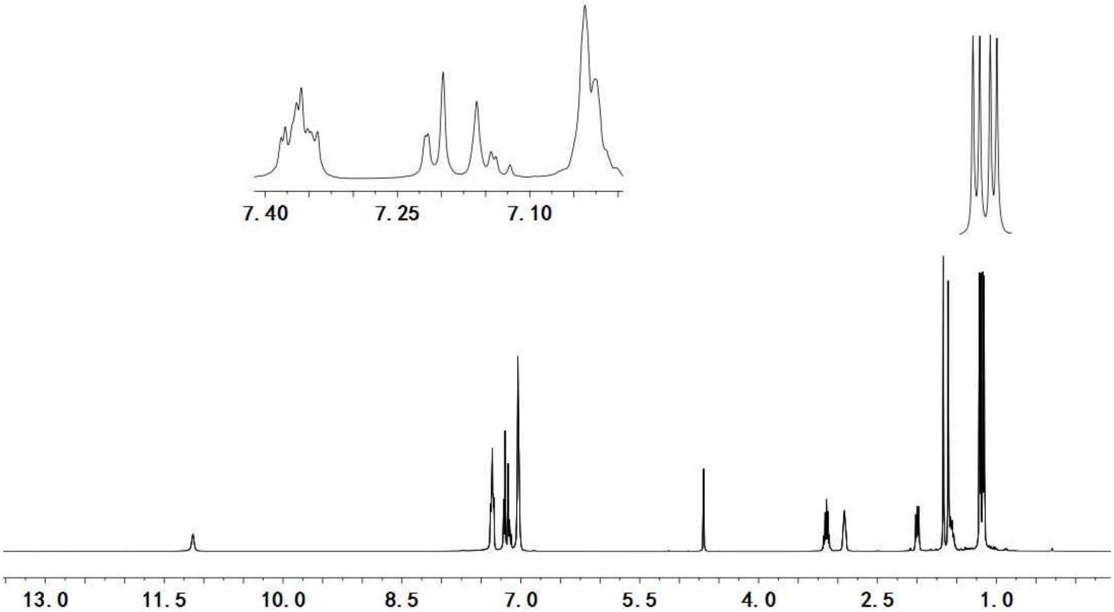


Fig. S1. ^{1}H NMR (400 MHz, C_6D_6, 298 K)

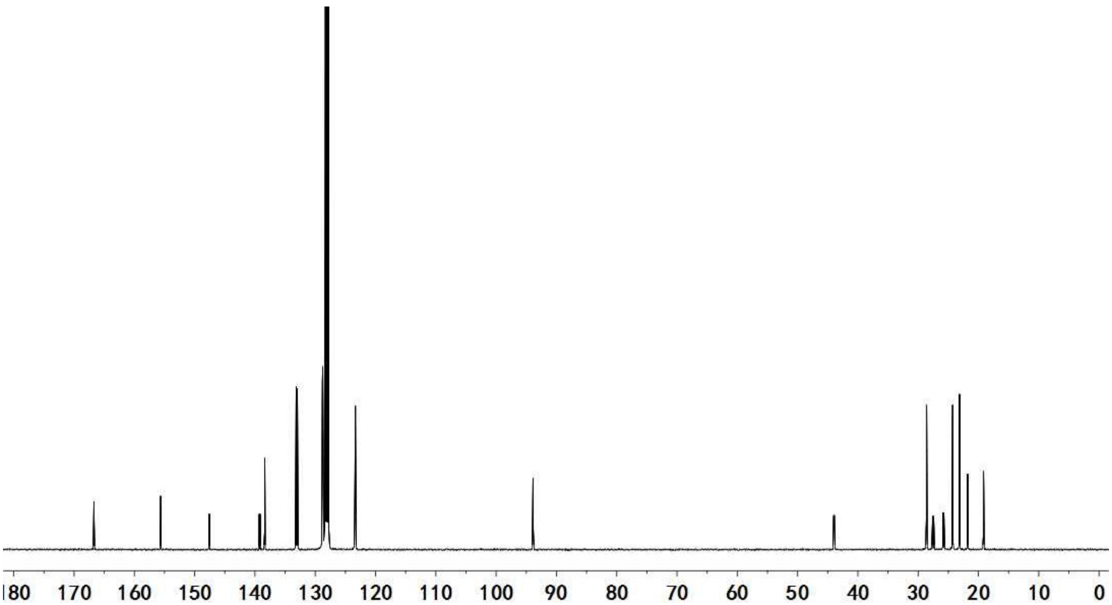


Fig. S2. ^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 298 K)

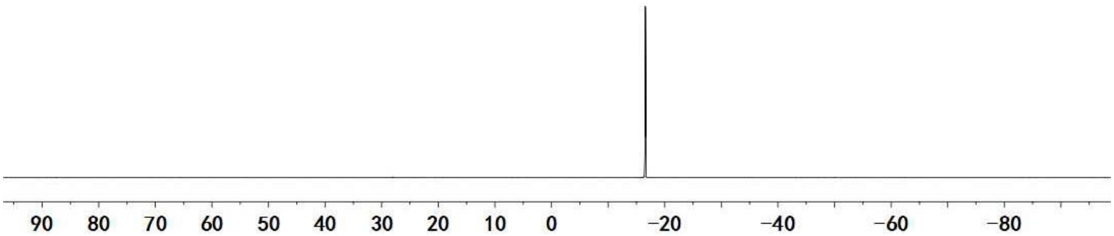
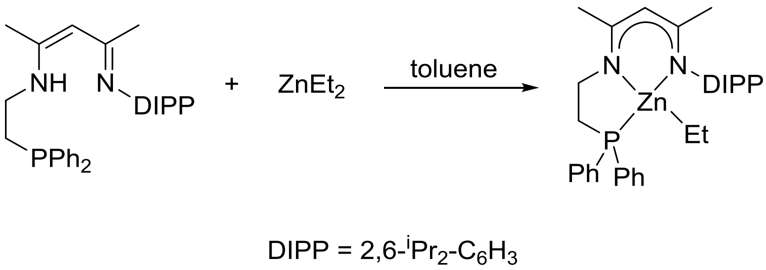


Fig. S3. ^{31}P{^{1}H} NMR (162 MHz, C_6D_6, 298 K)

Preparation of complex 1a:



HL[a] **1a**

Scheme S3.

$ZnEt_2$ (4.7 mL, 1.0 M in n-hexane) was slowly added to a solution of **HL[a]** (2.12 g, 4.5 mmol) in 15 mL of toluene at -35 ^oC. After stirring at room temperature overnight, all the volatiles of reaction mixture were removed in vacuum. The residue was recrystallized from hexane (4 mL) at -30 ^oC for 1 day to eventually afford **1a** as a yellow solid (2.08 g, 82% yield). Crystals suitable for the X-ray crystal structure analysis were grown from a layered toluene / hexane (v/v: 1:2) solution at -30^oC.

Elemental Analysis: calcd. for $C_{33}H_{43}N_2PZn$: C, 70.27; H, 7.68; N, 4.97. Found: C, 70.28; H, 7.25; N, 4.96.

^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 7.43 (m, 4H, *o-Ph*$_2$P), 7.12 (m, 3H, *m*, *p*-N*Ar*), 7.08 (m, 4H, *m-Ph*$_2$P), 7.06 (m, 2H, *p-Ph*$_2$P), 4.79 (s, 1H, MeC(N)C*H*), 3.47 (m, 2H, NC*H*$_2$), 3.22 (sp, $^3J_{HH}$ = 6.8 Hz, 2H, ArC*H*Me$_2$), 2.34 (m, 2H, PC*H*$_2$), 1.67 (s, 3H, *Me*C), 1.64 (s, 3H, *Me*C), 1.24 (d, $^3J_{HH}$ = 6.8 Hz, 6H, ArCH*Me*$_2$), 1.21 (overlapped with ArCH*Me*$_2$, 3H, ZnCH$_2$C*H*$_3$), 1.15 (d, $^3J_{HH}$ = 6.8 Hz, 6H, ArCH*Me*$_2$), 0.50 (q, $^3J_{HH}$ = 8.1 Hz, 2H, ZnC*H*$_2$).

^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 298 K): δ = 167.6 (Me*C*), 166.2 (Me*C*), 145.5 (*i*-N*Ar*), 141.9 (*o*-N*Ar*), 138.8 (d, $^1J_{PC}$ = 12.8 Hz, *i-Ph*$_2$P), 133.2 (d, $^2J_{PC}$=18.5 Hz, *o-Ph*$_2$P), 128.9 (*p-Ph*$_2$P), 128.8 (d, $^3J_{PC}$ = 6.7 Hz, *m-Ph*$_2$P), 125.7 (*p*-N*Ar*), 123.7 (*m*-N*Ar*), 95.9 (MeC(N)*C*H), 48.2 (d, $^2J_{PC}$ = 18.8 Hz, N*C*H$_2$), 32.2 (d, $^1J_{PC}$ = 11.3 Hz, P*C*H$_2$), 24.4 (ArCH*Me*$_2$), 23.7 (ArCH*Me*$_2$), 23.3 (*Me*C), 21.9 (*Me*C), 12.9 (ZnCH$_2$*C*H$_3$), -0.1 (d, $^2J_{PC}$ = 7.1 Hz, Zn*C*H$_2$).

^{31}P{^{1}H} NMR (162 MHz, C_6D_6, 298 K): δ = -23.1.

^{1}H, ^{1}H GCOSY (400 MHz / 400 MHz, C_6D_6, 298 K) [selected traces]: δ ^{1}H / δ ^{1}H = 7.43 / 7.08 (*o-Ph*$_2$P / *m-Ph*$_2$P), 7.08 / 7.06 (*m-Ph*$_2$P / *p-Ph*$_2$P), 3.47 / 2.34 (NC*H*$_2$ / PC*H*$_2$), 3.22 / 1.24 (ArC*H*Me$_2$ / ArCH*Me*$_2$), 1.21 / 0.50 (ZnCH$_2$C*H*$_3$ / ZnC*H*$_2$).

^{1}H, ^{13}C GHSQC (400 MHz / 101 MHz, C_6D_6, 298 K): δ ^{1}H / δ ^{13}C = 7.43 / 133.2 (*o-Ph*$_2$P), 7.12 / 125.7 (*p*-N*Ar*), 7.12 / 123.7 (*m*-N*Ar*), 7.08 / 128.8 (*m-Ph*$_2$P), 7.06 / 128.9 (*p-Ph*$_2$P), 4.79 / 95.9 (MeC(N)*CH*), 3.47 / 48.2 (N*CH*$_2$), 3.22 / 28.4 (Ar*CH*Me$_2$), 2.34 / 32.2 (P*CH*$_2$), 1.67 / 23.3 (*Me*C), 1.64 / 21.9 (*Me*C), 1.24 / 24.4 (ArCH*Me*$_2$), 1.21 / 12.9 (ZnCH$_2$*CH*$_3$), 1.15 / 23.7 (ArCH*Me*$_2$), 0.50 / -0.1 (Zn*CH*$_2$).

^{1}H, ^{13}C GHMBC (400 MHz / 101 MHz, C_6D_6, 298 K) [selected traces]: δ ^{1}H / δ ^{13}C = 7.43 / 128.9 (*o-Ph*$_2$P / *p-Ph*$_2$P), 3.47 / 167.6 (NC*H*$_2$ / Me*C*), 3.22 / 145.5, 123.7 (ArC*H*Me$_2$ / *i*-N*Ar*, *m*-N*Ar*), 2.34 / 138.8 (PC*H*$_2$ / *i-Ph*$_2$P).

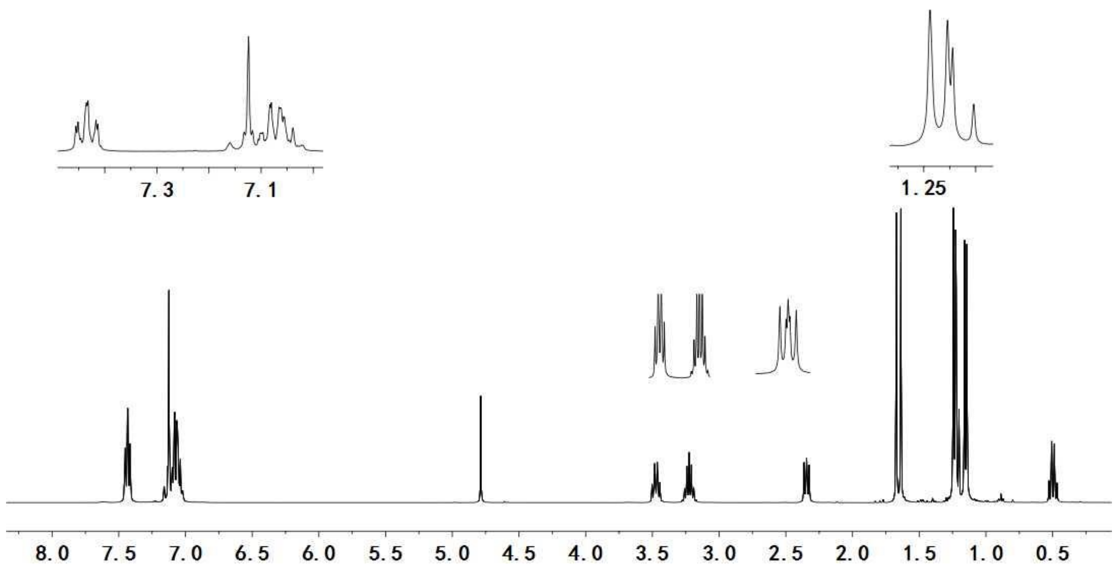


Fig. S4. ^{1}H NMR (400 MHz, C_6D_6, 298 K)

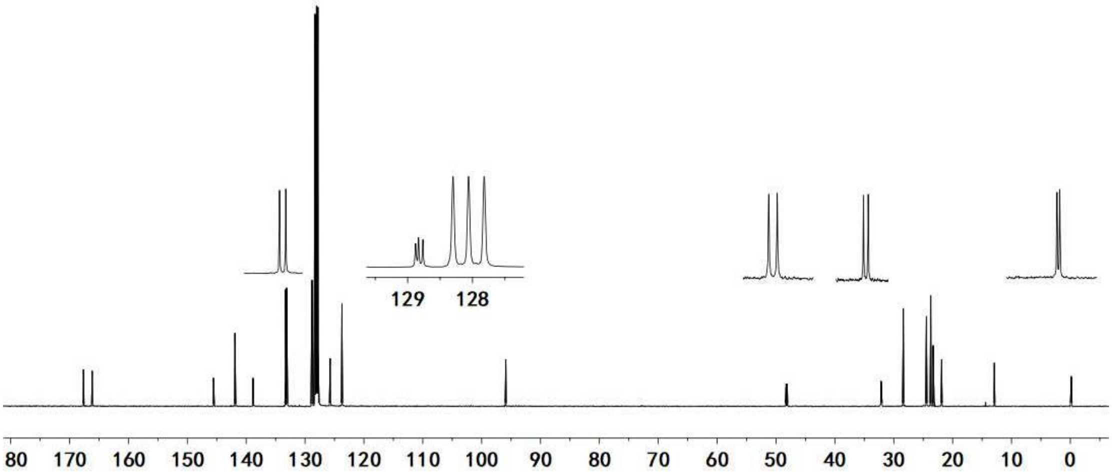


Fig. S5. ^{13}**C{**^{1}**H} NMR** (101 MHz, C_6D_6, 298 K)

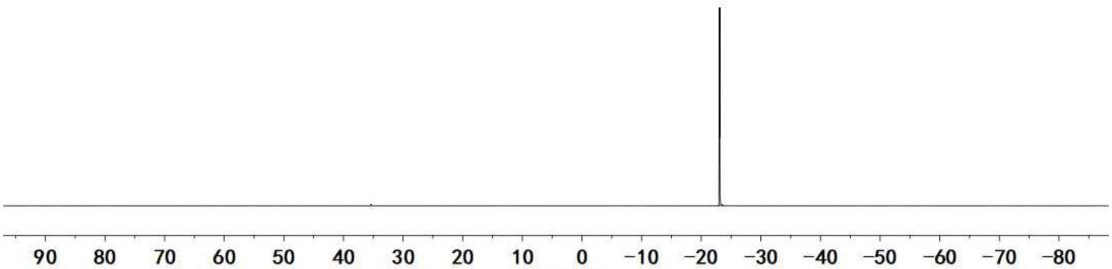


Fig. S6. ^{31}**P{**^{1}**H} NMR** (162 MHz, C_6D_6, 298 K)

X-ray crystal structure analysis of complex 1a: formula $C_{33}H_{43}N_2PZn$, M = 564.05 gmol^{-1}, colorless, 0.20 x 0.18 x 0.15 mm, Monoclinic, space group $P2_1/n$, a = 9.7230(9), b = 21.559(2), c = 14.9159(14) Å, β = 104.556(3)°, V = 3026.3(5) Å^3, ρ_{calc} = 1.238 gcm^{-3}, μ = 0.888 mm^{-1}, empirical absorption correction (0.6866 ≤ T ≤ 0.7455), Z = 4, λ = 0.71073 Å, T = 120(2) K, 112848 reflections collected (-12 ≤ h ≤ 12, -27 ≤ k ≤ 27, -19 ≤ l ≤ 19), 6990 independent (R_{int} = 0.0459) and 5823 observed reflections [I>2σ(I)], 340 refined parameters, the final R_1 was 0.0298 (I > 2σ(I)) and wR_2 was 0.0974 (all data). max. (min.) residual electron density 0.281 (-0.464) e.Å^{-3}, hydrogen atoms were placed in calculated positions and refined using a riding model.

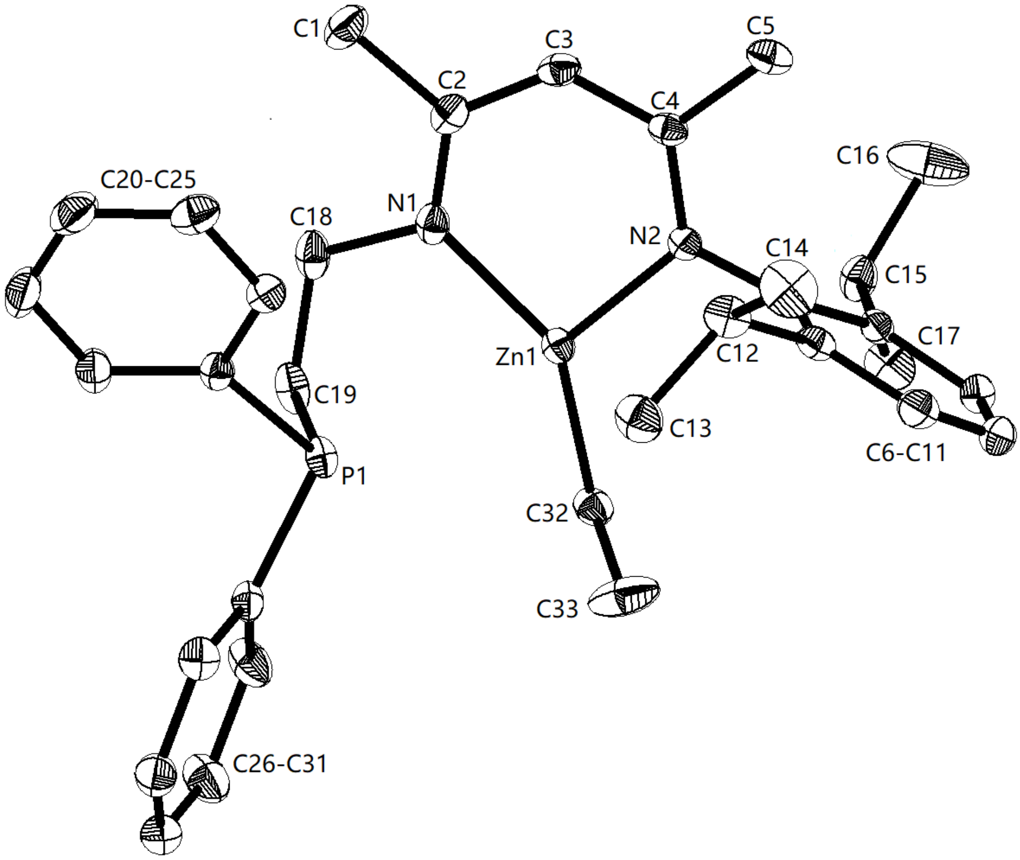
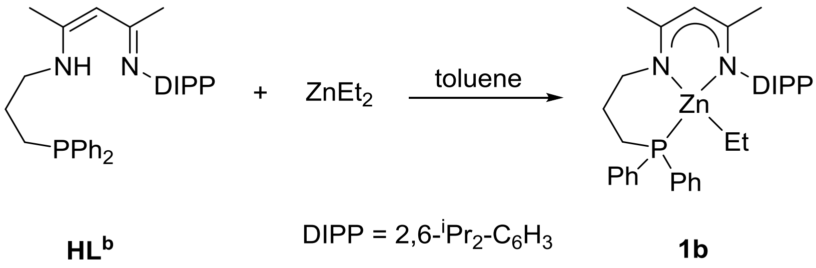


Fig. S7. Molecular structure of complex **1a**.

Preparation of Complex 1b:



Scheme S4.

Following the procedure described for **1a**, reaction of $ZnEt_2$ (5.3 mL, 1.0 M in n-hexane) with **HL**$^{\mathbf{b}}$ (2.42 g, 5.0 mmol) gave **1b** as a pale yellow crystalline solid (2.40 g, 83%). Crystals suitable for the X-ray crystal structure analysis were grown from a layered toluene / hexane (v/v: 1:2) solution at -30^{o}C.

Elemental Analysis: calcd. for $C_{34}H_{45}N_2PZn$: C, 70.64; H, 7.85; N, 4.85. Found: C, 70.94; H, 8.06; N, 4.47.

^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 7.46 (m, 4H, *o-Ph*$_2$P), 7.12 (m, 1H, *p*-N*Ar*), 7.11 (m, 2H, *m*-N*Ar*), 7.09 (m, 4H, *m-Ph*$_2$P), 7.06 (m, 2H, *p-Ph*$_2$P), 4.77 (s, 1H, MeC(N)C*H*), 3.41 (m, 2H, NC*H*$_2$), 3.30 (sp, $^{3}J_{HH}$ = 6.9 Hz, 2H, ArC*H*Me$_2$), 2.08 (m, 2H, PC*H*$_2$), 1.71 (s, 3H, *Me*C), 1.63 (s, 3H, *Me*C), 1.53 (m, 2H, NCH$_2$C*H*$_2$), 1.28 (t, $^{3}J_{HH}$ = 8.1 Hz, 3H, ZnCH$_2$C*H*$_3$), 1.16 (d, $^{3}J_{HH}$ = 6.9 Hz, 12H, ArCH*Me*$_2$), 0.54 (m, 2H, ZnC*H*$_2$).

^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 298 K): δ = 167.5 (Me*C*), 165.9 (Me*C*), 145.9 (*i*-N*Ar*), 142.1 (*o*-N*Ar*), 138.3 (d, $^{1}J_{PC}$ = 9.5 Hz, *i-Ph*$_2$P), 133.3 (d, $^{2}J_{PC}$=17.5 Hz, *o-Ph*$_2$P), 129.0 (*p-Ph*$_2$P), 128.7 (d, $^{3}J_{PC}$ = 6.6 Hz, *m-Ph*$_2$P), 125.5 (*p*-N*Ar*), 123.7 (*m*-N*Ar*), 95.7 (MeC(N)*C*H), 52.7 (d, $^{3}J_{PC}$ = 6.3 Hz, N*C*H$_2$), 28.4 (Ar*C*HMe$_2$), 28.1 (d, $^{2}J_{PC}$ = 8.9 Hz, NCH$_2$*C*H$_2$), 27.4 (d, $^{1}J_{PC}$ = 9.5 Hz, P*C*H$_2$), 24.4 (ArCH*Me*$_2$), 23.8 (ArCH*Me*$_2$), 23.5 (*Me*C), 21.1 (*Me*C), 13.3 (ZnCH$_2$*C*H$_3$), -0.8 (d, $^{2}J_{PC}$ = 14.9 Hz, Zn*C*H$_2$).

^{31}P{^{1}H} NMR (162 MHz, C_6D_6, 298 K): δ = -17.4.

^{1}H, ^{1}H GCOSY (400 MHz / 400 MHz, C_6D_6, 298 K) [selected traces]: δ ^{1}H / δ ^{1}H = 7.46 / 7.09 (*o-Ph*$_2$P / *m-Ph*$_2$P), 7.09 / 7.06 (*m-Ph*$_2$P / *p-Ph*$_2$P), 3.41 / 1.53 (NC*H*$_2$ / NCH$_2$C*H*$_2$), 3.29 / 1.16 (ArC*H*Me$_2$ / ArCH*Me*$_2$), 2.08 / 1.53 (PC*H*$_2$ / NCH$_2$C*H*$_2$), 1.28

/ 0.54 (ZnCH$_2$C*H*$_3$ / ZnC*H*$_2$).

^{1}H, ^{13}C GHSQC (400 MHz / 101 MHz, C_6D_6, 298 K): δ ^{1}H / δ ^{13}C = 7.46 / 133.3 (*o-Ph*$_2$P), 7.12 / 125.5 (*p*-N*Ar*), 7.11 / 123.7 (*m*-N*Ar*), 7.09 / 128.7 (*m-Ph*$_2$P), 7.06 / 129.0 (*p-Ph*$_2$P), 4.77 / 95.7 (MeC(N)*CH*), 3.41 / 52.7 (N*CH*$_2$), 3.30 / 28.4 (Ar*CH*Me$_2$), 2.08 / 27.4 (P*CH*$_2$), 1.71 / 23.5 (*Me*C), 1.63 / 21.1 (*Me*C), 1.53 / 28.1 (NCH$_2$*CH*$_2$), 1.28 / 13.3 (ZnCH$_2$*CH*$_3$), 1.16 / 24.4, 23.8 (ArCH*Me*$_2$), 0.54 / -0.8 (Zn*CH*$_2$).

^{1}H, ^{13}C GHMBC (400 MHz / 101 MHz, C_6D_6, 298 K) [selected traces]: δ ^{1}H / δ ^{13}C = 7.46 / 133.3, 128.7 (*o-Ph*$_2$P / *o-Ph*$_2$P, *m-Ph*$_2$P), 7.12 / 142.1 (*p*-N*Ar* / *o*-N*Ar*), 7.11 / 145.9, 123.7 (*m*-N*Ar* / *i*-N*Ar, m*-N*Ar*), 7.09 / 138.3, 128.7 (*m-Ph*$_2$P / *i-Ph*$_2$P, *m-Ph*$_2$P), 3.30 / 145.9, 142.1, 123.7, 23.8 (ArC*H*Me$_2$ / *i*-N*Ar*, *o*-N*Ar*, *m*-N*Ar*, ArCH*Me*$_2$), 2.08 / 138.3 (PC*H*$_2$ / *i-Ph*$_2$P), 1.16 / 142.1 (ArCH*Me*$_2$ / *o*-N*Ar*).

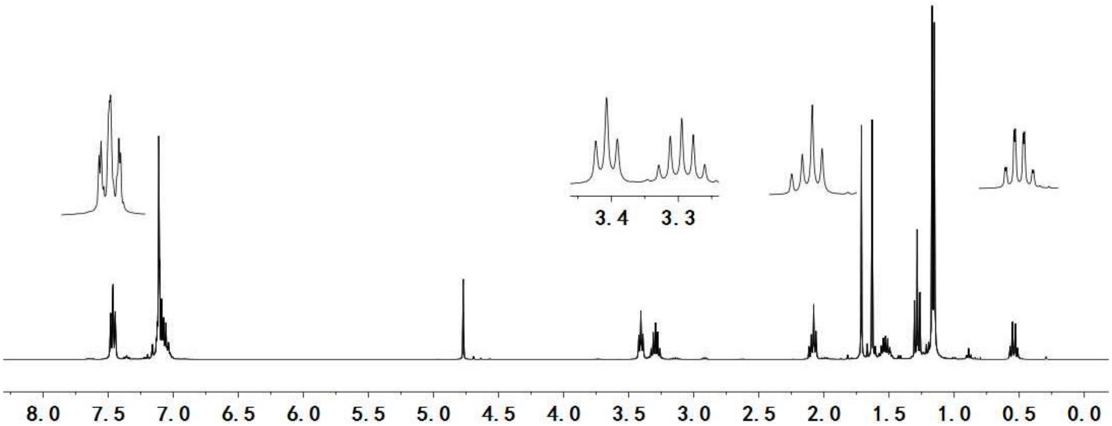


Fig. S8. ^{1}H NMR (400 MHz, C_6D_6, 298 K)

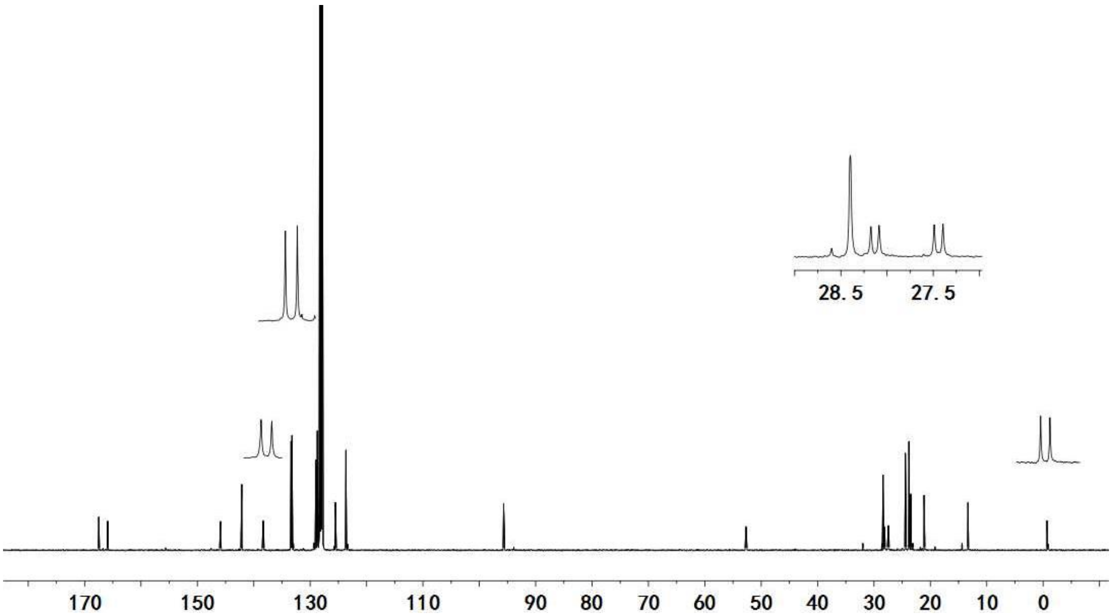


Fig. S9. $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6, 298 K)

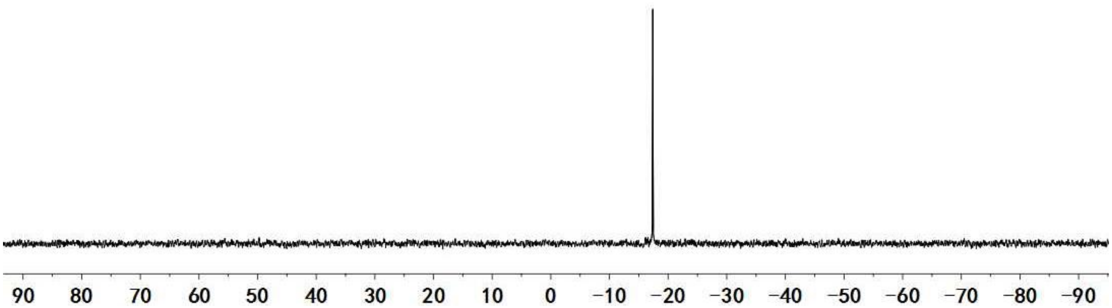


Fig. S10. $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6, 298 K)

X-ray crystal structure analysis of complex 1b: formula $C_{34}H_{45}N_2PZn$, M = 578.06 gmol^{-1}, colorless, 0.50 x 0.28 x 0.10 mm, Monoclinic, space group $P2_1/c$, a = 18.287(3), b = 11.4487(14), c = 18.253(3) Å, β = 113.024(3)°, V = 3517.1(9) Å^3, ρ_{calc} = 1.092 gcm^{-3}, μ = 0.769 mm^{-1}, empirical absorption correction (0.8203 ≤ T ≤1.0000), Z = 4, λ = 0.71073 Å, T = 157.15 K, 23099 reflections collected (-21 ≤ h ≤ 23, -13 ≤ k ≤ 14, -23 ≤ l ≤ 19), 7993 independent (R_{int} = 0.0405) and 6340 observed reflections [I>2σ(I)], 340 refined parameters, the final R_1 was 0.0603 (I > 2σ(I)) and wR_2 was 0.1618 (all data). max. (min.) residual electron density 0.517 (-0.378) e.Å^{-3}, hydrogen atoms were placed in calculated positions and refined using a riding model.

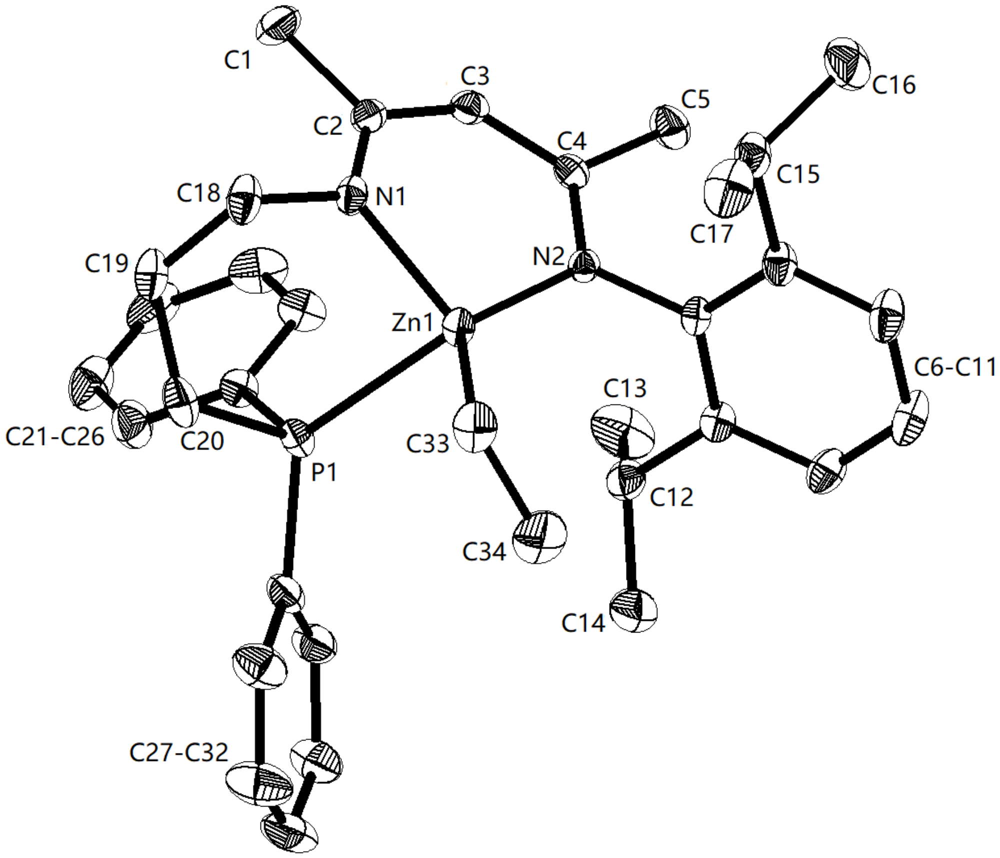
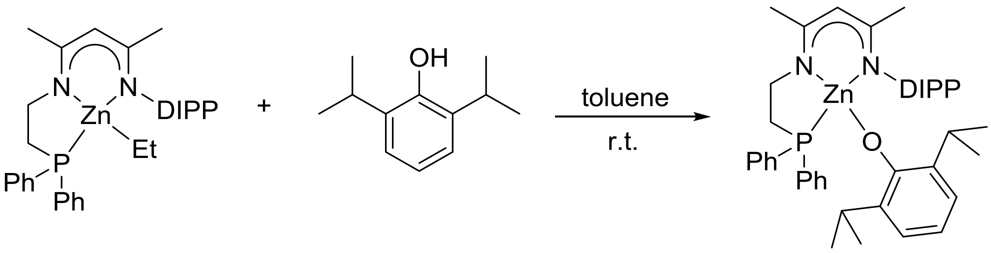


Fig. S11. Molecular structure of complex **1b**.

Preparation of complex 2a:



1a DIPP = 2,6-$^{i}Pr_2$-C_6H_3 2a

Scheme S5.

2,6-Di-*iso*-propylphenol (535 mg, 3.0 mmol) was added to a solution of **1a** (1.70 g, 3.0 mmol) in toluene (15 mL). The reaction mixture was stirred at room temperature for 8 h. The volatiles were removed under vacuum and then the residue was washed with hexane (3*2 mL) to eventually give **2a** as a white solid (1.77 g, 83%). Crystals suitable for the X-ray crystal structure analysis were grown from a layered toluene / hexane (v/v: 1:2) solution at room temperature.

Elemental Analysis: calcd. for $C_{43}H_{55}N_2OPZn$: C, 72.51; H, 7.78; N, 3.93. Found: C, 72.48; H, 7.74; N, 3.74.

^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 7.15 (m, 3H, *m*, *p*-N*Ar*), 7.05 (m, 2H, *m*-O*Ar)*, 7.04 (m, 4H, *o*-*Ph*$_2$P), 7.00 (m, 2H, *p*-*Ph*$_2$P), 6.98 (m, 4H, *m*-*Ph*$_2$P), 6.89 (m, 1H, *p*-O*Ar*), 4.67 (s, 1H, MeC(N)C*H*), 3.59 (sp, $^3J_{HH}$ = 6.8 Hz, 2H, NArC*H*Me$_2$), 3.30 (m, 2H, OArC*H*Me$_2$), 3.10 (m, 2H, NC*H*$_2$), 2.23 (m, 2H, PC*H*$_2$), 1.72 (s, 3H, *Me*C), 1.38 (d, $^3J_{HH}$ = 6.8 Hz, 6H, NArCH*Me*$_2$), 1.35 (s, 3H, *Me*C), 1.26 (d, $^3J_{HH}$ = 6.9 Hz, 6H, NArCH*Me*$_2$), 1.08 (d, $^3J_{HH}$ = 6.8 Hz, 12H, OArCH*Me*$_2$).

^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 298 K): δ = 168.6 (Me*C*), 168.2 (Me*C*), 161.3 (*i*-O*Ar*), 144.7 (*i*-N*Ar*), 142.6 (*o*-N*Ar*), 137.9 (*o*-O*Ar*), 133.4 (d, $^2J_{PC}$= 13.6 Hz, *o*-*Ph*$_2$P), 132.2 (d, $^1J_{PC}$ = 15.0 Hz, *i*-*Ph*$_2$P), 129.8 (*p*-*Ph*$_2$P), 128.7 (d, $^3J_{PC}$ = 8.2 Hz, *m*-*Ph*$_2$P), 126.1 (*p*-N*Ar*), 124.1 (*m*-N*Ar*), 123.1 (*m*-O*Ar*), 115.8 (*p*-O*Ar*), 94.6 (MeC(N)*C*H), 44.5 (N*C*H$_2$), 28.7 (NAr*C*HMe$_2$), 27.8 (OAr*C*HMe$_2$), 27.7 (overlapped with OAr*C*HMe$_2$, P*C*H$_2$), 24.6 (NArCH*Me*$_2$), 24.3 (NArCH*Me*$_2$), 23.8 (*Me*C), 23.4 (OArCH*Me*$_2$), 22.3 (*Me*C).

^{31}P{^{1}H} NMR (162 MHz, C_6D_6, 298 K): δ = -26.4.

^{1}H, ^{1}H GCOSY (400 MHz / 400 MHz, C_6D_6, 298 K) [selected traces]: δ ^{1}H / δ ^{1}H = 7.05 / 6.89 (*m*-O*Ar* / *p*-O*Ar*), 7.04 / 6.98 (*o*-Ph_2P / *m*-Ph_2P), 3.59 / 1.38, 1.26 (NArC*H*Me_2 / NArCHMe_2), 3.30 / 1.08 (OArC*H*Me_2 / OArCHMe_2), 3.10 / 2.23 (NCH_2 / PCH_2).

^{1}H, ^{13}C GHSQC (400 MHz / 101 MHz, C_6D_6, 298 K): δ ^{1}H / δ ^{13}C = 7.15 / 126.1, 124.1 (*p*-N*Ar*, *m*-N*Ar*), 7.05 / 123.1 (*m*-O*Ar*), 7.04 / 133.4 (*o*-Ph_2P), 7.00 / 129.8 (*p*-Ph_2P), 6.98 / 128.7 (*m*-Ph_2P), 6.89 / 115.8 (*p*-O*Ar*), 4.67 / 94.6 (MeC(N)*CH*), 3.59 / 28.7 (NAr*CH*Me_2), 3.30 / 27.8 (OAr*CH*Me_2), 3.10 / 44.5 (NCH_2), 2.23 / 27.7 (PCH_2), 1.72 / 23.8 (*Me*C), 1.38 / 24.3 (NArCHMe_2), 1.35 / 22.3 (*Me*C), 1.26 / 24.6 (NArCHMe_2), 1.08 / 23.4(OArCHMe_2).

^{1}H, ^{13}C GHMBC (400 MHz / 101 MHz, C_6D_6, 298 K) [selected traces]: δ ^{1}H / δ ^{13}C = 7.15 / 144.7 (m-N*Ar* / *i*-N*Ar*), 7.05 / 161.3 (*m*-O*Ar* / *i*-O*Ar*), 7.00 / 133.4 (*p*-Ph_2P / *o*-Ph_2P), 6.89 / 137.9 (*p*-O*Ar* / *o*-O*Ar*), 3.10 / 168.6, 27.7 (NCH_2 / Me*C*, PCH_2), 3.59 / 144.7, 142.6, 124.1, (NArC*H*Me_2 / *i*-N*Ar*, *o*-N*Ar*, *m*-N*Ar*), 3.30 / 161.3, 137.9, 123.1 (OArC*H*Me_2 / *i*-O*Ar*, *o*-O*Ar*, *m*-O*Ar*), 1.38 / 142.6 (NArCHMe_2 / *o*-N*Ar*), 1.35 / 168.6 (*Me*C / Me*C*), 2.23 / 132.2 (PCH_2 / *i*-Ph_2P), 1.08 / 137.9 (OArCHMe_2 / *o*-O*Ar*).

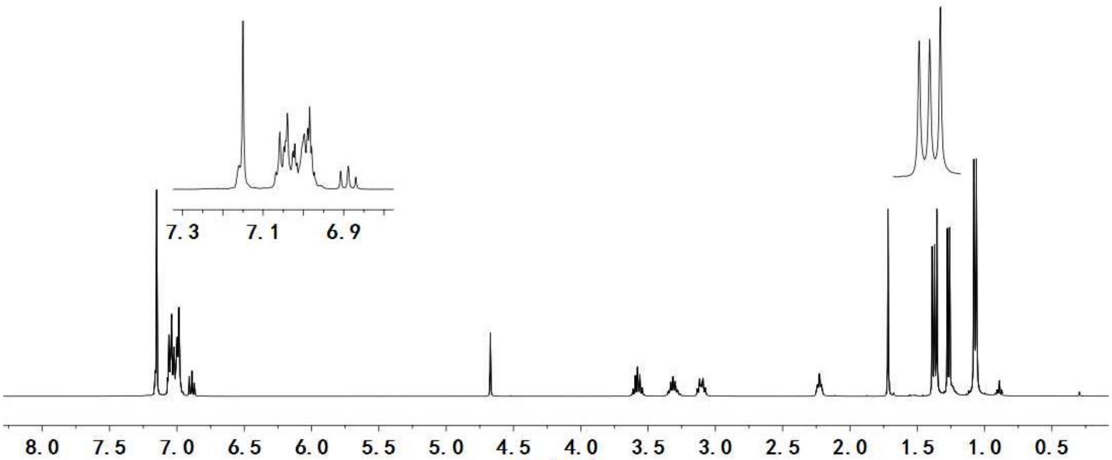


Fig. S12. ^{1}H NMR (400 MHz, C_6D_6, 298 K)

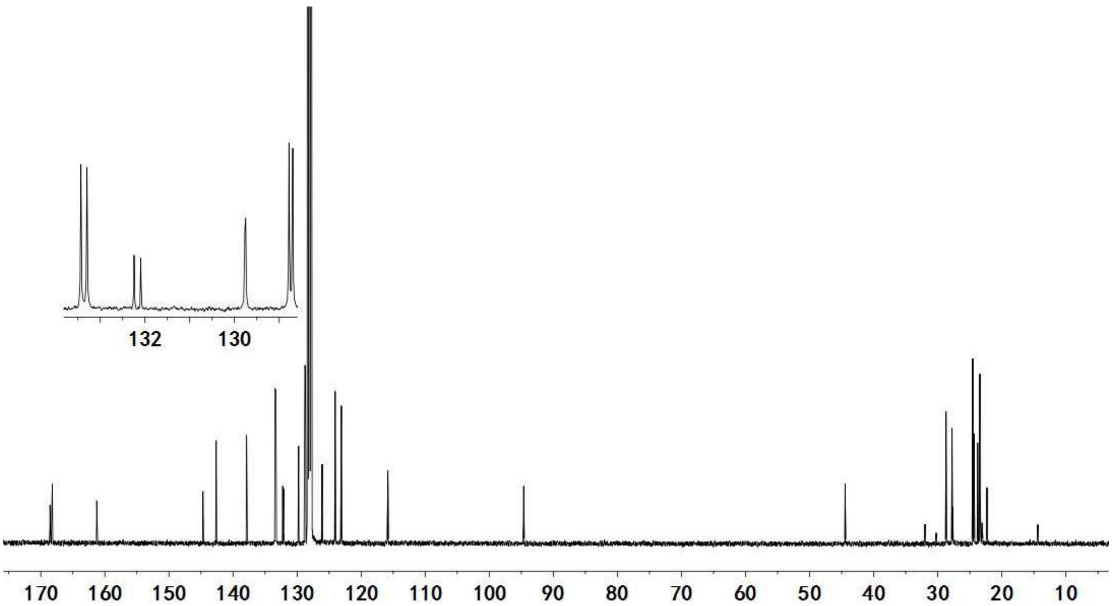


Fig. S13. ^{13}**C{**^{1}**H} NMR** (101 MHz, C_6D_6, 298 K)

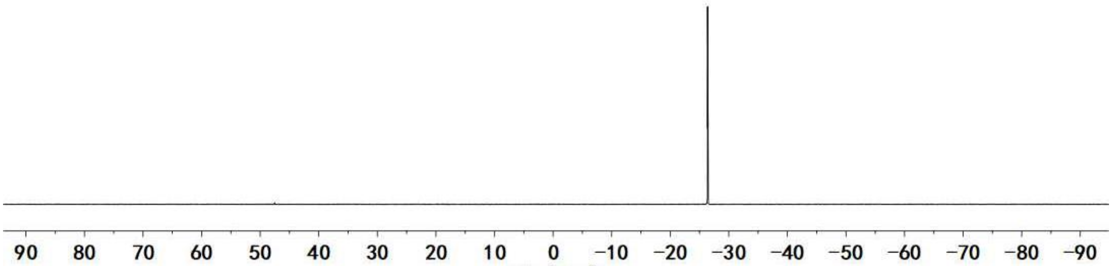


Fig. S14. ^{31}**P{**^{1}**H} NMR** (162 MHz, C_6D_6, 298 K)

X-ray crystal structure analysis of complex 2a: formula $C_{43}H_{55}N_2OPZn$, M = 712.25 gmol^{-1}, colorless, 0.12 x 0.10 x 0.08 mm, Orthorhombic, space group *Pccn*, a = 19.9034(11), b = 22.2475(12), c = 17.4182(8) Å, V = 7712.8(7) Å^3, ρ_{calc} = 1.227 gcm^{-3}, μ = 0.713 mm^{-1}, empirical absorption correction (0.6924 ≤ T ≤ 0.7455), Z = 8, λ = 0.71073 Å, T = 120(2) K, 110312 reflections collected (-25 ≤ h ≤ 24, -28 ≤ k ≤ 28, -22 ≤ l ≤ 22), 8858 independent (R_{int} = 0.0845) and 6499 observed reflections [I>2σ(I)], 340 refined parameters, the final R_1 was 0.0355 (I > 2σ(I)) and wR_2 was 0.0991 (all data). max. (min.) residual electron density 0.484 (-0.453) e.Å^{-3}, hydrogen atoms were placed in calculated positions and refined using a riding model.

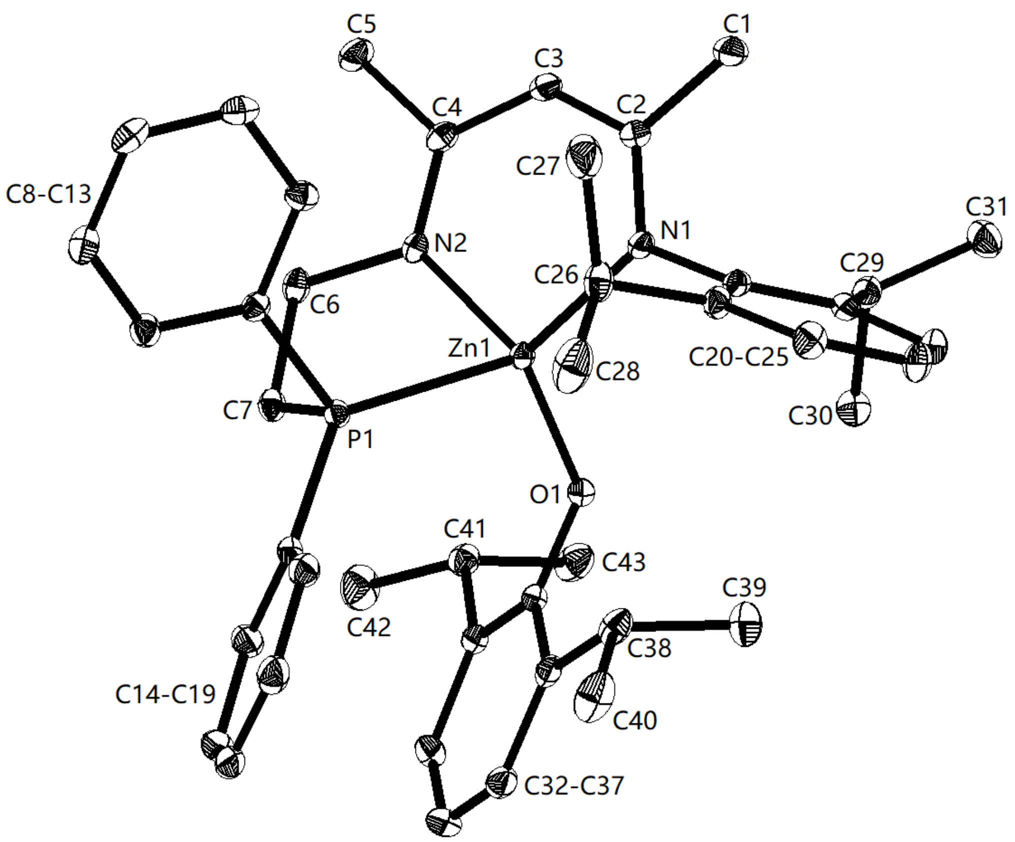
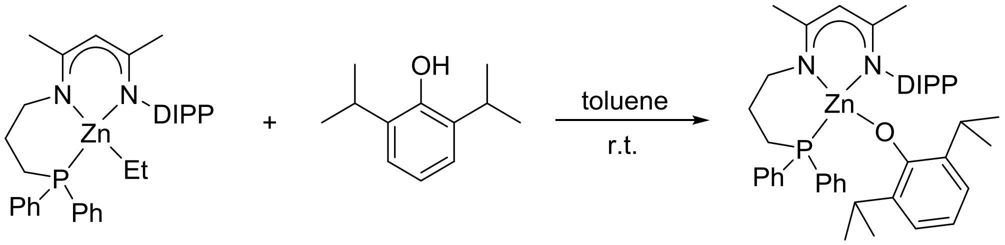


Fig. S15. Molecular structure of complex **2a**.

Preparation of Complex 2b:



1b DIPP = 2,6-$^{i}Pr_2$-C_6H_3 **2b**

Scheme S6.

Following the procedure described for **2a**, reaction of 2,6-di-*iso*-propylphenol (178 mg, 1.0 mmol) with **1b** (578 mg, 1.0 mmol) gave **2b** as a colorless crystalline solid (595 mg, 82%). Crystals suitable for the X-ray crystal structure analysis were grown from a layered toluene / hexane (v/v: 1:2) solution at -30^{o}C.

Elemental Analysis: calcd. for $C_{44}H_{57}N_2OPZn$: C, 72.76; H, 7.91; N, 5.09. Found: C, 72.55; H, 7.89; N, 4.77.

^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 7.18 (m, 4H, *o-Ph*$_2$P), 7.11 (m, 2H, *m*-O*Ar*), 7.09 (m, 3H, *m, p*-N*Ar*), 7.04 (m, 6H, *m, p-Ph*$_2$P), 6.93 (m, 1H, *p*-O*Ar*), 4.71 (s, 1H, MeC(N)C*H*), 3.62 (m, 2H, NC*H*$_2$), 3.48 (m, 2H, NArC*H*Me$_2$), 3.44 (m, 2H, OArC*H*Me$_2$), 2.08 (m, 2H, PC*H*$_2$), 1.70 (s, 3H, *Me*C), 1.43 (s, 3H, *Me*C), 1.20 (d, $^3J_{HH}$ = 6.9 Hz, 12H, NArCH*Me*$_2$), 1.18 (overlapped with NArCH*Me*$_2$, 2H, NCH$_2$C*H*$_2$), 1.03 (d, $^3J_{HH}$ = 6.6 Hz, 12H, OArCH*Me*$_2$).

^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 298 K): δ = 167.7 (Me*C*), 167.5 (Me*C*), 162.0 (*i*-O*Ar*), 145.7 (*i*-N*Ar*), 142.7 (*o*-N*Ar*), 137.7 (*o*-O*Ar*), 133.9 (d, $^2J_{PC}$=13.3 Hz, *o-Ph*$_2$P), 132.9 (d, $^1J_{PC}$ = 18.4 Hz, *i-Ph*$_2$P), 130.1 (*p-Ph*$_2$P), 128.7 (d, $^3J_{PC}$ = 8.3 Hz, *m-Ph*$_2$P), 126.0 (*p*-N*Ar*), 124.1 (*m*-N*Ar*), 123.1 (*m*-O*Ar*), 115.4 (*p*-O*Ar*), 94.6 (MeC(N)*C*H), 51.2 (N*C*H$_2$), 29.0 (d, $^1J_{PC}$ = 6.7 Hz, P*C*H$_2$), 28.7 (NAr*C*HMe$_2$), 27.4 (OAr*C*HMe$_2$), 26.4 (NCH$_2$*C*H$_2$), 24.5 (NArCH*Me*$_2$), 24.3 (*Me*C), 23.8 (OArCH*Me*$_2$), 21.1 (*Me*C).

^{31}P{^{1}H} NMR (162 MHz, C_6D_6, 298 K): δ = -14.9.

^{1}H, ^{1}H GCOSY (400 MHz / 400 MHz, C_6D_6, 298 K) [selected traces]: δ ^{1}H / δ ^{1}H = 7.18 / 7.04 (*o-Ph*$_2$P / *m-Ph*$_2$P), 7.11 / 6.93 (*m*-O*Ar* / *p*-O*Ar*), 3.62 / 1.18 (NC*H*$_2$ / NCH$_2$C*H*$_2$), 3.48 / 1.20 (NArC*H*Me$_2$ / NArCH*Me*$_2$), 3.44 / 1.03 (OArC*H*Me$_2$ /

OArCH*Me*$_2$), 2.08 / 1.18 (PC*H*$_2$ / NCH$_2$C*H*$_2$).

^{1}H, ^{13}C GHSQC (400 MHz / 101 MHz, C_6D_6, 298 K): δ ^{1}H / δ ^{13}C = 7.18 / 133.9 (*o-Ph*$_2$P), 7.11 / 123.1 (*m*-O*Ar*), 7.09 / 124.1, 126.0 (*m, p*-N*Ar*), 7.04 / 130.1, 128.7 (*m, p-Ph*$_2$P), 6.93 / 115.4 (*p*-O*Ar*), 4.71 / 94.6(MeC(N)*CH*), 3.62 / 51.2 (N*CH*$_2$), 3.48 / 28.7 (NAr*CH*Me$_2$), 3.44 / 27.4 (OAr*CH*Me$_2$), 2.08 / 29.0 (P*CH*$_2$), 1.70 / 24.3 (*Me*C), 1.43 / 21.1 (*Me*C), 1.20 / 24.5 (NArCH*Me*$_2$), 1.18 / 26.4 (NCH$_2$*CH*$_2$), 1.03 / 23.8 (OArCH*Me*$_2$).

^{1}H, ^{13}C GHMBC (400 MHz / 101 MHz, C_6D_6, 298 K) [selected traces]: δ ^{1}H / δ ^{13}C = 7.18 / 133.9, 130.1 (*o-Ph*$_2$P / *o-Ph*$_2$P, *p-Ph*$_2$P), 7.11 / 162.0, 123.1 (*m*-O*Ar* / *i*-O*Ar*, *m*-O*Ar*), 7.09 / 145.7, 142.7, 124.1 (*m, p*-N*Ar* / *i*-N*Ar*, *o*-N*Ar, m*-N*Ar*), 7.04 / 133.9, 132.9, 128.7 (*m, p- Ph*$_2$P / *o- Ph*$_2$P, *i- Ph*$_2$P, *m- Ph*$_2$P), 6.93 / 137.7 (*p*-O*Ar* / *o*-O*Ar*), 3.48 / 145.7, 142.7, 124.1, 24.5 (NArC*H*Me$_2$ / *i*-N*Ar*, *o*-N*Ar*, *m*-N*Ar*, NArCH*Me*$_2$), 2.08 / 132.9 (PC*H*$_2$ / *i-Ph*$_2$P), 1.70 / 145.7 (*Me*C / *i*-N*Ar*), 1.20 / 142.7 (NArCH*Me*$_2$ / *o*-N*Ar*), 1.03 / 137.7 (OArCH*Me*$_2$ / *o*-O*Ar*).

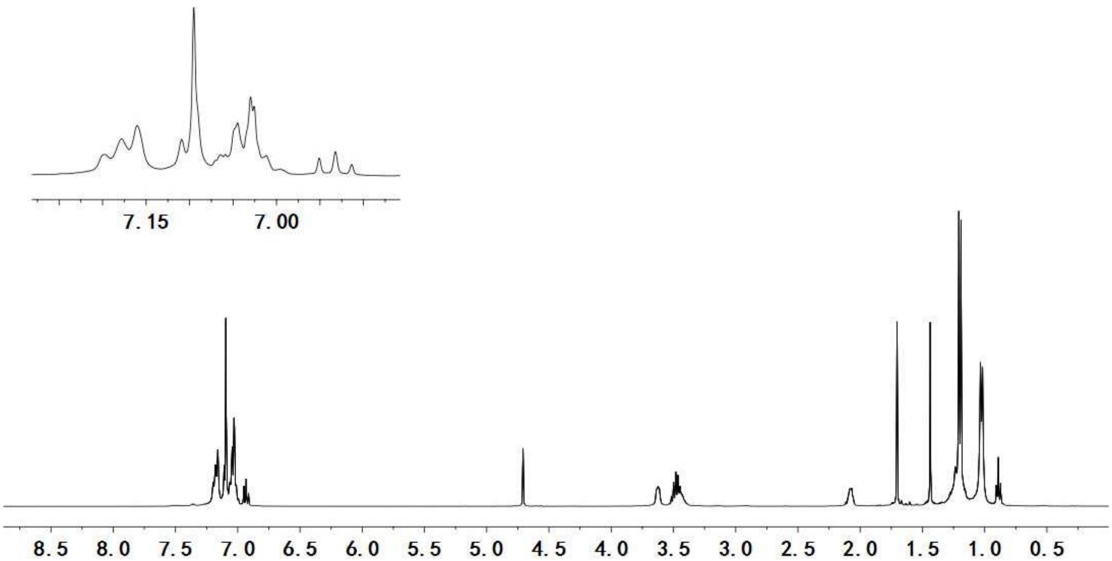


Fig. S16. ^{1}H NMR (400 MHz, C_6D_6, 298 K)

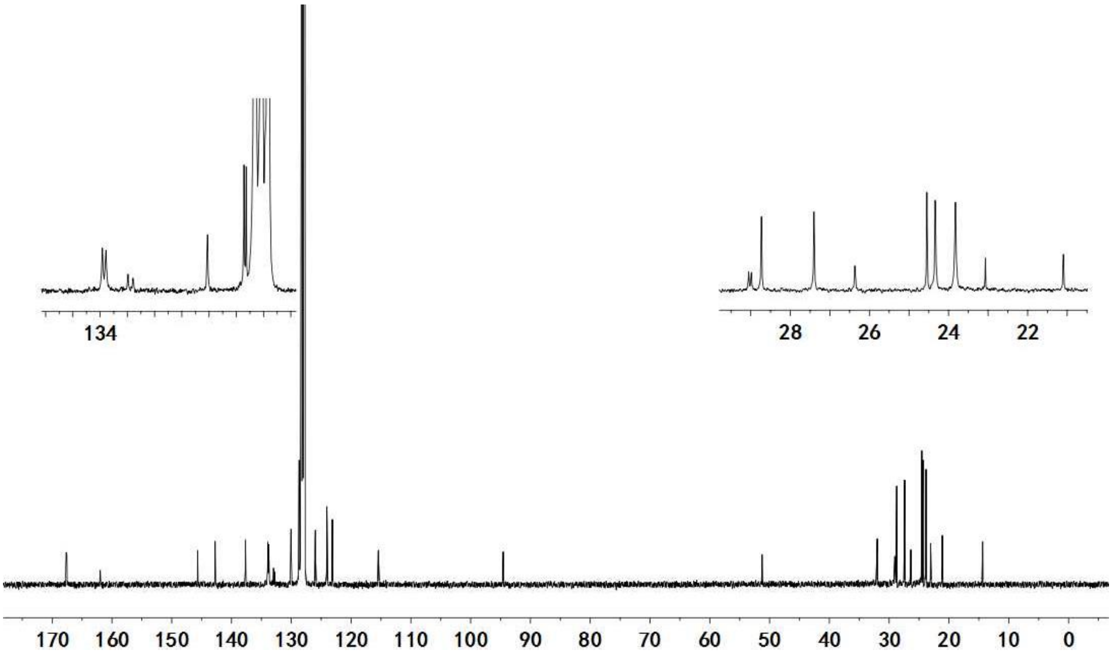


Fig. S17. ^{13}**C{**^{1}**H} NMR** (101 MHz, C_6D_6, 298 K)

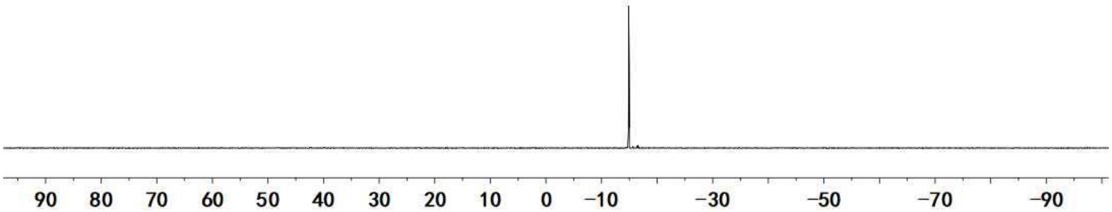


Fig. S18. ^{31}**P{**^{1}**H} NMR** (162 MHz, C_6D_6, 298 K)

X-ray crystal structure analysis of complex 2b: formula $C_{44}H_{57}N_2OPZn$, M = 726.28 gmol^{-1}, colorless, 0.30 x 0.15 x 0.10 mm, Monoclinic, space group $P2_1/n$, a = 12.8320(5), b = 17.0896(5), c = 18.1726(6) Å, β = 90.809(3)°, V = 3984.7(2) Å^3, ρ_{calc} = 1.211 gcm^{-3}, μ = 0.691 mm^{-1}, empirical absorption correction (0.81292 ≤ T ≤ 1.00000), Z = 4, λ = 0.71073 Å, T = 223 K, 29941 reflections collected (-17 ≤ h ≤ 15, -22 ≤ k ≤ 22, -24 ≤ l ≤ 24), 11028 independent (R_{int} = 0.0603) and 6056 observed reflections [I>2σ(I)], 452 refined parameters, the final R_1 was 0.0540 (I > 2σ(I)) and wR_2 was 0.1243 (all data). max. (min.) residual electron density 0.514 (-0.375) e.Å^{-3}, hydrogen atoms were placed in calculated positions and refined using a riding model.

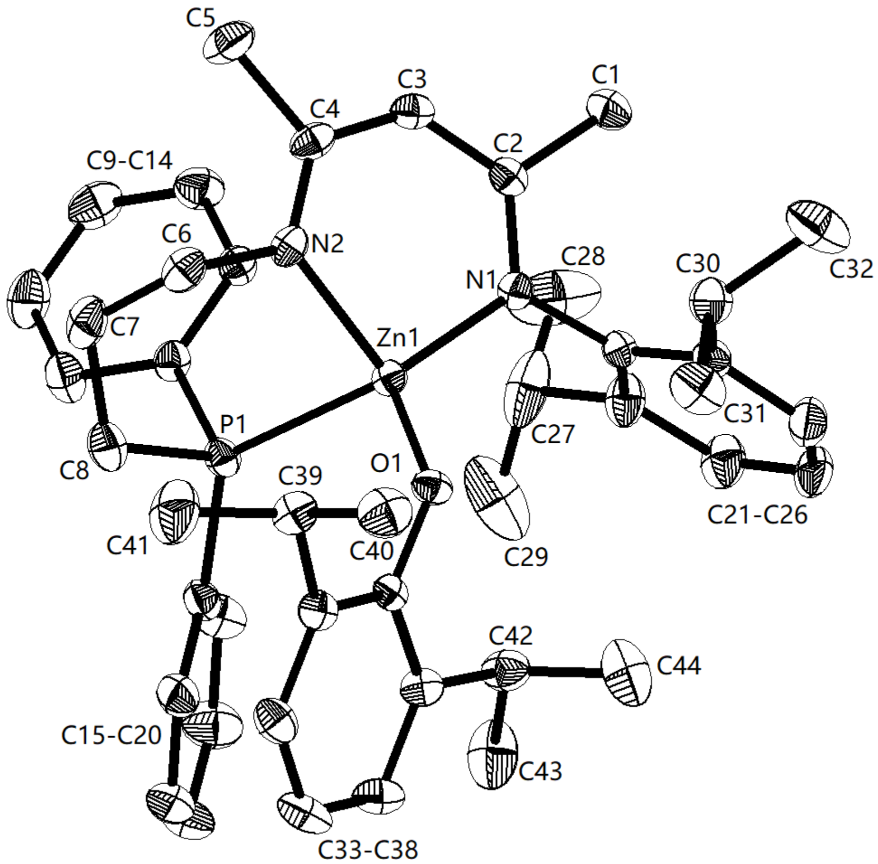
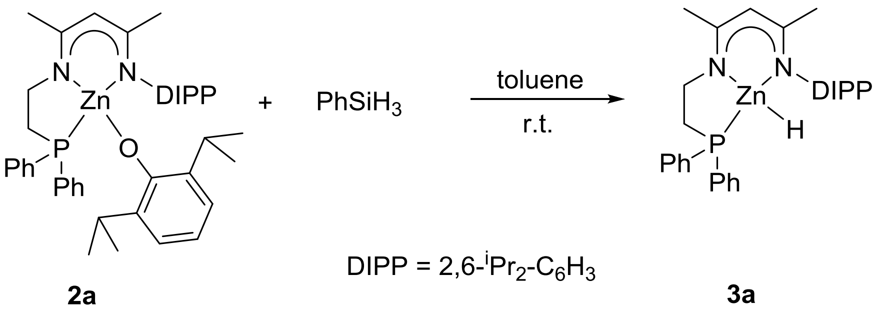


Fig. S19. Molecular structure of complex **2b**.

Preparation of complex 3a:



2a **3a**

Scheme S7.

$PhSiH_3$ (227 mg, 2.1 mmol) was added to a solution of **2a** (1.50 g, 2.1 mmol) in toluene (10 mL). The reaction mixture was stirred at room temperature for 1 h. The volatiles were removed under vacuum, and then the residue was washed with hexane (3*2 mL) to eventually give **3a** as a white solid (979 mg, 87%). Crystals suitable for the X-ray crystal structure analysis were grown from a layered toluene / hexane (v/v: 1:2) solution at room temperature.

Elemental Analysis: calcd. for $C_{31}H_{39}N_2PZn$: C, 69.46; H, 7.33; N, 5.23. Found: C, 69.95; H, 7.36; N, 4.93.

IR: ν(Zn-H) = 1742 cm^{-1}.

^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 7.45 (m, 4H, *o-Ph*$_2$P), 7.16 (m, 1H, *p*-N*Ar*), 7.14 (m, 2H, *m*-N*Ar*), 7.05 (m, 6H, *m*, *p-Ph*$_2$P), 4.78 (s, 1H, MeC(N)C*H*), 4.72 (s, 1H, Zn*H*), 3.36 (m, 4H, NC*H*$_2$, ArC*H*Me$_2$), 2.36 (t, $^3J_{HH}$ = 7.0 Hz, 2H, PC*H*$_2$), 1.68 (s, 3H, *Me*C), 1.60 (s, 3H, *Me*C), 1.29 (d, $^3J_{HH}$ = 6.8 Hz, 6H, ArCH*Me*$_2$), 1.18 (d, $^3J_{HH}$ = 6.9 Hz, 6H, ArCH*Me*$_2$).

^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 298 K): δ = 167.8 (Me*C*), 166.4 (Me*C*), 145.5 (*i*-N*Ar*), 142.4 (*o*-N*Ar*), 137.4 (d, $^1J_{PC}$ = 8.5 Hz, *i-Ph*$_2$P), 133.4 (d, $^2J_{PC}$= 17.5 Hz, *o-Ph*$_2$P), 129.0 (*p-Ph*$_2$P), 128.8 (d, $^3J_{PC}$ = 6.9 Hz, *m-Ph*$_2$P), 125.8 (*p*-N*Ar*), 123.9 (*m*-N*Ar*), 95.8 (MeC(N)*C*H), 47.2 (d, $^2J_{PC}$ = 12.8 Hz, N*C*H$_2$), 31.9 (d, $^1J_{PC}$ = 4.3 Hz, P*C*H$_2$), 28.3 (Ar*C*HMe$_2$), 25.1 (ArCH*Me*$_2$), 23.7 (ArCH*Me*$_2$), 23.5 (*Me*C), 21.8 (*Me*C).

^{31}P{^{1}H} NMR (162 MHz, C_6D_6, 298 K): δ = -27.4.

^{1}H, ^{1}H GCOSY (400 MHz / 400 MHz, C_6D_6, 298 K) [selected traces]: δ ^{1}H / δ ^{1}H = 7.45 / 7.05 (*o-Ph*$_2$P / *m-Ph*$_2$P), 3.36 / 2.36 (N*CH$_2$* / PC*H$_2$*), 3.36 / 1.29, 1.18 (ArC*H*Me$_2$ / ArCH*Me*$_2$).

^{1}H, ^{13}C GHSQC (400 MHz / 101 MHz, C_6D_6, 298 K): δ ^{1}H / δ ^{13}C = 7.45 / 133.4 (*o-Ph*$_2$P), 7.16 / 125.8 (*p*-N*Ar*), 7.14 / 123.9 (*m*-N*Ar*), 7.05 / 129.0, 128.8 (*p-Ph*$_2$P, *m-Ph*$_2$P), 4.78 / 95.8 (MeC(N)*CH*), 3.36 / 47.2, 28.3 (N*CH*$_2$, Ar*CH*Me$_2$,), 2.36 / 31.9 (P*CH*$_2$), 1.68 / 23.5 (*Me*C), 1.60 / 21.8 (*Me*C), 1.29 / 25.1 (ArCH*Me*$_2$), 1.18 / 23.7 (ArCH*Me*$_2$).

^{1}H, ^{13}C GHMBC (400 MHz / 101 MHz, C_6D_6, 298 K) [selected traces]: δ ^{1}H / δ ^{13}C = 7.45 / 129.0 (o-*Ph*$_2$P / *p-Ph*$_2$P), 7.16 / 142.4, 123.9 (*p*-N*Ar* / *o*-N*Ar*, *m*-N*Ar*), 4.78 / 167.8, 145.5, 47.2 (MeC(N)C*H* / Me*C*, *i*-N*Ar* , N*C*H$_2$), 3.36 / 167.8, 31.9 (NC*H$_2$* / Me*C*, P*C*H$_2$), 3.36 / 25.1, 23.7 (PC*H$_2$* / ArCH*Me$_2$*), 2.36 / 137.4 (PC*H$_2$* / *i-Ph*$_2$P), 1.68 / 166.4 (*Me*C / Me*C*), 1.29, 1.18 / 142.4 (ArCH*Me*$_2$ / *o*-N*Ar*).

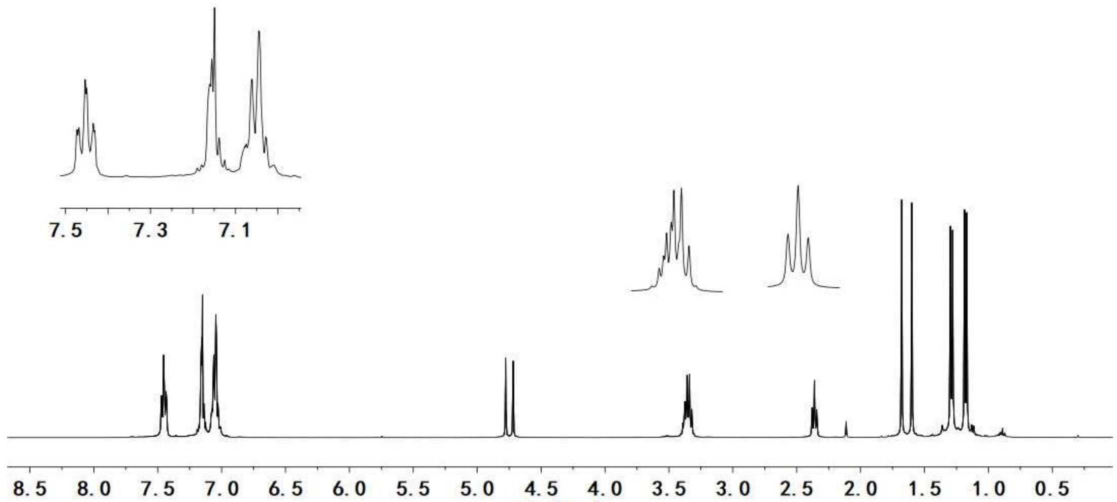


Fig. S20. ^{1}H NMR (400 MHz, C_6D_6, 298 K)

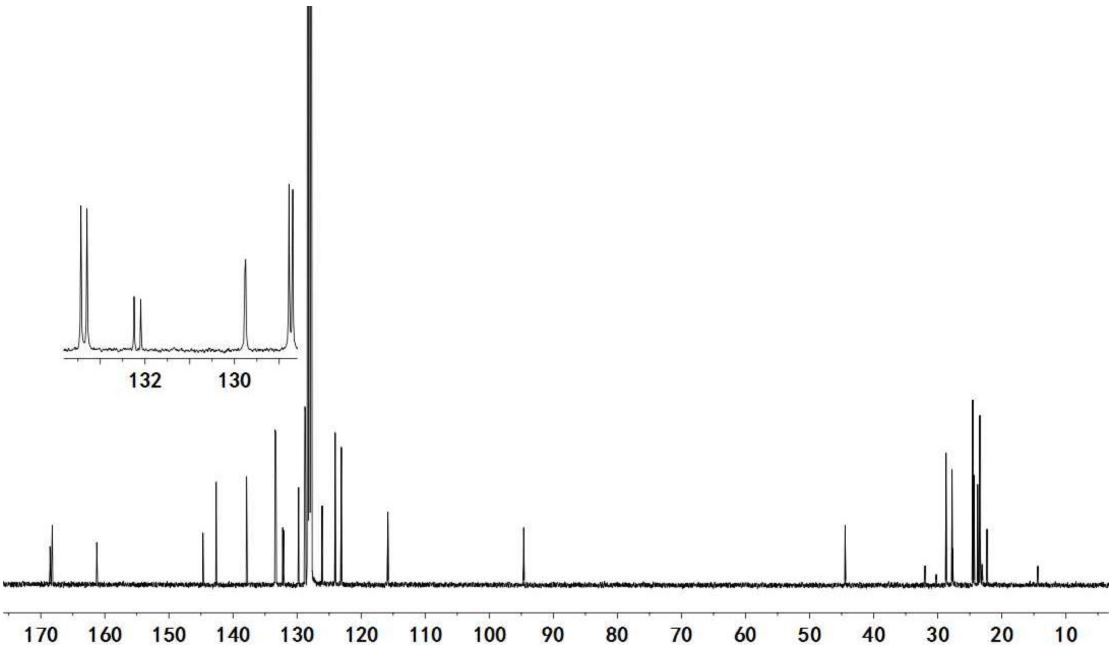


Fig. S21. ^{13}**C{**^{1}**H} NMR** (101 MHz, C_6D_6, 298 K)

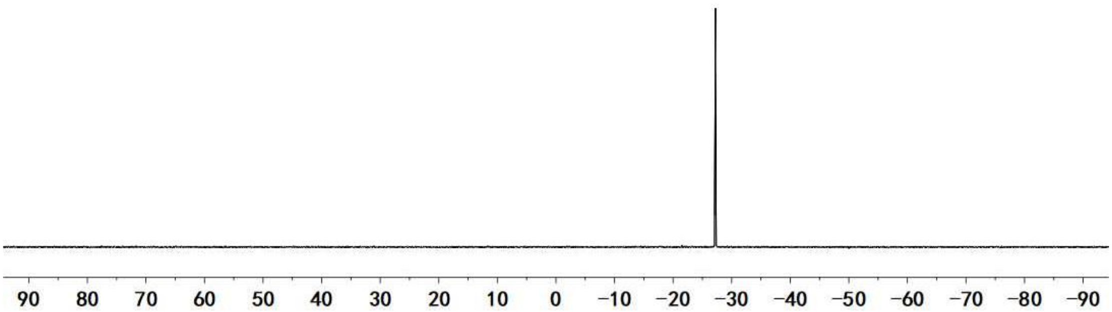


Fig. S22. ^{31}**P{**^{1}**H} NMR** (162 MHz, C_6D_6, 298 K)

X-ray crystal structure analysis of complex 3a: formula $C_{31}H_{39}N_2PZn$, M = 536.00 gmol^{-1}, colorless, 0.22 x 0.15 x 0.10mm, Triclinic, space group P-1, a = 8.6965(4), b = 11.5479(5), c = 14.1617(6) Å, α = 95.6760(10)°, β = 98.3260(10)°, γ = 96.3300(10)° V = 1389.06(11) Å^3, ρ_{calc} = 1.281 gcm^{-3}, μ = 0.963 mm^{-1}, empirical absorption correction (0.6912 ≤ T ≤ 0.7456), Z = 2, λ = 0.71073 Å, T = 120(2) K, 46146 reflections collected (-11 ≤ h ≤ 11, -14 ≤ k ≤ 14, -18 ≤ l ≤ 18), 6369 independent (R_{int} = 0.0503) and 5455 observed reflections [I>2σ(I)], 326 refined parameters, the final R_1 was 0.0276 (I > 2σ(I)) and wR_2 was 0.0719 (all data). max. (min.) residual electron density 0.377 (-0.263) e.Å^{-3}, hydrogen atoms except for hydrides were placed in calculated positions and refined using a riding model, the hydride atom in this structure was located in a Fourier difference map and was refined with isotropic displacement parameters.

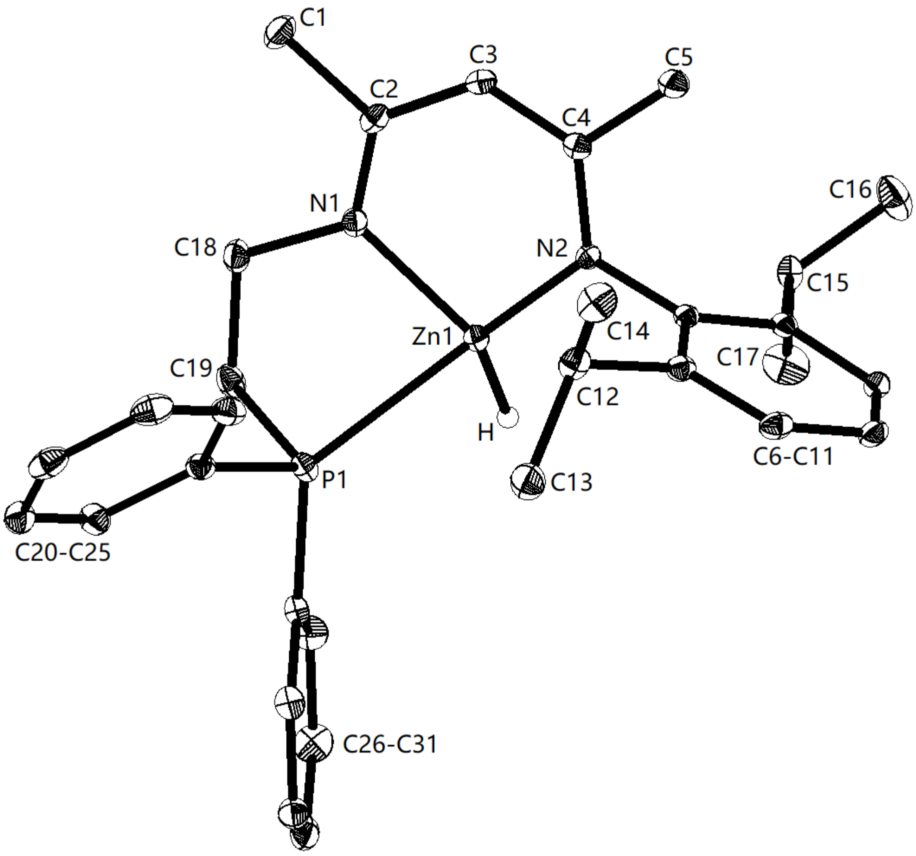
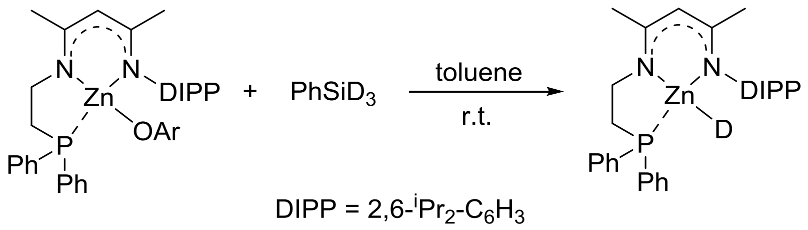


Fig. S23. Molecular structure of complex **3a**.

Preparation of complex 3a-*D*:



2a **3a-*D***

Scheme S8.

Following the procedure described for **3a**, reaction of $PhSiD_3$ (77 mg, 0.7 mmol) with **2a** (500 mg, 0.7 mmol) gave **3a-*D*** as a white solid (274 mg, 74% yield).

FTIR Spectrum: *ν*(Zn-D) = 1255 cm^{-1}.

^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 7.45 (m, 4H, *o-Ph*$_2$P), 7.16 (m, H, *p*-N*Ar*), 7.14 (m, 2H, *m*-N*Ar*), 7.05 (m, 6H, *m*, *p-Ph*$_2$P), 4.78 (s, 1H, MeC(N)C*H*), 3.36 (m, 4H, NCH_2, ArC*H*Me$_2$), 2.36 (t, $^3J_{HH}$ = 7.0 Hz, 2H, PCH_2), 1.68 (s, 3H, *Me*C), 1.60 (s, 3H, *Me*C), 1.29 (d, $^3J_{HH}$ = 6.8 Hz, 6H, ArCH*Me*$_2$), 1.18 (d, $^3J_{HH}$ = 6.9 Hz, 3H, ArCH*Me*$_2$).

^{31}P{^{1}H} NMR (162 MHz, C_6D_6, 298 K): δ = -27.2

^{2}H NMR (92 MHz, C_6H_6 / C_6D_6 (100:1), 298 K): δ = 4.75 (Zn*D*).

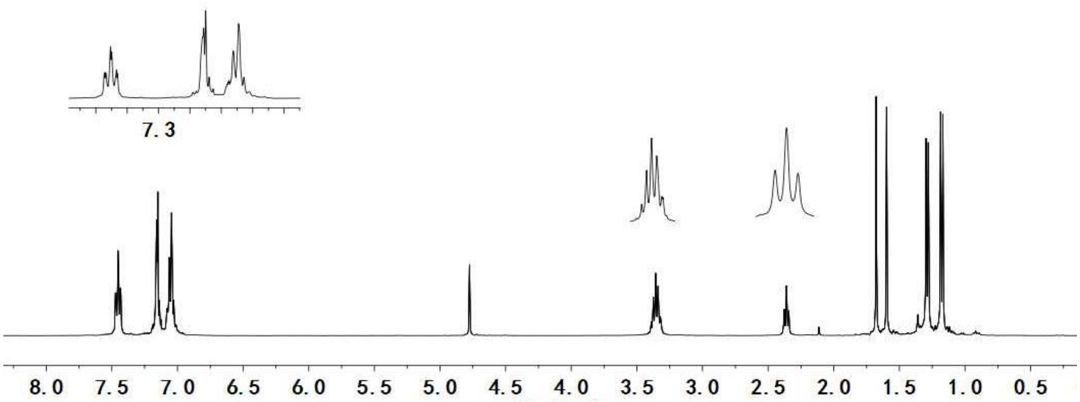


Fig. S24. ^{1}H NMR (400 MHz, C_6D_6, 298 K)

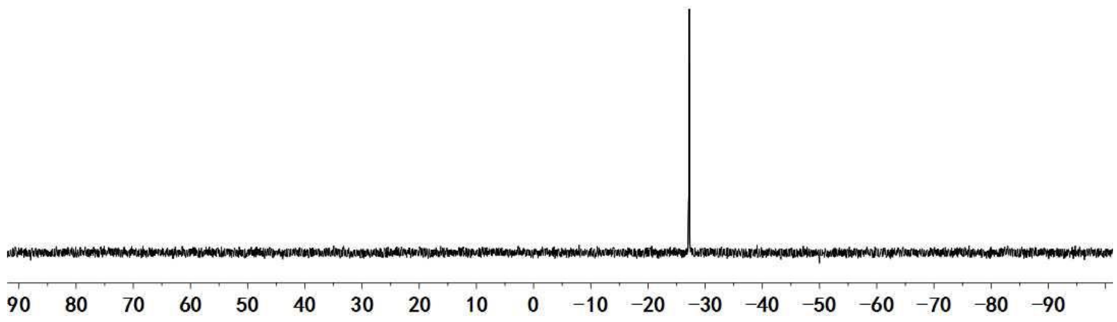


Fig. S25. ^{31}P{^{1}H} NMR (162 MHz, C_6D_6, 298 K)

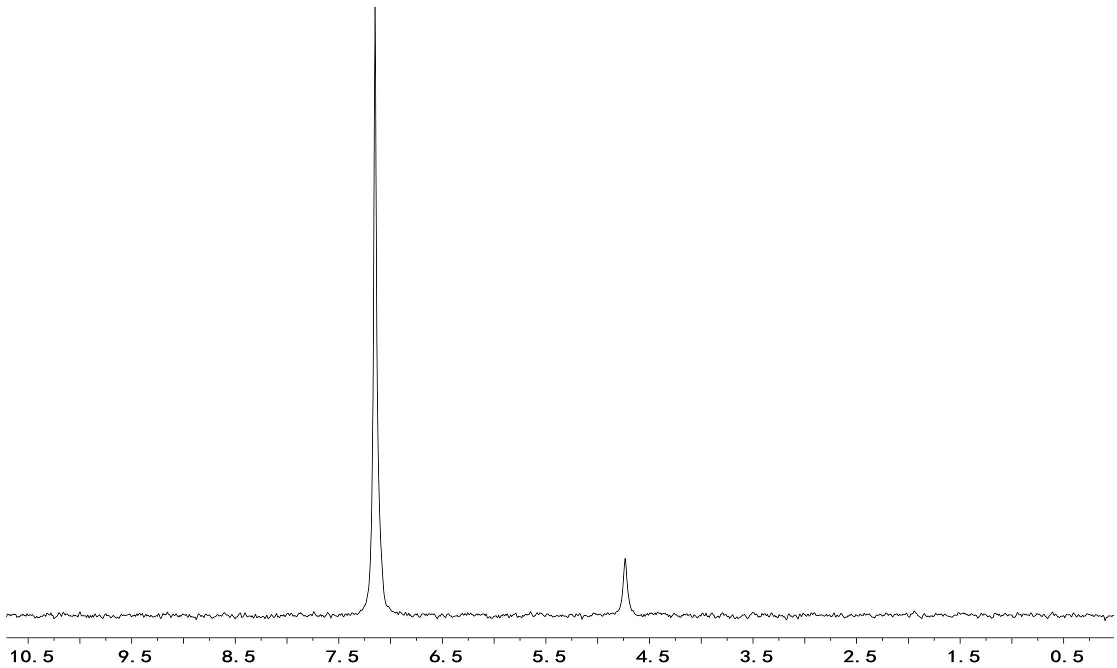
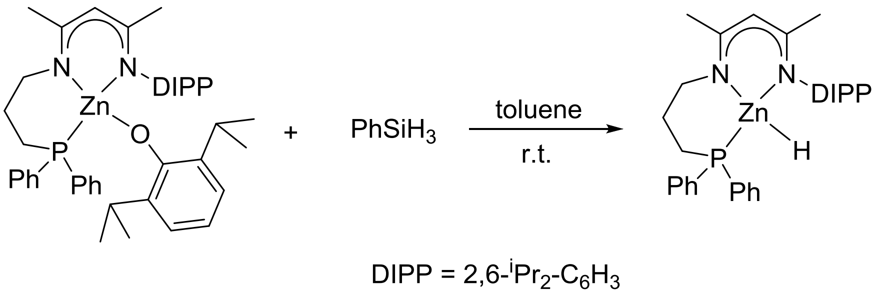


Fig. S26. ^{2}H NMR (92 MHz, C_6H_6 / C_6D_6 (100:1), 298 K)

Preparation of complex 3b:



2b **3b**

Scheme S9.

Following the procedure described for **3a**, reaction of $PhSiH_3$ (108 mg, 1.0 mmol) with **2b** (726 mg, 1.0 mmol) gave **3b** as a white solid (418 mg, 76%). Crystals suitable for the X-ray crystal structure analysis were grown from a layered toluene / hexane (v/v: 1:2) solution at -30^{o}C.

Elemental Analysis: calcd. for $C_{32}H_{41}N_2PZn$: C, 69.88; H, 7.51; N, 5.09. Found: C, 69.96; H, 7.64; N, 4.77.

IR: ν(Zn-H) = 1733 cm^{-1}.

^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 7.55 (m, 4H, *o*-*Ph*$_2$P), 7.10 (m, 2H, *m*-N*Ar*), 7.09 (m, 1H, *p*-N*Ar*), 7.08 (m, 4H, *m*-*Ph*$_2$P), 7.05 (m, 2H, *p*-*Ph*$_2$P), 4.72 (s, 1H, MeC(N)C*H*), 4.71 (s, 1H, Zn*H*), 3.46 (m, 2H, ArC*H*Me$_2$), 3.35 (m, 2H, NC*H*$_2$), 2.10 (m, 2H, PC*H*$_2$), 1.71 (s, 3H, *Me*C), 1.60 (s, 3H, *Me*C), 1.40 (m, 2H, NCH$_2$C*H*$_2$), 1.18 (d, $^3J_{HH}$ = 6.8 Hz, 6H, ArCH*Me*$_2$), 1.16 (d, $^3J_{HH}$ = 6.8 Hz, 6H, ArCH*Me*$_2$).

^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 298 K): δ = 167.4 (Me*C*), 166.1 (Me*C*), 146.2 (*i*-N*Ar*), 142.7 (*o*-N*Ar*), 135.8 (br, *i*-*Ph*$_2$P), 133.6 (d, $^2J_{PC}$ = 16.1 Hz, *o*-*Ph*$_2$P), 129.4 (*p*-*Ph*$_2$P), 128.7 (d, $^3J_{PC}$ = 7.2 Hz, *m*-*Ph*$_2$P), 125.5 (*p*-N*Ar*), 123.9 (*m*-N*Ar*), 95.1 (MeC(N)*C*H), 52.6 (N*C*H$_2$), 28.4 (br, P*C*H$_2$), 28.3 (Ar*C*HMe$_2$), 26.9 (d, $^2J_{PC}$ = 4.5 Hz, NCH$_2$*C*H$_2$), 25.0 (ArCH*Me*$_2$), 24.0 (ArCH*Me*$_2$), 23.7 (*Me*C), 20.9 (*Me*C).

^{31}P{^{1}H} NMR (162 MHz, C_6D_6, 298 K): δ = -18.9.

^{1}H, ^{1}H GCOSY (400 MHz / 400 MHz, C_6D_6, 298 K) [selected traces]: δ ^{1}H / δ ^{1}H = 7.55 / 7.08 (*o*-*Ph*$_2$P / *m*-*Ph*$_2$P), 3.46 / 1.18, 1.16 (ArC*H*Me$_2$ / ArCH*Me*$_2$), 3.35 / 1.40 (NC*H*$_2$ / NCH$_2$C*H*$_2$), 2.10 / 1.40 (PC*H*$_2$ / NCH$_2$C*H*$_2$).

^{1}H, ^{13}C GHSQC (400 MHz / 101 MHz, C_6D_6, 298 K): δ ^{1}H / δ ^{13}C = 7.55 / 133.6 (*o*-*Ph*$_2$P), 7.10 / 123.9 (*m*-N*Ar*), 7.09 / 125.5 (*p*-N*Ar*), 7.08 / 128.7 (*m*-*Ph*$_2$P), 7.05 /

129.4 (*p*-*Ph*$_2$P), 4.72 / 95.1 (MeC(N)*CH*), 3.46 / 28.3 (Ar*CH*Me$_2$), 3.35 / 52.6 (N*CH*$_2$), 2.10 / 28.4 (P*CH*$_2$), 1.71 / 23.7 (*Me*C), 1.60 / 20.9 (*Me*C), 1.40 / 26.9 (NCH$_2$*CH*$_2$), 1.18 / 25.0 (ArCH*Me*$_2$), 1.16 / 24.0 (ArCH*Me*$_2$).

^{1}H, ^{13}C GHMBC (400 MHz / 101 MHz, C_6D_6, 298 K) [selected traces]: δ ^{1}H / δ ^{13}C = 7.55 / 133.6, 129.4 (*o*-*Ph*$_2$P / *o*-*Ph*$_2$P, *p*-*Ph*$_2$P), 7.10 / 146.2, 123.9 (*m*-N*Ar* / *i*-N*Ar*, *m*-N*Ar*), 7.09 / 142.7 (*p*-N*Ar* / *o*-N*Ar*), 3.46 / 146.2, 142.7, 123.9 (ArC*H*Me$_2$ / *i*-N*Ar*, *o*-N*Ar*, *m*-N*Ar*), 2.10 / 135.8 (PC*H*$_2$ / *i*-*Ph*$_2$P), 1.18, 1.16 / 142.7 (ArCH*Me*$_2$ / *o*-N*Ar*).

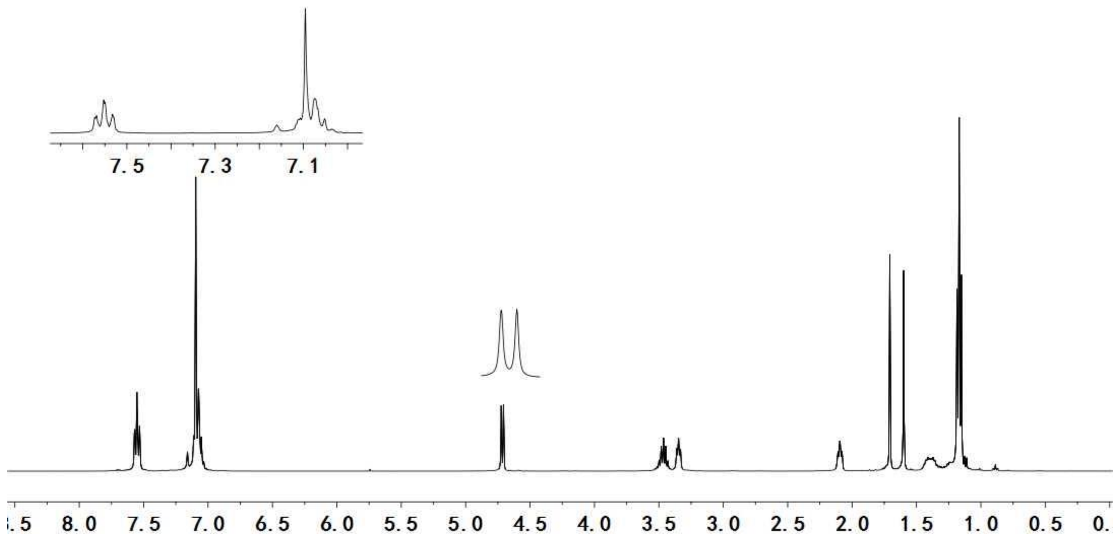


Fig. S27. ^{1}H NMR (400 MHz, C_6D_6, 298 K)

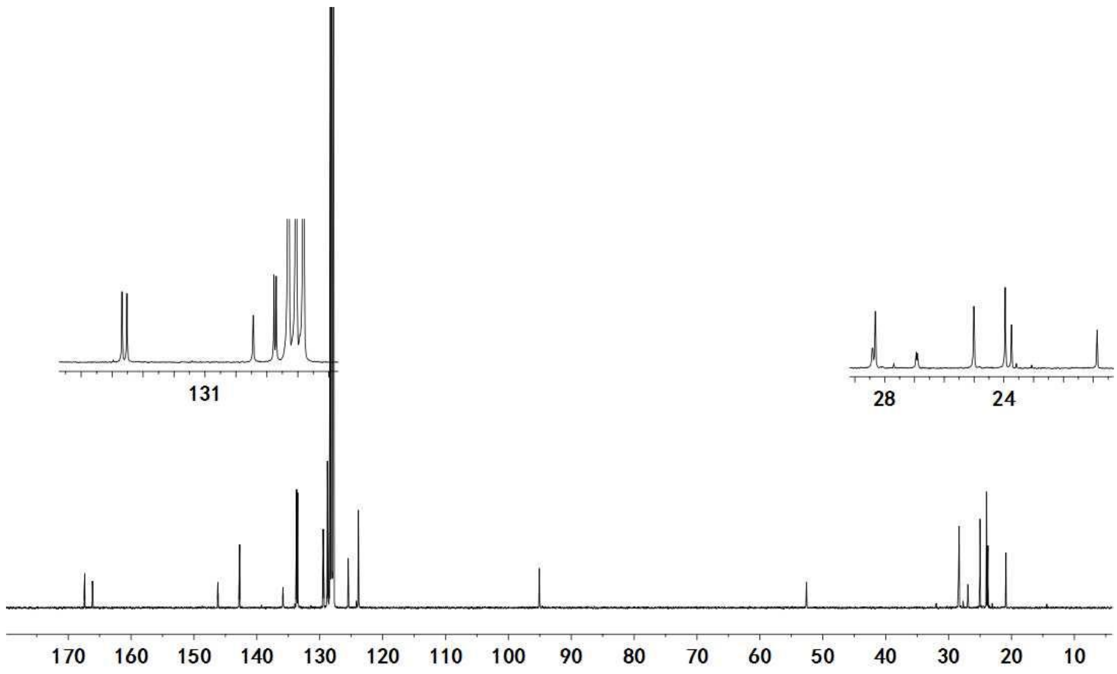


Fig. S28. ^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 298 K)

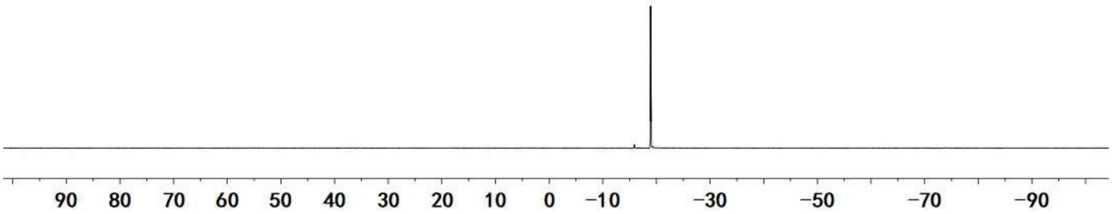


Fig. S29. ^{31}**P{**^{1}**H} NMR** (162 MHz, C_6D_6, 298 K)

X-ray crystal structure analysis of complex 3b: formula $C_{32}H_{41}N_2PZn$, M = 550.03 gmol^{-1}, colorless, 0.300 x 0.250 x 0.100 mm, Triclinic, space group P-1, a = 9.9277(11), b = 10.6844(14), c = 15.122(2) Å, α = 72.783(12)°, β = 78.335(10)°, γ = 86.922(10)° V = 1500.5(3) Å^3, ρ_{calc} = 1.217 gcm^{-3}, μ = 0.890 mm^{-1}, empirical absorption correction (0.82329 ≤ T ≤ 1.00000), Z = 2, λ = 0.71073 Å, T = 223(2) K, 13114 reflections collected (-11 ≤ h ≤ 11, -12 ≤ k ≤ 10, -17 ≤ l ≤ 17), 5285 independent (R_{int} = 0.1225) and 2273 observed reflections [I>2σ(I)], 331 refined parameters, the final R_1 was 0.0787 (I > 2σ(I)) and wR_2 was 0.1635 (all data). max. (min.) residual electron density 0.706 (-0.468) e.Å^{-3}, hydrogen atoms except for hydrides were placed in calculated positions and refined using a riding model, the hydride atom in this structure was located in a Fourier difference map and was refined with isotropic displacement parameters.

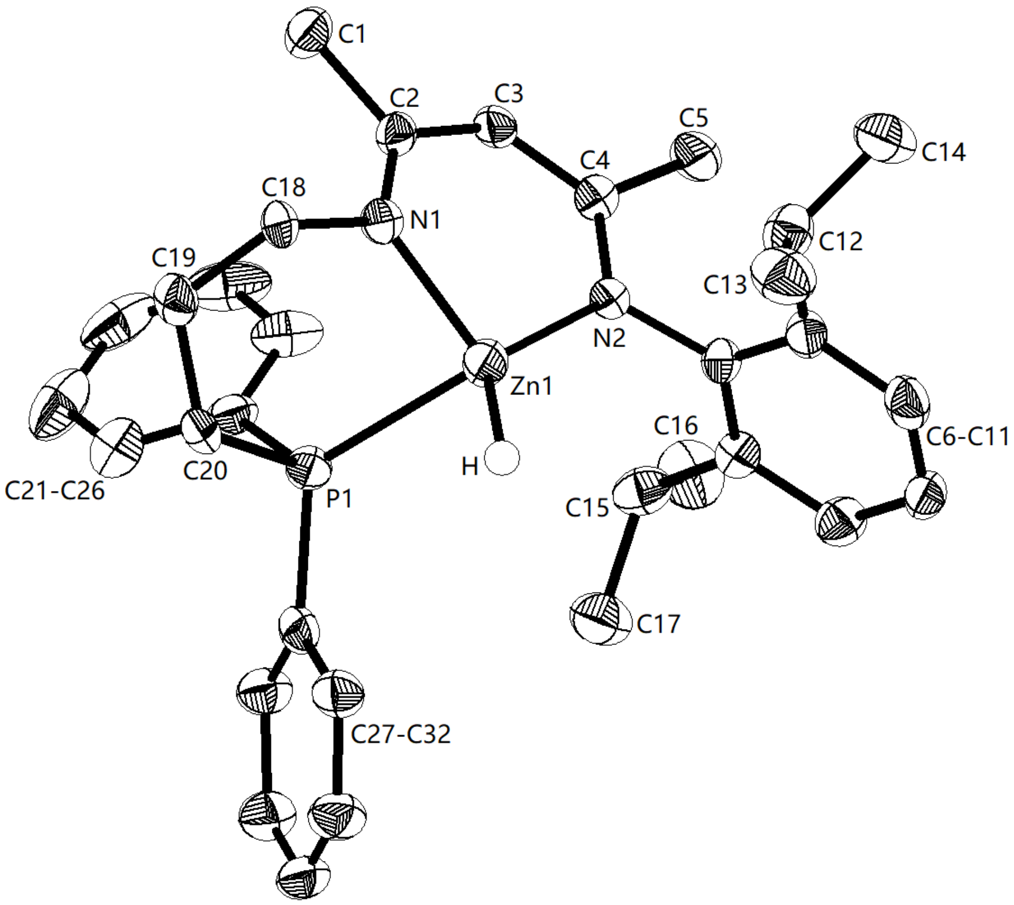
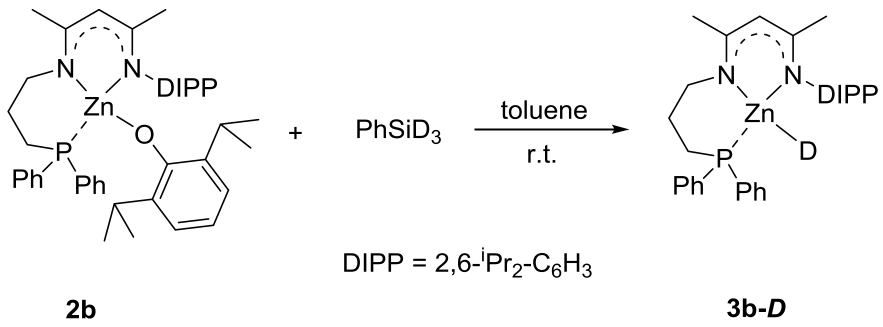


Fig. S30. Molecular structure of complex **3b**.

Preparation of complex 3b-*D*:



Scheme S10.

Following the procedure described for **3b**, reaction of $PhSiD_3$ (56 mg, 0.5 mmol) with **2b** (363 mg, 0.5 mmol) gave **3b-*D*** as a white solid (218 mg, 79% yield).

FTIR Spectrum: ν(Zn-D) = 1247 cm^{-1}.

^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 7.56 (m, 4H, *o-Ph*$_2$P), 7.11 (m, 3H, *m,p*-N*Ar*), 7.08 (m, 4H, *m-Ph*$_2$P), 7.04 (m, 2H, *p-Ph*$_2$P), 4.74 (s, 1H, MeC(N)C*H*), 3.48 (m, 2H, ArC*H*Me$_2$), 3.43 (m, 2H, NC*H*$_2$), 2.11 (m, 2H, PC*H*$_2$), 1.73 (s, 3H, *Me*C), 1.58 (s, 3H, *Me*C), 1.38 (m, 2H, NCH$_2$C*H*$_2$), 1.17 (d, $^3J_{HH}$ = 6.9 Hz, 6H, ArCH*Me*$_2$), 1.16 (d, $^3J_{HH}$ = 6.8 Hz, 6H, ArCH*Me*$_2$).

^{31}P{^{1}H} NMR (162 MHz, C_6D_6, 298 K): δ = -19.3.

^{2}H NMR (92 MHz, C_6H_6 / C_6D_6 (100:1), 298 K): δ = 4.73 (Zn*D*).

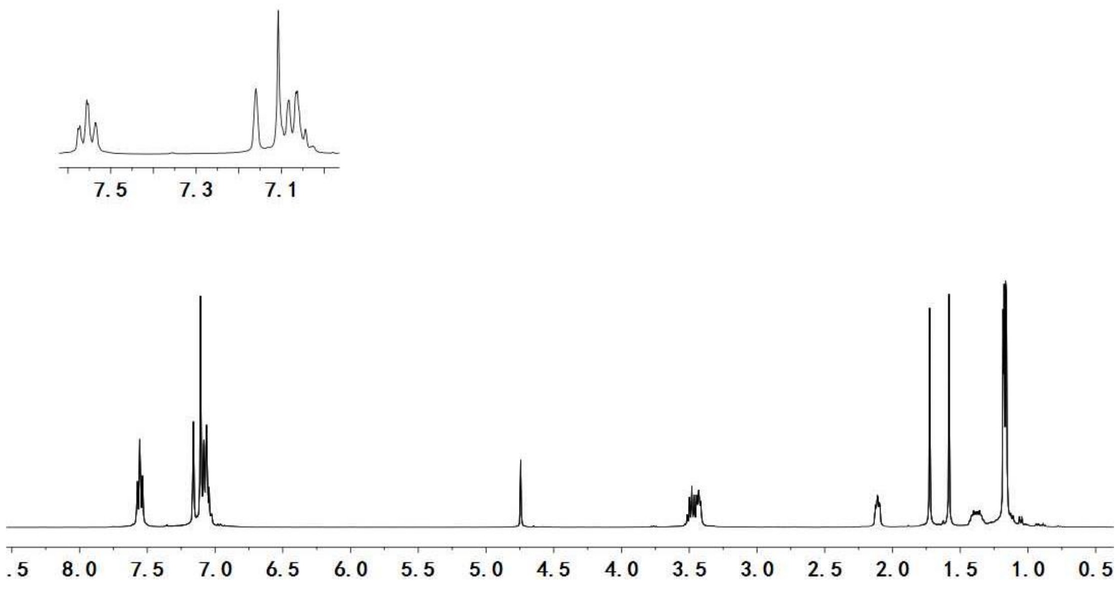


Fig. S31. ^{1}H NMR (400 MHz, C_6D_6, 298 K)

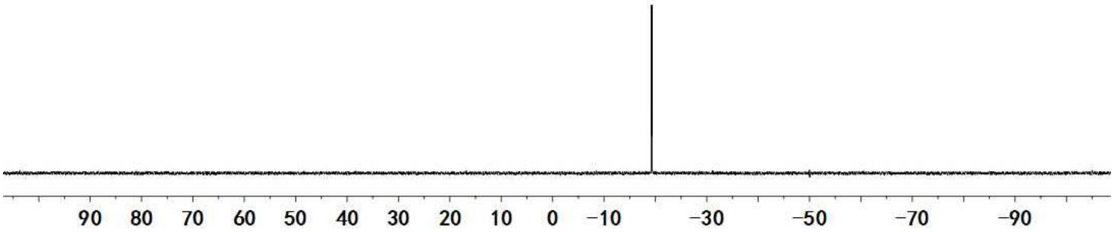


Fig. S32. $^{31}P\{^{1}H\}$ NMR (162 MHz, C_6D_6, 298 K)

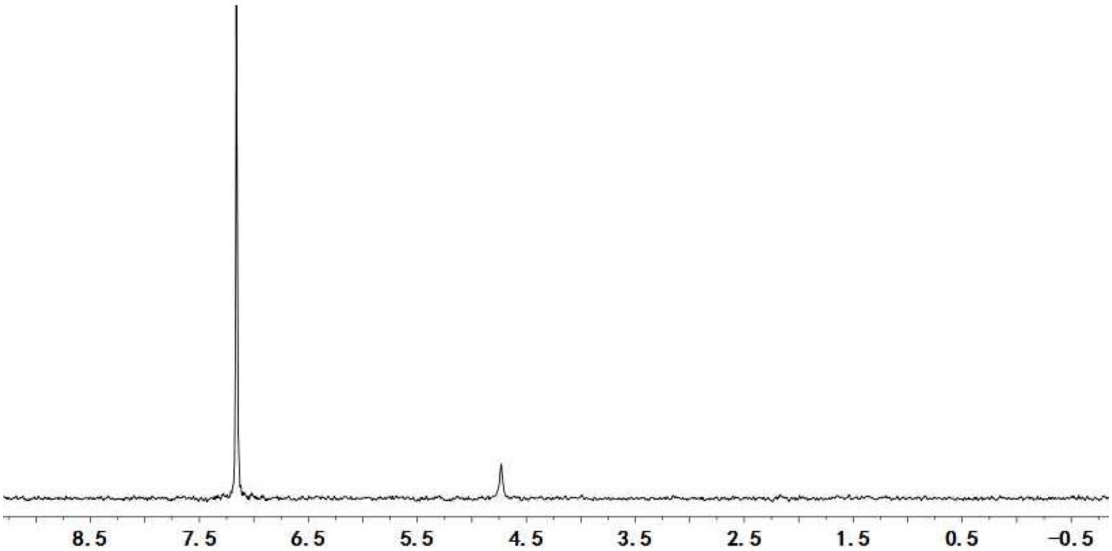
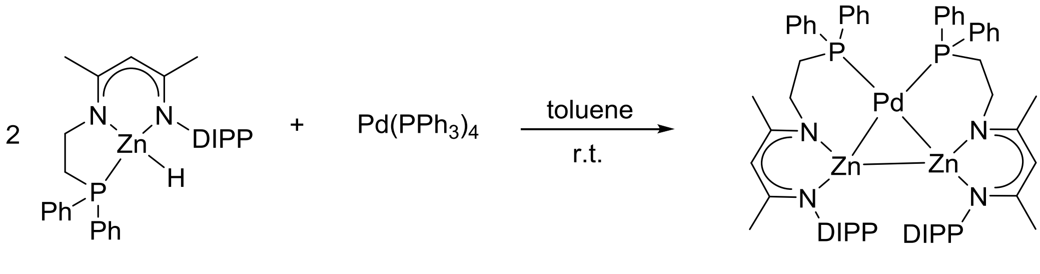


Fig. S33. ^{2}H NMR (92 MHz, C_6H_6 / C_6D_6 (100:1), 298 K)

Preparation of complex 4a:



DIPP = 2,6-$^{i}Pr_2$-C_6H_3

3a **4a**

Scheme S11.

$Pd(PPh_3)_4$ (324 mg, 0.28 mmol) was added to a solution of **3a** (300 mg, 0.56 mmol) in toluene (4 mL) and the reaction mixture was stirred for 1 h at room temperature. The volatiles were removed under vacuum, and then the residue was washed with hexane (4*1 mL) to finally give **4a** as a pale orange solid (263 mg, 80%). Crystals suitable for the X-ray crystal structure analysis were grown from a layered toluene / hexane (v/v: 1:2) solution at room temperature.

Elemental Analysis: calcd. for $C_{62}H_{76}N_4P_2PdZn_2$: C, 63.30; H, 6.51; N, 4.76. Found: C, 63.04; H, 6.61; N, 4.37.

^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 7.70 (m, 4H, *o-Ph*$_2$P), 7.24 (m, 4H, *o-Ph*$_2$P), 7.18 (m, 2H, *m*-N*Ar*), 7.11 (m, 2H, *p*-N*Ar*), 7.08 (m, 6H, *m, p-Ph*$_2$P), 7.03 (m, 6H, *m, p-Ph*$_2$P), 6.87 (m, 2H, *m*-N*Ar*), 4.96 (s, 2H, MeC(N)C*H*), 3.50 (m, 4H, NC*H*$_2$, ArC*H*Me$_2$), 3.17 (m, 2H, NC*H*$_2$), 2.64 (m, 2H, ArC*H*Me$_2$), 2.40 (m, 2H, PC*H*$_2$), 2.01 (m, 2H, PC*H*$_2$), 1.96 (s, 6H, *MeC*), 1.76 (s, 6H, *MeC*), 1.36 (d, $^3J_{HH}$ = 7.0 Hz, 6H, ArCH*Me*$_2$), 1.28 (d, $^3J_{HH}$ = 6.8 Hz, 6H, ArCH*Me*$_2$), 0.96 (d, $^3J_{HH}$ = 6.9 Hz, 6H, ArCH*Me*$_2$), 0.30 (d, $^3J_{HH}$ = 6.7 Hz, 6H, ArCH*Me*$_2$).

^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 298 K): δ = 165.1 (Me*C*), 164.7 (Me*C*), 146.5 (*i*-N*Ar*), 145.7 (d, $^1J_{PC}$ = 9.6 Hz, *i-Ph*$_2$P), 145.6 (d, $^1J_{PC}$ = 9.3 Hz, *i-Ph*$_2$P), 143.3 (*o*-N*Ar*), 142.1 (*o*-N*Ar*), 141.5 (d, $^1J_{PC}$ = 9.4 Hz, *i-Ph*$_2$P), 141.4 (d, $^1J_{PC}$ = 9.6 Hz, *i-Ph*$_2$P), 136.6 (d, $^2J_{PC}$ = 11.3 Hz, *o-Ph*$_2$P), 136.5 (d, $^2J_{PC}$ = 10.9 Hz, *o-Ph*$_2$P), 131.1 (d, $^2J_{PC}$ = 6.4 Hz, *o-Ph*$_2$P), 131.0 (d, $^2J_{PC}$ = 6.2 Hz, *o-Ph*$_2$P), 129.4 (*p-Ph*$_2$P), 128.1 (overlapped with solvent, *m-Ph*$_2$P)[1], 126.7 (*p-Ph*$_2$P), 124.9 (*p*-N*Ar*), 123.6 (*m*-N*Ar*), 123.1 (*m*-N*Ar*), 96.5 (MeC(N)*C*H), 48.3 (N*C*H$_2$), 38.8 (d, $^1J_{PC}$ = 12.8 Hz, P*C*H$_2$), 38.7

(d, $^{1}J_{PC}$ = 12.9 Hz, P*C*H_2), 28.9 (Ar*C*HMe$_2$), 28.1 (Ar*C*HMe$_2$), 26.9 (ArCH*Me*$_2$), 25.2 (ArCH*Me*$_2$), 24.2 (ArCH*Me*$_2$), 24.0 (*Me*C), 23.0 (ArCH*Me*$_2$), 21.7 (*Me*C) [^{1}from the ^{1}H, ^{13}C GHSQC experiment].

^{31}P{^{1}H} NMR (162 MHz, C_6D_6, 298 K): δ = 15.2.

^{1}H, ^{1}H GCOSY (400 MHz / 400 MHz, C_6D_6, 298 K) [selected traces]: δ ^{1}H / δ ^{1}H = 7.70 / 7.08 (*o-Ph*$_2$P / *m-Ph*$_2$P), 6.87 / 7.11 (*m*-N*Ar* / *p*-N*Ar*), 3.50 / 3.17, 2.40 (NC*H*$_2$ / NC*H*$_2$, PC*H*$_2$), 2.64 / 0.96, 0.30 (ArC*H*Me$_2$ / ArCH*Me*$_2$), 2.40 / 2.01 (PC*H*$_2$ / PC*H*$_2$), 1.36 / 3.50 (ArCH*Me*$_2$ / NC*H*$_2$).

^{1}H, ^{13}C GHSQC (400 MHz / 101 MHz, C_6D_6, 298 K): δ ^{1}H / δ ^{13}C = 7.70 / 136.6, 136.5 (*o-Ph*$_2$P), 7.24 / 131.1, 131.0 (*o-Ph*$_2$P), 7.18 / 123.6 (*m*-N*Ar*), 7.11 / 124.9 (*p*-N*Ar*), 7.08 / 129.4 (*p-Ph*$_2$P), 7.08 / 128.1 (*m-Ph*$_2$P), 7.03 / 126.7 (*p-Ph*$_2$P), 7.03 / 128.1 (m-*Ph*$_2$P), 6.87 / 123.6 (*m*-N*Ar*), 4.96 / 96.5 (MeC(N)*CH*), 3.50, 3.17 / 48.3 (N*CH*$_2$), 3.50 / 28.9 (Ar*CH*Me$_2$), 2.64 / 28.1 (Ar*CH*Me$_2$), 2.40, 2.01 / 38.8 (P*CH*$_2$), 2.40, 2.01 / 38.7 (P*CH*$_2$), 1.96 / 21.7 (*MeC*), 1.76 / 24.0 (*MeC*), 1.36 / 24.2 (ArCH*Me*$_2$), 1.28 / 25.2 (ArCH*Me*$_2$), 0.96 / 23.0 (ArCH*Me*$_2$), 0.30 / 26.9 (ArCH*Me*$_2$).

^{1}H, ^{13}C GHMBC (400 MHz / 101 MHz, C_6D_6, 298 K) [selected traces]: δ ^{1}H / δ ^{13}C = 7.70 / 129.4 (*o-Ph*$_2$P / *m-Ph*$_2$P), 7.24 / 126.7 (*o-Ph*$_2$P / *m-Ph*$_2$P), 7.18 / 146.5 (*m*-N*Ar* / *i*-N*Ar*), 7.11 / 142.1 (*p*-N*Ar* / *o*-N*Ar*), 4.96 / 146.5 (MeC(N)C*H* / *i*-N*Ar*), 3.50 / 142.1 (ArC*H*Me$_2$ / *o*-N*Ar*), 2.64 / 143.3 (ArC*H*Me$_2$ / *o*-N*Ar*), 1.96 / 164.7 (*Me*C / Me*C*), 1.36 1.28 / 28.9 (ArCH*Me*$_2$ / Ar*C*HMe$_2$), 0.96, 0.30 / 28.1 (ArCH*Me*$_2$ / Ar*C*HMe$_2$).

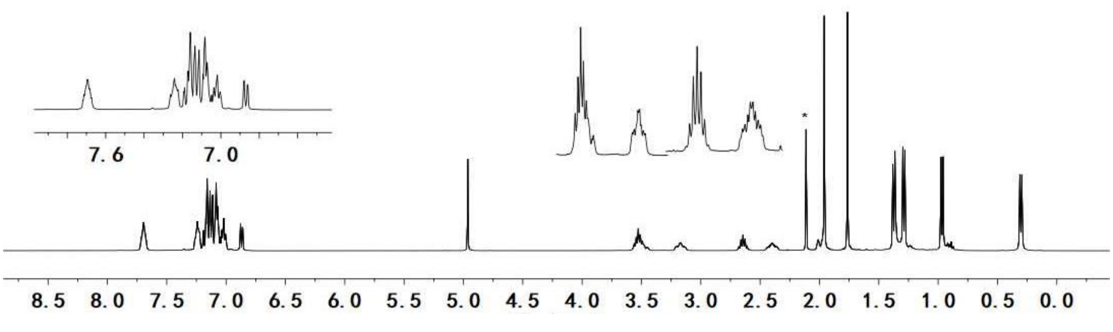


Fig. S34. ^{1}H NMR (400 MHz, C_6D_6, 298 K) [*: toluene]

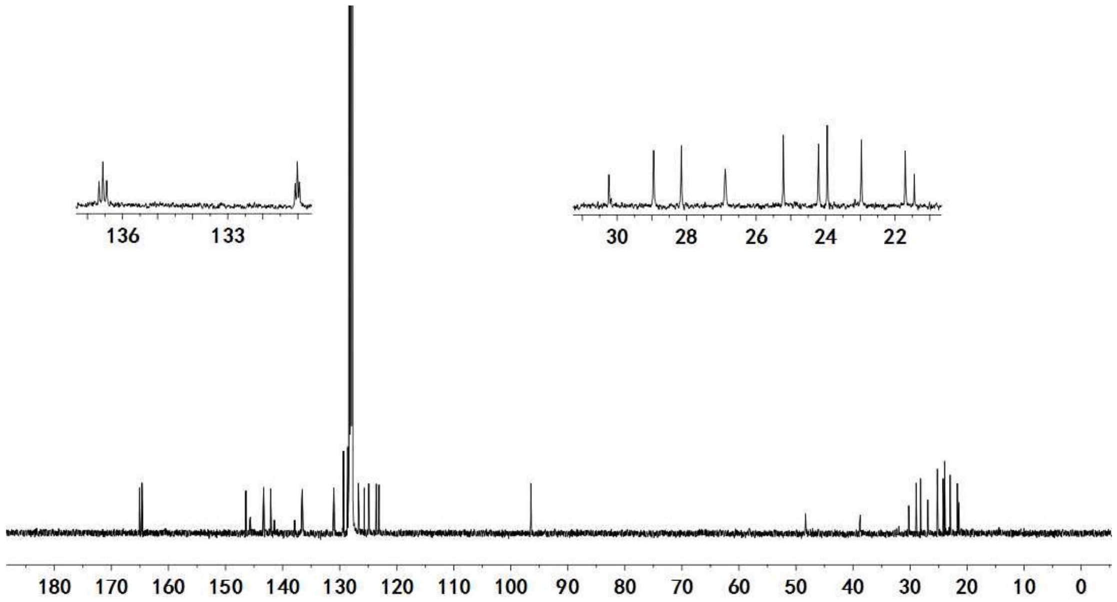


Fig. S35. ^{13}**C{**^{1}**H} NMR** (101 MHz, C_6D_6, 298 K)

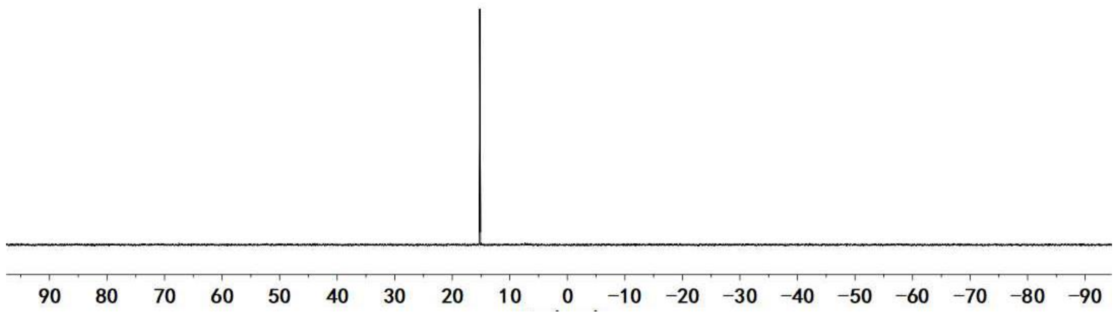


Fig. S36. ^{31}**P{**^{1}**H} NMR** (162 MHz, C_6D_6, 298 K)

X-ray crystal structure analysis of complex 4a: formula $C_{62}H_{76}N_4P_2PdZn_2$ $2C_7H_8$, M = 1360.66 gmol^{-1}, orange, 0.25 x 0.2 x 0.15 mm, Triclinic, space group P-1, a = 13.2882(9), b = 13.5207(9), c = 19.9980(14) Å, α = 83.034(2)°, β = 73.547(2)°, γ = 81.356(2)° V = 3394.9(4) Å^3, ρ_{calc} = 1.331 gcm^{-3}, μ = 1.055 mm^{-1}, empirical absorption correction (0.6912 ≤ T ≤ 0.7456), Z = 2, λ = 0.71073 Å, T = 120(2) K, 124299 reflections collected (-17 ≤ h ≤ 17, -17 ≤ k ≤ 17, -25 ≤ l ≤ 25), 15654 independent (R_{int} = 0.0851) and 11206 observed reflections [I>2σ(I)], 780 refined parameters, the final R_1 was 0.0389 (I > 2σ(I)) and wR_2 was 0.1006 (all data). max. (min.) residual electron density 1.121 (-0.705) e.Å^{-3}, hydrogen atoms were placed in calculated positions and refined using a riding model.

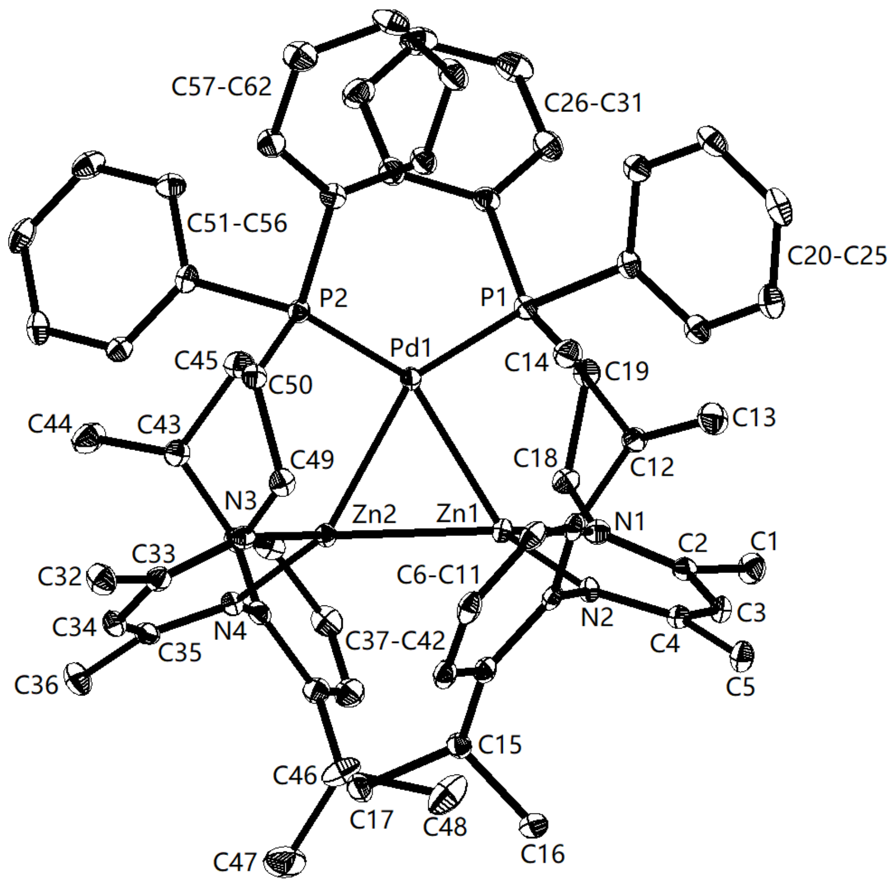
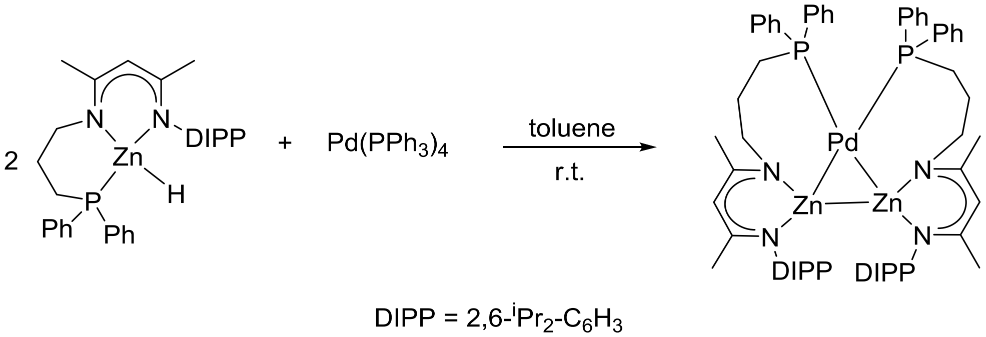


Fig. S37. Molecular structure of complex **4a**.

Preparation of Complex 4b:



3b **4b**

Scheme S12.

Following the procedure described for **4a**, reaction of $Pd(PPh_3)_4$ (289 mg, 0.25 mmol) with **3b** (275 mg, 0.50 mmol) gave **4b** as a yellow crystalline solid (196 mg, 65%). Crystals suitable for the X-ray crystal structure analysis were grown from a layered toluene / hexane (v/v: 1:2) solution at room temperature.

Elemental Analysis: calcd. for $C_{64}H_{80}N_4P_2PdZn_2$: C, 63.82; H, 6.69; N, 4.65. Found: C, 64.38; H, 7.01; N, 4.18.

^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 7.38 (m, 4H, *o-Ph*$_2$P), 7.22 (m, 4H, *o-Ph*$_2$P), 7.17 (m, 2H, *m*-N*Ar*), 7.12 (m, 2H, *p*-N*Ar*), 7.07 (m, 2H, *m*-N*Ar*), 7.04 (m, 4H, *m-Ph*$_2$P), 7.02 (m, 2H, *p-Ph*$_2$P), 6.99 (m, 2H, *p-Ph*$_2$P), 6.90 (m, 4H, *m-Ph*$_2$P), 4.85 (s, 2H, MeC(N)C*H*), 3.42 (m, 2H, NC*H*$_2$), 3.38 (m, 2H, ArC*H*Me$_2$), 3.34 (m, 2H, ArC*H*Me$_2$), 2.82 (m, 2H, NC*H*$_2$), 2.43 (m, 2H, PC*H*$_2$), 2.03 (m, 2H, PC*H*$_2$), 1.79 (s, 6H, *Me*C), 1.78 (s, 6H, *Me*C), 1.54 (m, 2H, NCH$_2$C*H*$_2$), 1.38 (m, 2H, NCH$_2$C*H*$_2$), 1.31 (d, $^3J_{HH}$ = 6.8 Hz, 6H, ArCH*Me*$_2$), 1.26 (d, $^3J_{HH}$ = 6.8 Hz, 6H, ArCH*Me*$_2$), 1.25 (d, $^3J_{HH}$ = 6.9 Hz, 6H, ArCH*Me*$_2$), 0.95 (d, $^3J_{HH}$ = 6.8 Hz, 6H, ArCH*Me*$_2$).

^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 298 K): δ = 165.4 (Me*C*), 164.6 (Me*C*), 147.5 (*i*-N*Ar*), 142.8 (*o*-N*Ar*), 142.7 (*o*-N*Ar*), 142.4 (d, $^1J_{PC}$ = 8.0 Hz, *i-Ph*$_2$P), 142.3 (d, $^1J_{PC}$ = 8.2 Hz, *i-Ph*$_2$P), 140.1 (d, $^1J_{PC}$ = 8.3 Hz, *i-Ph*$_2$P), 140.0 (d, $^1J_{PC}$ = 8.0 Hz, *i-Ph*$_2$P), 134.8 (d, $^2J_{PC}$ = 8.7 Hz, *o-Ph*$_2$P), 134.7 (d, $^2J_{PC}$ = 8.8 Hz, *o-Ph*$_2$P), 132.5 (d, $^2J_{PC}$ = 6.5 Hz, *o-Ph*$_2$P), 132.4 (d, $^2J_{PC}$ = 6.6 Hz, *o-Ph*$_2$P), 128.5 (*p-Ph*$_2$P), 128.1 (overlapped with solvent, *m-Ph*$_2$P)[1], 127.9 (overlapped with solvent, *m-Ph*$_2$P)[1], 127.3 (*p-Ph*$_2$P), 124.8 (*p*-N*Ar*), 123.5 (*m*-N*Ar*), 123.4 (*m*-N*Ar*), 97.1 (MeC(N)*C*H), 46.6 (N*C*H$_2$), 30.2 (d,

$^{1}J_{PC}$ = 12.0 Hz, P*C*H$_2$), 30.1 (d, $^{1}J_{PC}$ = 11.9 Hz, P*C*H$_2$), 29.2 (Ar*C*HMe$_2$), 28.4 (Ar*C*HMe$_2$), 26.0 (ArCH*Me*$_2$), 25.0 (ArCH*Me*$_2$), 24.9 (NCH$_2$*C*H$_2$), 24.9 (ArCH*Me*$_2$), 24.4 (*Me*C), 24.1 (ArCH*Me*$_2$), 20.9 (*Me*C) [^{1}from the ^{1}H, ^{13}C GHSQC experiment].

^{31}P{^{1}H} NMR (162 MHz, C_6D_6, 298 K): δ = 3.5.

^{1}H, ^{1}H GCOSY (400 MHz / 400 MHz, C_6D_6, 298 K) [selected traces]: δ ^{1}H / δ ^{1}H = 7.38 / 6.90 (*o-Ph*$_2$P / *m-Ph*$_2$P), 7.22 / 7.04 (*o-Ph*$_2$P / *m-Ph*$_2$P), 3.42 / 2.82 (NC*H*$_2$ / NC*H*$_2$), 2.43 / 2.03 (PC*H*$_2$ / PC*H*$_2$), 1.54 / 1.38 (NCH$_2$C*H*$_2$ / NCH$_2$C*H*$_2$).

^{1}H, ^{13}C GHSQC (400 MHz / 101 MHz, C_6D_6, 298 K): δ ^{1}H / δ ^{13}C = 7.38 / 134.8, 134.7 (*o-Ph*$_2$P), 7.22 / 132.5, 132.4 (*o-Ph*$_2$P), 7.17 / 123.5 (*m*-N*Ar*), 7.12 / 124.8 (*p*-N*Ar*), 7.07 / 123.4 (*m*-N*Ar*), 7.04 / 128.1 (*m-Ph*$_2$P), 7.02 / 127.3 (*p-Ph*$_2$P), 6.99 / 128.5 (*p-Ph*$_2$P), 6.90 / 127.9 (*m-Ph*$_2$P), 4.85 / 97.1 (MeC(N)*CH*), 3.42, 2.82 / 46.6 (N*CH*$_2$), 3.38 / 29.2 (Ar*CH*Me$_2$), 3.34 / 28.4 (Ar*CH*Me$_2$), 2.43, 2.03 / 30.2 (P*CH*$_2$), 2.43, 2.03 / 30.1 (P*CH*$_2$), 1.79 / 24.4 (*Me*C), 1.78 / 20.9 (*Me*C), 1.54, 1.38 /24.9 (NCH$_2$*CH*$_2$), 1.31 / 25.0 (ArCH*Me*$_2$), 1.26 / 24.9 (ArCH*Me*$_2$), 1.25 / 24.1(ArCH*Me*$_2$), 0.95 / 26.0 (ArCH*Me*$_2$).

^{1}H, ^{13}C GHMBC (400 MHz / 101 MHz, C_6D_6, 298 K) [selected traces]: δ ^{1}H / δ ^{13}C = 7.38 / 134.8, 128.5 (*o-Ph*$_2$P / *o-Ph*$_2$P, *p-Ph*$_2$P), 7.22 / 132.4, 127.3 (*o-Ph*$_2$P / *o-Ph*$_2$P, *p-Ph*$_2$P), 7.12 / 142.8, 142.7 (*p*-N*Ar* / *o*-N*Ar*), 7.17 / 147.5, 123.5 (*m*-N*Ar* / *i*-N*Ar*, *m*-N*Ar*), 7.07 / 147.5, 123.5 (*m*-N*Ar* / *i*-N*Ar*, *m*-N*Ar*), 7.04 / 142.4 (*m-Ph*$_2$P / *i-Ph*$_2$P), 7.02 / 132.4 (*p-Ph*$_2$P / *o-Ph*$_2$P), 6.99 / 134.8 (*p-Ph*$_2$P / *o-Ph*$_2$P), 6.90 / 140.1, 127.9 (*m-Ph*$_2$P / *i-Ph*$_2$P, *m-Ph*$_2$P), 3.38 / 147.5, 142.7, 123.4 (ArC*H*Me$_2$ / *i*-N*Ar*, *o*-N*Ar*, *m*-N*Ar*), 3.34 / 147.5, 142.8, 123.5 (ArC*H*Me$_2$ / *i*-N*Ar*, *o*-N*Ar*, *m*-N*Ar*), 2.43, 2.03 / 142.4, 140.1 (PC*H*$_2$ / *i-Ph*$_2$P), 1.31, 1.26 / 142.8 (ArCH*Me*$_2$ / *o*-N*Ar*), 1.25, 0.95 / 142.7 (ArCH*Me*$_2$ / *o*-N*Ar*).

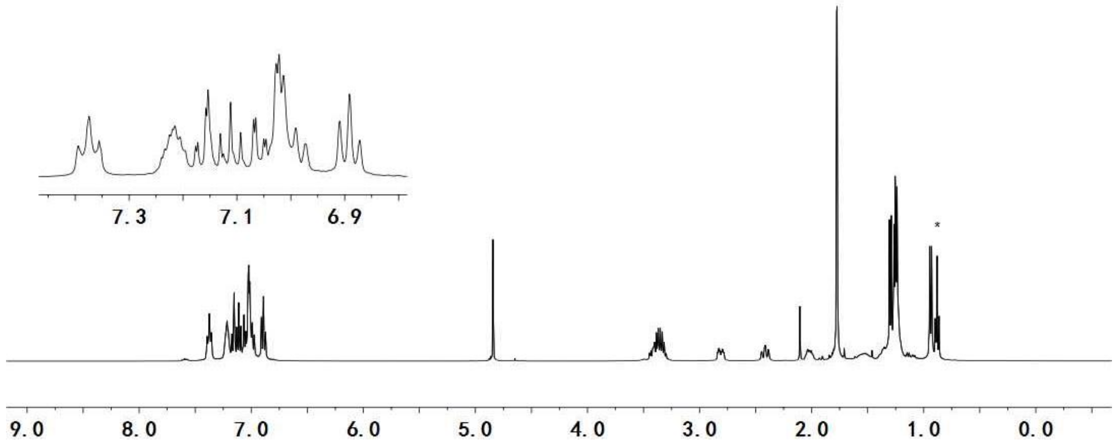


Fig. S38. [1]H NMR (400 MHz, C_6D_6, 298 K) [*: hexane]

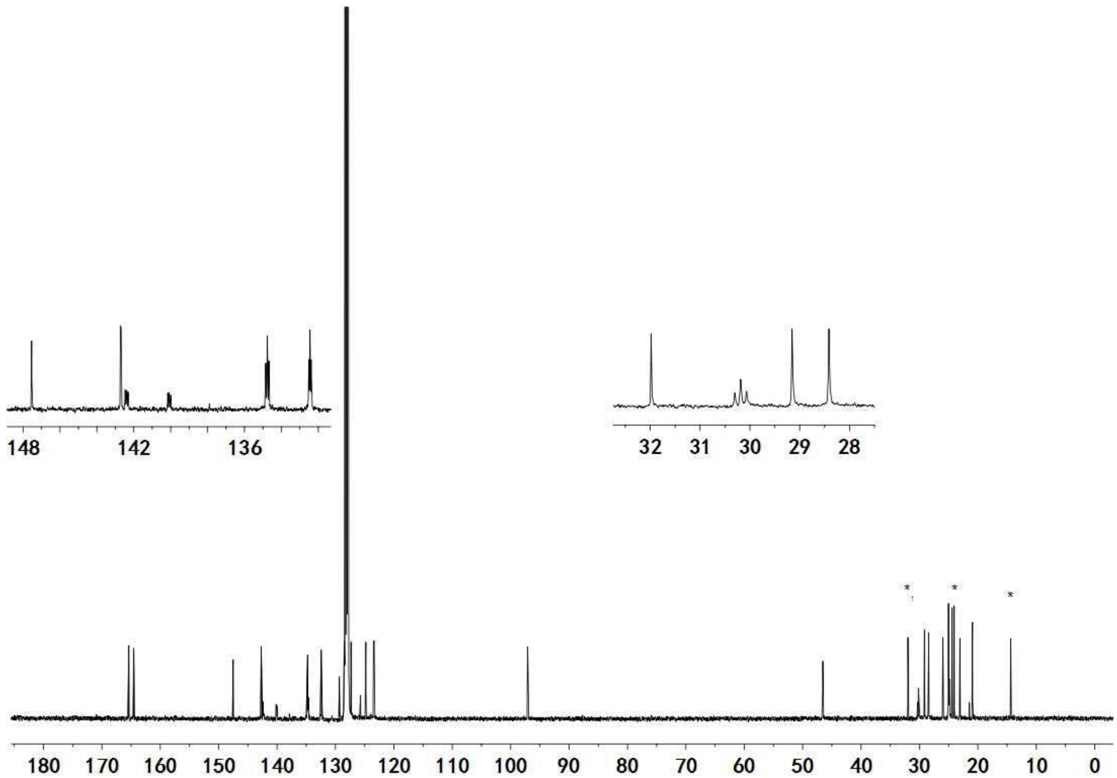


Fig. S39. [13]C {[1]H} NMR (101 MHz, C_6D_6, 298 K) [*: hexane]

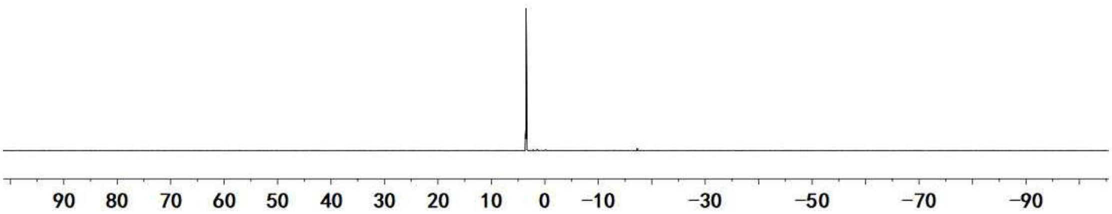


Fig. S40. $^{31}P\{^{1}H\}$ NMR (162 MHz, C_6D_6, 298 K)

X-ray crystal structure analysis of complex 4b: formula $C_{64}H_{80}N_4P_2PdZn_2$, M = 1204.45 gmol^{-1}, yellow, 0.18 x 0.16 x 0.15 mm, Triclinic, space group P-1, a = 11.9735(6), b = 14.1036(8), c = 20.0885(10) Å, α = 93.312(2)°, β = 105.224(2)°, γ = 108.871(2)° V = 3059.3(3) Å^3, ρ_{calc} = 1.307 gcm^{-3}, μ = 1.161 mm^{-1}, empirical absorption correction (0.5708 ≤ T ≤ 0.7456), Z = 2, λ = 0.71073 Å, T = 120(2) K, 82895 reflections collected (-15 ≤ h ≤ 15, -18 ≤ k ≤ 18, -26 ≤ l ≤ 26), 14131 independent (R_{int} = 0.0883) and 10556 observed reflections [I>2σ(I)], 670 refined parameters, the final R_1 was 0.0401 (I > 2σ(I)) and wR_2 was 0.1138 (all data). max. (min.) residual electron density 0.756 (-0.550) e.Å^{-3}, hydrogen atoms were placed in calculated positions and refined using a riding model.

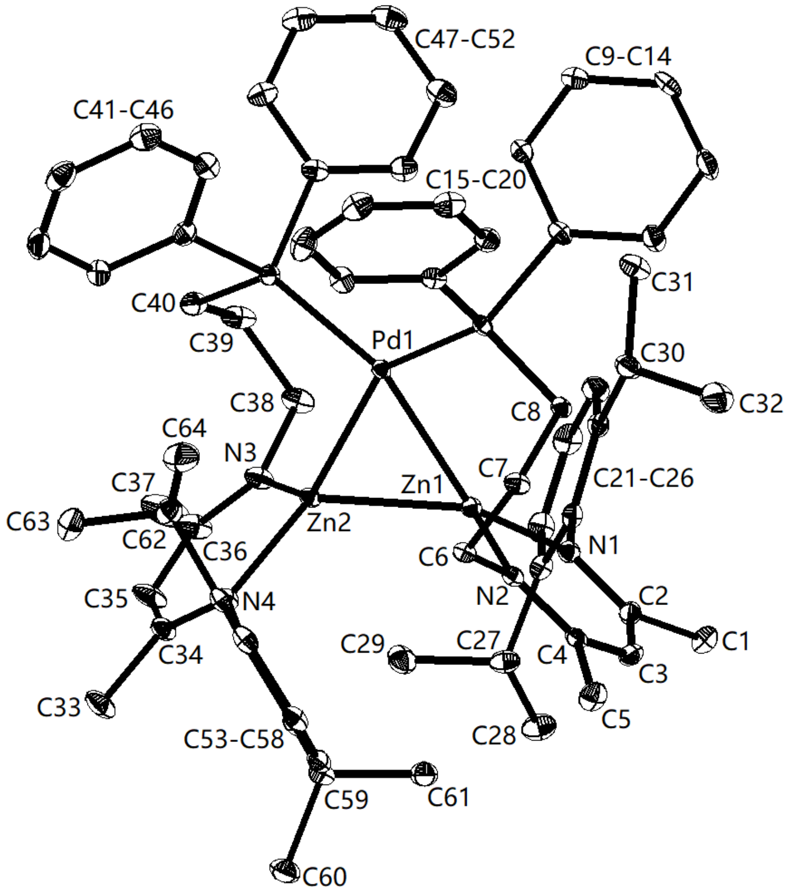
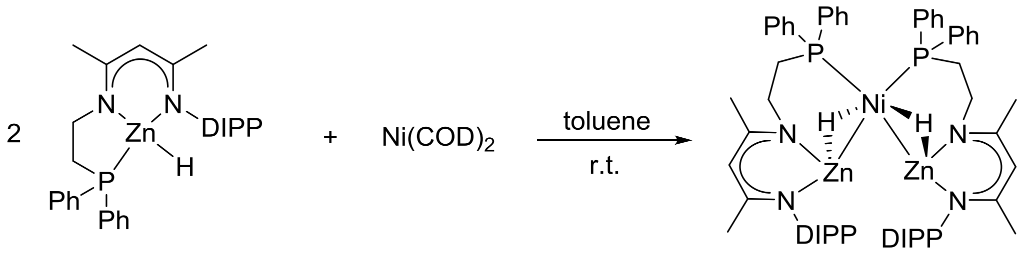


Fig. S41. Molecular structure of complex **4b**.

Preparation of complex 5a:



3a DIPP = 2,6-$^{i}Pr_2$-C_6H_3 **5a**

Scheme S13.

$Ni(COD)_2$ (55 mg, 0.2 mmol) was added to a solution of **3a** (214 mg, 0.4 mmol) in toluene (4 mL). The reaction mixture was stirred at room temperature for 1 h and then the solvent was removed under vacuum. The residue was washed with hexane (3*1 mL) to finally give **5a** as an orange crystalline solid (199 mg, 88% yield). Crystals suitable for the X-ray crystal structure analysis were grown from a layered toluene / hexane (v/v: 1:2) solution at room temperature.

Elemental Analysis: calcd. for $C_{62}H_{78}N_4NiP_2Zn_2$: C, 65.86; H, 6.95; N, 4.96. Found: C, 65.86; H, 6.64; N, 4.62.

^{1}H NMR (400 MHz, C_6D_6 / C_6D_5Br (5:1), 298 K): δ = 7.35 (m, 4H, *o-Ph*$_2$P), 7.13 (m, 4H, *o-Ph*$_2$P), 7.07 (m, 6H, *m, p*-N*Ar*), 6.99 (m, 12H, *m, p-Ph*$_2$P), 4.74 (s, 2H, MeC(N)C*H*), 3.31 (m, 2H, ArC*H*Me$_2$), 3.16 (m, 4H, NC*H*$_2$), 3.09 (m, 2H, ArC*H*Me$_2$), 1.99, 2.29 (m, 4H, PC*H*$_2$), 1.73 (s, 6H, *MeC*), 1.66 (s, 6H, *MeC*), 1.27 (overlapped with hexane, 6H, ArCH*Me*$_2$), 1.22 (overlapped with hexane, 6H, ArCH*Me*$_2$), 1.11 (d, $^3J_{HH}$ = 6.8 Hz, 6H ArCH*Me*$_2$), 0.82 (d, $^3J_{HH}$ = 6.8 Hz, 6H ArCH*Me*$_2$), -6.58 (br d, $^2J_{PH}$ = 5.6 Hz, 2H, Ni*H*$_2$).

^{13}C{^{1}H} NMR (101 MHz, C_6D_6 / C_6D_5Br (5:1), 298 K): δ = 165.5 (Me*C*), 165.3 (Me*C*), 146.4 (*i*-N*Ar*), 143.1 (*o*-N*Ar*), 142.7 (*i-Ph*$_2$P), 134.0 (*o-Ph*$_2$P), 132.0 (*m-Ph*$_2$P), 127.8, 127.7 (overlapped with solvent, *m*, *p-Ph*$_2$P)[1], 125.7 (*p*-N*Ar*), 125.4 (*p-Ph*$_2$P), 123.9 (m-N*Ar*), 123.4 (*o-Ph*$_2$P), 95.8 (MeC(N)*C*H), 47.0 (N*C*H$_2$), 38.8 (d, $^1J_{PC}$ = 11.1 Hz, P*C*H$_2$), 38.7 (d, $^1J_{PC}$ = 16.6 Hz, P*C*H$_2$), 28.4 (Ar*C*HMe$_2$), 28.3 (Ar*C*HMe$_2$), 25.0 (ArCH*Me*$_2$), 24.9 (ArCH*Me*$_2$), 24.3 (ArCH*Me*$_2$), 24.2 (ArCH*Me*$_2$), 24.1 (*Me*C), 22.7 (*Me*C) [[1]from the ^{1}H, ^{13}C GHSQC experiment].

^{31}P{^{1}H} NMR (162 MHz, C_6D_6 / C_6D_5Br (5:1), 298 K): δ = 22.7.

^{1}H, ^{1}H GCOSY (400 MHz / 400 MHz, C_6D_6 / C_6D_5Br (5:1), 298 K) [selected traces]: δ ^{1}H / δ ^{1}H = 7.35 / 6.99 (*o-Ph*$_2$P / *m-Ph*$_2$P), 3.31 / 1.25 (ArC*H*Me$_2$ / ArCH*Me*$_2$), 3.09 / 0.82 (ArC*H*Me$_2$ / ArCH*Me*$_2$), 2.29 / 3.16 (PC*H*$_2$ / NC*H*$_2$), 1.27 / 3.13 (ArCH*Me*$_2$ / ArC*H*Me$_2$).

^{1}H, ^{13}C GHSQC (400 MHz / 101 MHz, C_6D_6 / C_6D_5Br (5:1), 298 K): δ ^{1}H / δ ^{13}C = 7.35 / 134.0 (*o-Ph*$_2$P), 7.13 / 123.4 (*o-Ph*$_2$P), 7.07 / 123.9, 125.7 (*m*, *p*-N*Ar*), 6.99 / 132.0, 125.4 (*m*, *p-Ph*$_2$P), 6.99 / 127.7, 127.8 (*m*, *p-Ph*$_2$P), 4.74 / 95.8 (MeC(N)*CH*), 3.31 / 28.4 (Ar*CH*Me$_2$), 3.16 / 47.0 (N*CH*$_2$), 3.09 / 28.3 (Ar*CH*Me$_2$), 2.29, 1.99 / 38.8 (P*CH*$_2$), 2.29, 1.99 / 38.7 (P*CH*$_2$), 1.73 / 22.7 (*MeC*), 1.66 / 24.1 (*MeC*), 1.27 / 24.3 (ArCH*Me*$_2$), 1.22 / 24.9 (ArCH*Me*$_2$), 1.11 / 24.2 (ArCH*Me*$_2$), 0.82 / 25.0 (ArCH*Me*$_2$).

^{1}H, ^{13}C GHMBC (400 MHz / 101 MHz, C_6D_6 / C_6D_5Br (5:1), 298 K) [selected traces]: δ ^{1}H / δ ^{13}C = 7.13 / 142.7 (*o-Ph*$_2$P / *i-Ph*$_2$P), 7.07 / 146.4 (*m*-N*Ar* / *i*-N*Ar*), 6.99 / 132.0 (*p-Ph*$_2$P / *m-Ph*$_2$P), 4.74 / 146.4 (MeC(N)C*H* / *i*-N*Ar*), 3.31, 3.09 / 143.1 (ArC*H*Me$_2$ / *o*-N*Ar*), 1.73 / 165.5 (*Me*C / Me*C*), 1.66 / 165.3 (*Me*C / Me*C*).

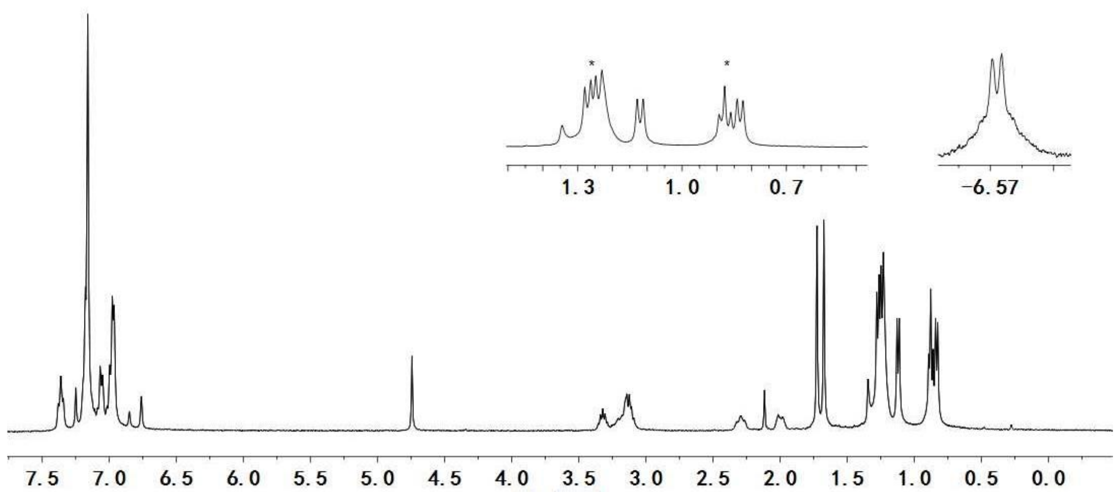


Fig. S42. ^{1}H NMR (400 MHz, C_6D_6 / C_6D_5Br (5:1), 298 K) [*: hexane]

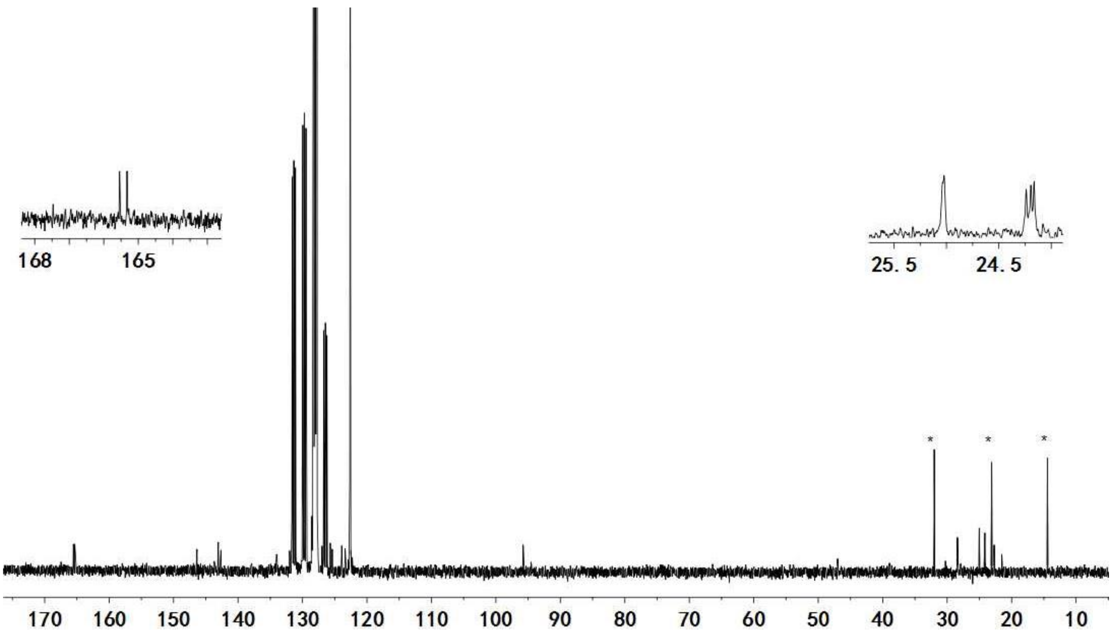


Fig. S43. ^{13}**C {^{1}H} NMR** (101 MHz, C_6D_6 / C_6D_5Br (5:1), 298 K) [*: hexane]

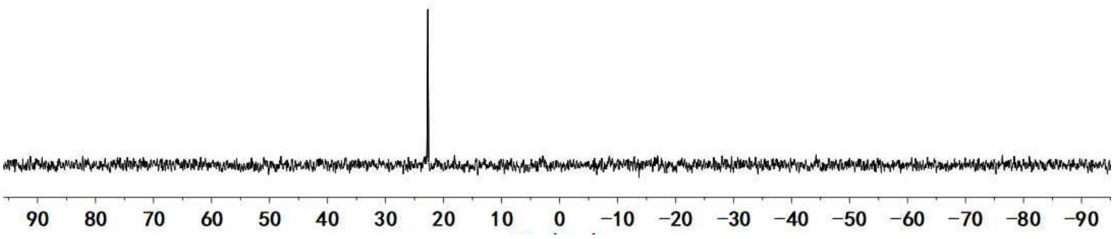


Fig. S44. ^{31}**P{^{1}H} NMR** (162 MHz, C_6D_6 / C_6D_5Br (5:1), 298 K)

X-ray crystal structure analysis of complex 5a: formula $C_{62}H_{78}N_4NiP_2Zn_2$, M = 1130.70 gmol^{-1}, orange, 0.350 x 0.250 x 0.150 mm, Triclinic, space group P-1, a = 13.9465(7), b = 15.3871(7), c = 18.6906(9) Å, α = 99.879(2)°, β = 110.923(2)°, γ = 101.287(2)° V = 3544.0(3) Å^3, ρ_{calc} = 1.060 gcm^{-3}, μ = 1.013 mm^{-1}, empirical absorption correction (0.6206 ≤ T ≤ 0.7456), Z = 2, λ = 0.71073 Å, T = 120(2) K, 197525 reflections collected (-18 ≤ h ≤ 18, -19 ≤ k ≤ 20, -24 ≤ l ≤ 24), 16519 independent (R_{int} = 0.0461) and 13405 observed reflections [I>2σ(I)], 660 refined parameters, the final R_1 was 0.0315 (I > 2σ(I)) and wR_2 was 0.0914 (all data). max. (min.) residual electron density 0.321 (-0.419) e.Å^{-3}, hydrogen atoms except for hydrides were placed in calculated positions and refined using a riding model, the hydride atoms in this structure were located in a Fourier difference map and were refined with isotropic displacement parameters.

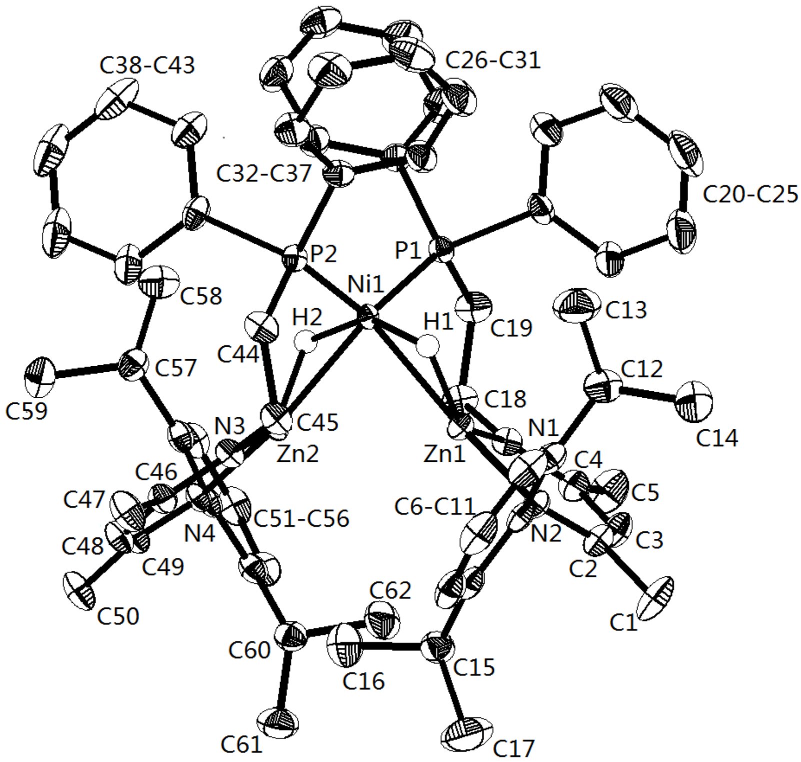
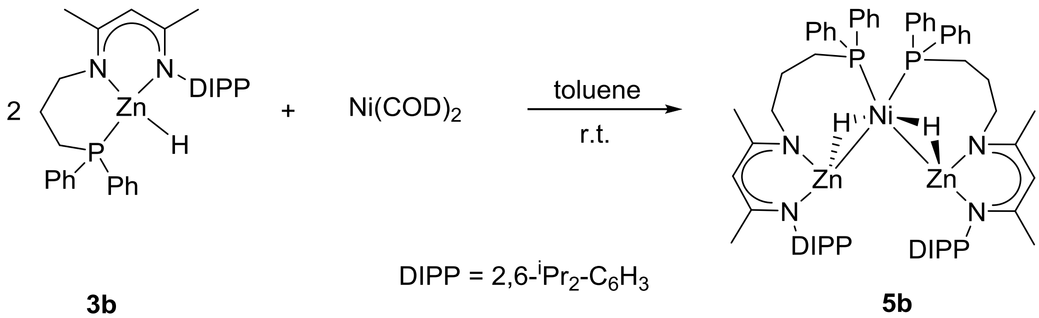


Fig. S45. Molecular structure of complex **5a**.

Preparation of Complex 5b:



3b **5b**

Scheme S14.

Following the procedure described for **5a**, reaction of $Ni(COD)_2$ (69 mg, 0.25 mmol) with **3b** (275 mg, 0.50 mmol) in toluene (4 mL) gave **5b** as a red crystalline solid (243 mg, 84%). Crystals suitable for the X-ray crystal structure analysis were grown from a layered toluene / hexane (v/v: 1:2) solution at room temperature.

Elemental Analysis: calcd. for $C_{64}H_{82}N_4NiP_2Zn_2$: C, 66.34; H, 7.13; N, 4.84. Found: C, 66.18; H, 7.02; N, 4.60.

^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 7.37 (m, 4H, *o-Ph*$_2$P), 7.19 (m, 2H, *m*-N*Ar*), 7.17 (m, 2H, *m*-N*Ar*), 7.14 (m, 2H, *p*-N*Ar*), 7.10 (m, 2H, *p-Ph*$_2$P), 7.05 (m, 4H, *o-Ph*$_2$P), 7.02 (m, 4H, *m-Ph*$_2$P), 6.89 (m, 6H, *m*, *p-Ph*$_2$P), 4.83 (s, 2H, MeC(N)C*H*), 3.89 (m, 2H, NC*H*$_2$), 3.86 (m, 2H, ArC*H*Me$_2$), 3.24 (sp, $^3J_{HH}$ = 6.7 Hz, 2H, ArC*H*Me$_2$), 2.42 (m, 2H, NC*H*$_2$), 2.23 (m, 2H, PC*H*$_2$), 2.02 (m, 2H, PC*H*$_2$), 1.77 (s, 12H, *Me*C), 1.42 (d, $^3J_{HH}$ = 6.8 Hz, 6H, ArCH*Me*$_2$), 1.41 (overlapped with ArCH*Me*$_2$, 2H, NCH$_2$C*H*$_2$), 1.29 (d, $^3J_{HH}$ = 7.4 Hz, 6H, ArCH*Me*$_2$), 1.27 (d, $^3J_{HH}$ = 7.2 Hz, 6H, ArCH*Me*$_2$), 1.23 (d, $^3J_{HH}$ = 6.8 Hz, 6H, ArCH*Me*$_2$), 1.06 (m, 2H, NCH$_2$C*H*$_2$), -9.38 (br d, $^2J_{PH}$ = 5.6 Hz, 1H, Ni*H*$_2$), -9.42 (br d, $^2J_{PH}$ = 5.5 Hz, 1H, Ni*H*$_2$).

^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 298 K): δ = 166.3 (Me*C*), 165.4 (Me*C*), 147.3 (*i*-N*Ar*), 145.3 (d, $^1J_{PC}$ = 10.2 Hz, *i-Ph*$_2$P), 145.1 (d, $^1J_{PC}$ = 10.2 Hz, *i-Ph*$_2$P), 143.0 (*o*-N*Ar*), 142.7 (*o*-N*Ar*), 137.2 (d, $^1J_{PC}$ = 8.2 Hz, *i-Ph*$_2$P), 137.1 (d, $^1J_{PC}$ = 8.9 Hz, *i-Ph*$_2$P), 135.1 (d, $^2J_{PC}$ = 7.4 Hz, *o-Ph*$_2$P), 135.0 (d, $^2J_{PC}$ = 7.2 Hz, *o-Ph*$_2$P), 131.9 (d, $^2J_{PC}$ = 5.4 Hz, *o-Ph*$_2$P), 131.8 (d, $^2J_{PC}$ = 5.3 Hz, *o-Ph*$_2$P), 128.5 (*p-Ph*$_2$P), 127.7 (*m-Ph*$_2$P), 127.6 (*m-Ph*$_2$P), 127.0 (*p-Ph*$_2$P), 125.1 (*p*-N*Ar*), 123.8 (*m*-N*Ar*), 123.6 (*m*-N*Ar*), 96.6 (MeC(N)*C*H), 45.7 (N*C*H$_2$), 33.3 (d, $^1J_{PC}$ = 14.5 Hz, P*C*H$_2$), 33.1 (d, $^1J_{PC}$ = 13.7 Hz, P*C*H$_2$), 29.1 (Ar*C*HMe$_2$), 28.3 (Ar*C*HMe$_2$), 25.9 (NCH$_2$*C*H$_2$), 25.4

(ArCH*Me*$_2$), 25.0 (ArCH*Me*$_2$), 24.9 (ArCH*Me*$_2$), 24.6 (ArCH*Me*$_2$), 24.5 (*Me*C), 21.0 (*Me*C).

^{31}P{^{1}H} NMR (162 MHz, C_6D_6, 298 K): δ = 17.1.

^{1}H, ^{1}H GCOSY (400 MHz / 400 MHz, C_6D_6, 298 K) [selected traces]: δ ^{1}H / δ ^{1}H = 7.37 / 7.02 (*o-Ph*$_2$P / *m-Ph*$_2$P), 7.05 / 6.89 (*o-Ph*$_2$P / *m-Ph*$_2$P), 3.89 / 2.42 (NC*H*$_2$ / NC*H*$_2$), 3.89 / 1.06 (NC*H*$_2$ / NCH$_2$C*H*$_2$), 2.42 / 1.41, 1.06 (NC*H*$_2$ / NCH$_2$C*H*$_2$), 2.23 / 2.02 (PC*H*$_2$ / PC*H*$_2$), 2.23, 2.02 / 1.41, 1.06 (PC*H*$_2$ / NCH$_2$C*H*$_2$), 1.06 / 1.41 (NCH$_2$C*H*$_2$ / NCH$_2$C*H*$_2$).

^{1}H, ^{13}C GHSQC (400 MHz / 101 MHz, C_6D_6, 298 K): δ ^{1}H / δ ^{13}C = 7.37 / 135.1, 135.0 (*o-Ph*$_2$P), 7.19 / 123.8 (*m*-N*Ar*), 7.17 / 123.6 (*m*-N*Ar*), 7.14 / 125.1 (*p*-N*Ar*), 7.10 / 128.5 (*p-Ph*$_2$P), 7.05 / 131.9, 131.8 (*o-Ph*$_2$P), 7.02 / 127.7 (*m-Ph*$_2$P), 6.89 / 127.6, 127.0 (*m*, *p-Ph*$_2$P), 4.83 / 96.7 (MeC(N)*CH*), 3.89, 2.42 / 45.7 (N*CH*$_2$), 3.86 / 28.3 (Ar*CH*Me$_2$), 3.24 / 29.1 (Ar*CH*Me$_2$), 2.23, 2.02 / 33.2 (P*CH*$_2$), 2.23, 2.02 / 33.1 (P*CH*$_2$), 1.77 / 24.5, 21.0 (*Me*C), 1.42 / 25.4 (ArCH*Me*$_2$), 1.41, 1.06 / 25.9 (NCH$_2$*CH*$_2$), 1.29 / 24.6 (ArCH*Me*$_2$), 1.27 / 25.0 (ArCH*Me*$_2$), 1.23 / 24.9 (ArCH*Me*$_2$).

^{1}H, ^{13}C GHMBC (400 MHz / 101 MHz, C_6D_6, 298 K) [selected traces]: δ ^{1}H / δ ^{13}C = 7.37 / 135.1, 128.5 (*o-Ph*$_2$P / *o-Ph*$_2$P, *p-Ph*$_2$P), 7.19 / 147.3, 123.6 (*m*-N*Ar* / *i*-N*Ar*, *m*-N*Ar*), 7.17 / 147.3, 123.8 (*m*-N*Ar* / *i*-N*Ar*, *m*-N*Ar*), 7.14 / 143.0, 142.7 (*p*-N*Ar* / *o*-N*Ar*), 7.10 / 135.1 (*p-Ph*$_2$P / *o-Ph*$_2$P), 7.05 / 131.8, 127.0 (*o-Ph*$_2$P / *o-Ph*$_2$P, *p-Ph*$_2$P), 7.02 / 137.2, 127.7 (*m-Ph*$_2$P / *i-Ph*$_2$P, *m-Ph*$_2$P), 6.89 / 145.3, 131.8, 127.6 (*m*, *p-Ph*$_2$P / *i-Ph*$_2$P, *o-Ph*$_2$P, *m-Ph*$_2$P), 3.86 / 147.3, 142.7, 123.8 (ArC*H*Me$_2$ / *i*-N*Ar*, *o*-N*Ar*, *m*-N*Ar*), 3.24 / 147.3, 143.0, 123.6 (ArC*H*Me$_2$ / *i*-N*Ar*, *o*-N*Ar*, *m*-N*Ar*), 2.23, 2.02 / 145.3 (PC*H*$_2$ / *i-Ph*$_2$P), 2.23, 2.02 / 137.2 (PC*H*$_2$ / *i-Ph*$_2$P), 1.42, 1.27 / 143.0 (ArCH*Me*$_2$ / *o*-N*Ar*), 1.29, 1.23 / 142.7 (ArCH*Me*$_2$ / *o*-N*Ar*).

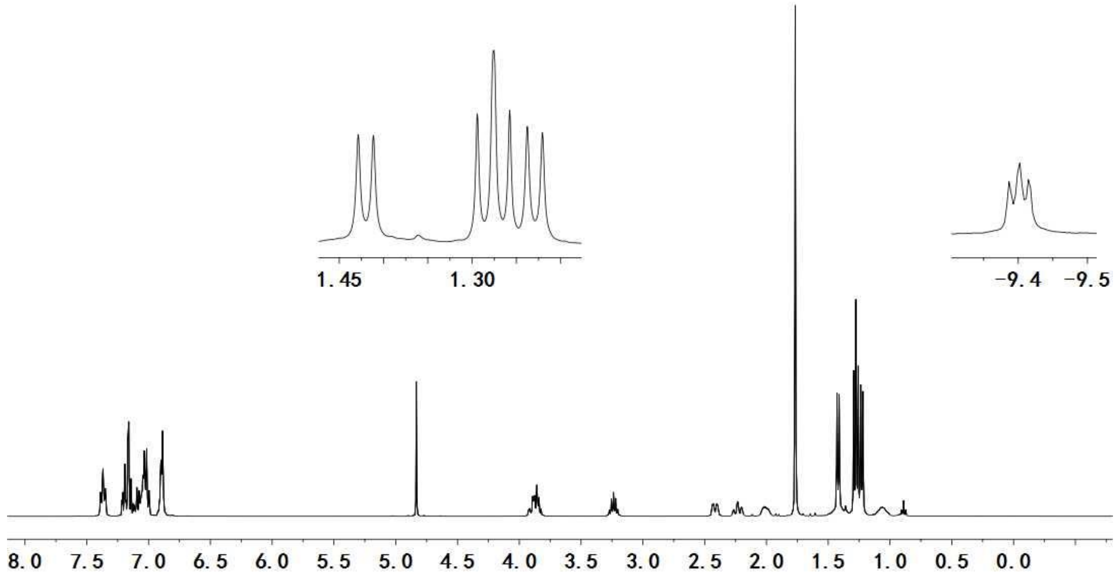


Fig. S46. ¹H NMR (400 MHz, C_6D_6, 298 K)

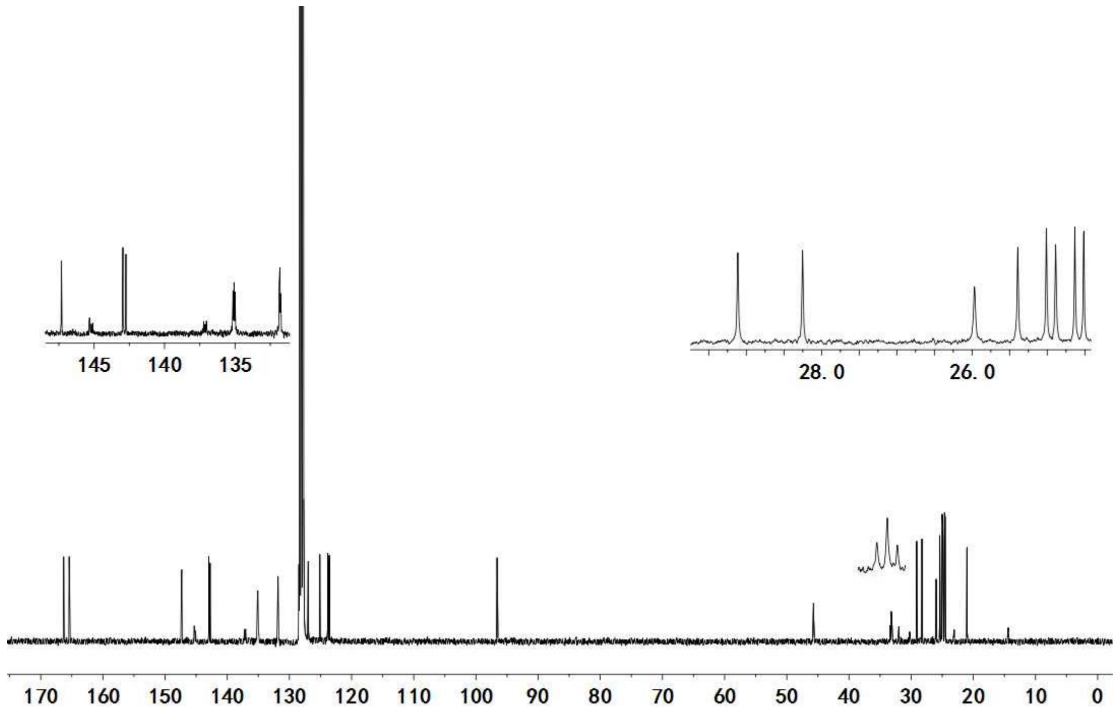


Fig. S47. ¹³C{¹H} NMR (101 MHz, C_6D_6, 298 K)

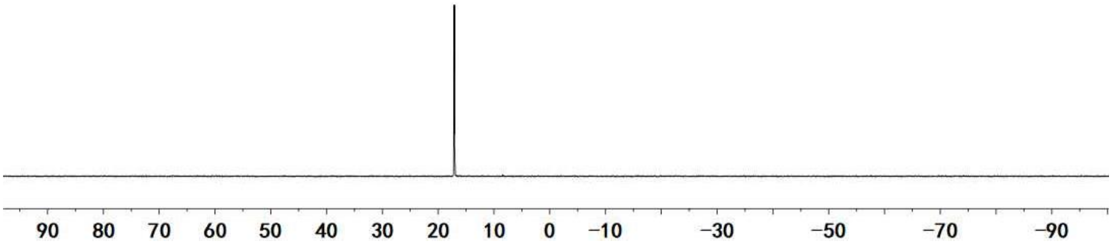


Fig. S48. ^{31}**P{**^{1}**H} NMR** (162 MHz, C_6D_6, 298 K)

X-ray crystal structure analysis of complex 5b: formula $C_{64}H_{82}N_4NiP_2Zn_2$, M = 1158.75 gmol^{-1}, orange, 0.30 x 0.20 x 0.15 mm, Monoclinic, space group *Ia*, a = 18.7842(10), b = 14.6521(8), c = 23.6304(11) Å, β = 111.760(3)°, V = 6040.3(6) Å^3, ρ_{calc} = 1.272 gcm^{-3}, μ = 1.190 mm^{-1}, empirical absorption correction (0.5516 ≤ T ≤ 0.7456), Z = 4, λ = 0.71073 Å, T = 223(2) K, 100209 reflections collected (-24 ≤ h ≤ 24, -19 ≤ k ≤ 19, -30 ≤ l ≤ 30), 13727 independent (R_{int} = 0.0846) and 11843 observed reflections [I>2σ(I)], 679 refined parameters, the final R_1 was 0.0331 (I > 2σ(I)) and wR_2 was 0.0656 (all data). max. (min.) residual electron density 0.246 (-0.507) e.Å^{-3}, hydrogen atoms except for hydrides were placed in calculated positions and refined using a riding model, the hydride atoms in this structure were located in a Fourier difference map and were refined with isotropic displacement parameters.

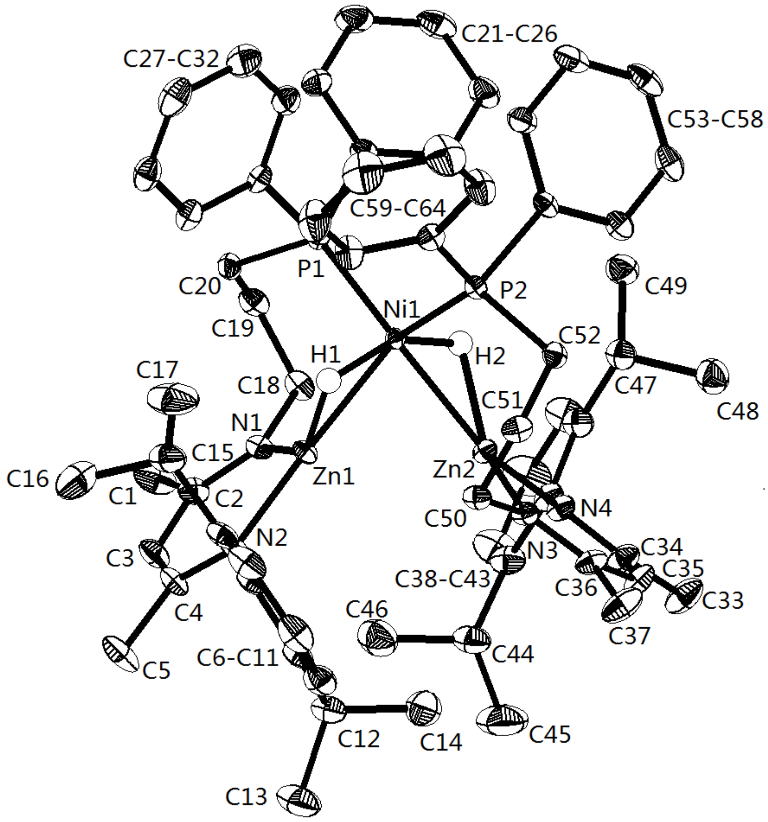
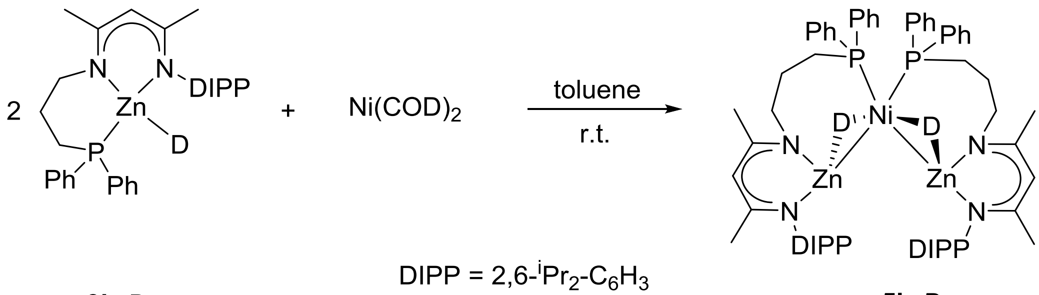


Fig. S49. Molecular structure of complex **5b**.

Preparation of complex 5b-*D*:



Scheme S15.

Following the procedure described for **5a**, reaction of $Ni(COD)_2$ (36 mg, 0.13 mmol) with **3b-*D*** (143 mg, 0.26 mmol) in toluene (4 mL) gave **5b-*D*** as a red crystalline solid (127 mg, 84%).

^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 7.37 (m, 4H, *o*-*Ph*$_2$P), 7.19 (m, 2H, *m*-N*Ar*), 7.17 (m, 2H, *m*-N*Ar*), 7.14 (m, 2H, *p*-N*Ar*), 7.10 (m, 2H, *p*-*Ph*$_2$P), 7.05 (m, 4H, *o*-*Ph*$_2$P), 7.02 (m, 4H, *m*-*Ph*$_2$P), 6.89 (m, 6H, *m*, *p*-*Ph*$_2$P), 4.83 (s, 2H, MeC(N)C*H*), 3.89 (m, 2H, NC*H*$_2$), 3.86 (m, 2H, ArC*H*Me$_2$), 3.24 (m, 2H, ArC*H*Me$_2$), 2.42 (m, 2H, NC*H*$_2$), 2.23 (m, 2H, PC*H*$_2$), 2.02 (m, 2H, PC*H*$_2$), 1.77 (s, 12H, *Me*C), 1.42 (d, $^3J_{HH}$ = 6.4 Hz, 6H, ArCH*Me*$_2$), 1.41 (overlapped with ArCH*Me*$_2$, 2H, NCH$_2$C*H*$_2$), 1.25 (m, 18H, ArCH*Me*$_2$), 1.06 (m, 2H, NCH$_2$C*H*$_2$).

^{31}P{^{1}H} NMR (162 MHz, C_6D_6, 298 K): δ = 17.1.

^{2}H NMR (92 MHz, C_6H_6 / C_6D_6 (100:1), 298 K): δ = -9.38 (Zn*D*).

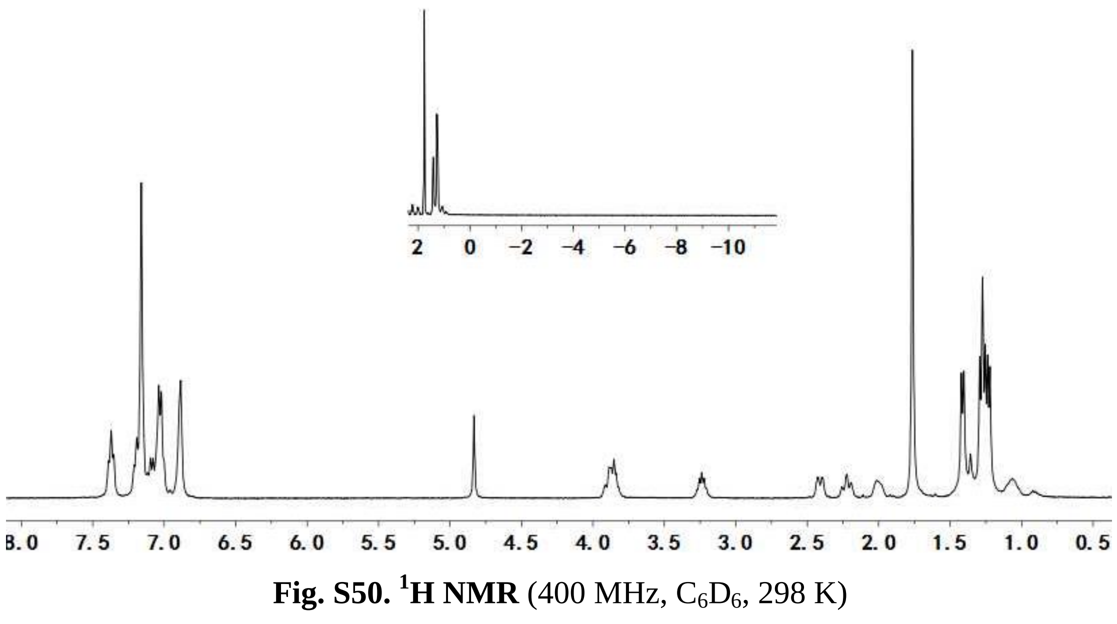


Fig. S50. **^{1}H NMR** (400 MHz, C_6D_6, 298 K)

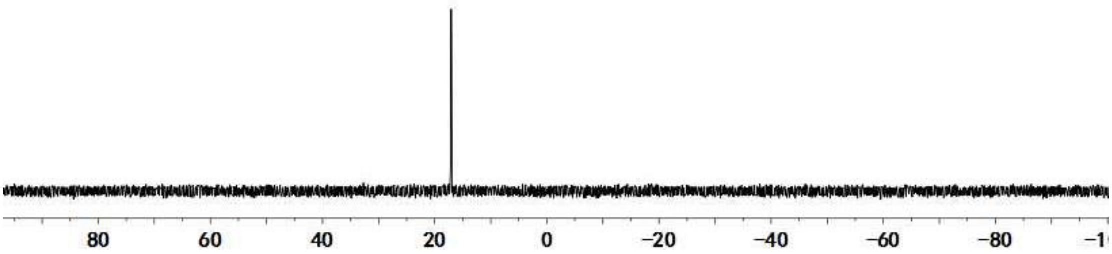


Fig. S51. ^{31}**P{**^{1}**H} NMR** (162 MHz, C_6D_6, 298 K)

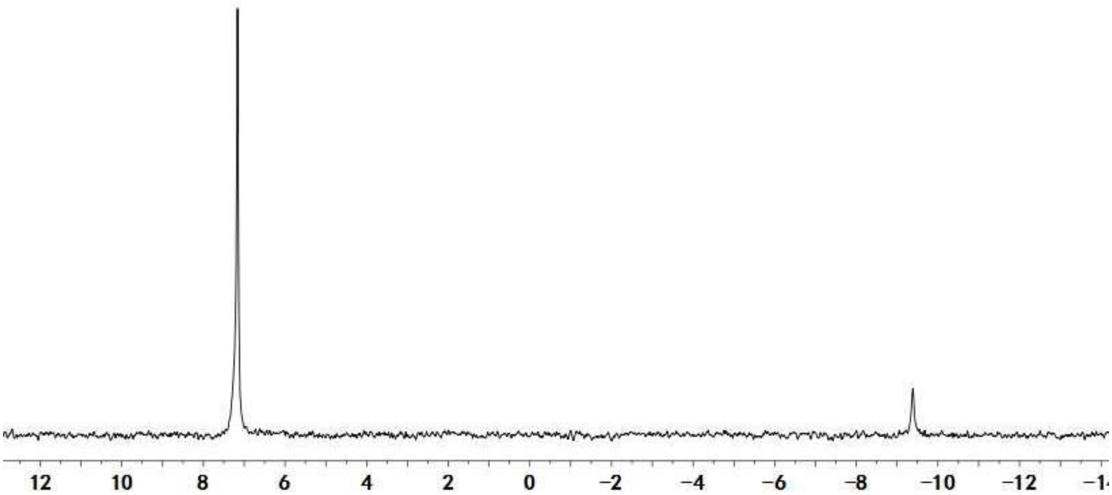


Fig. S52. ^{2}**H NMR** (92 MHz, C_6H_6 / C_6D_6 (100:1), 298 K)

Computational details:

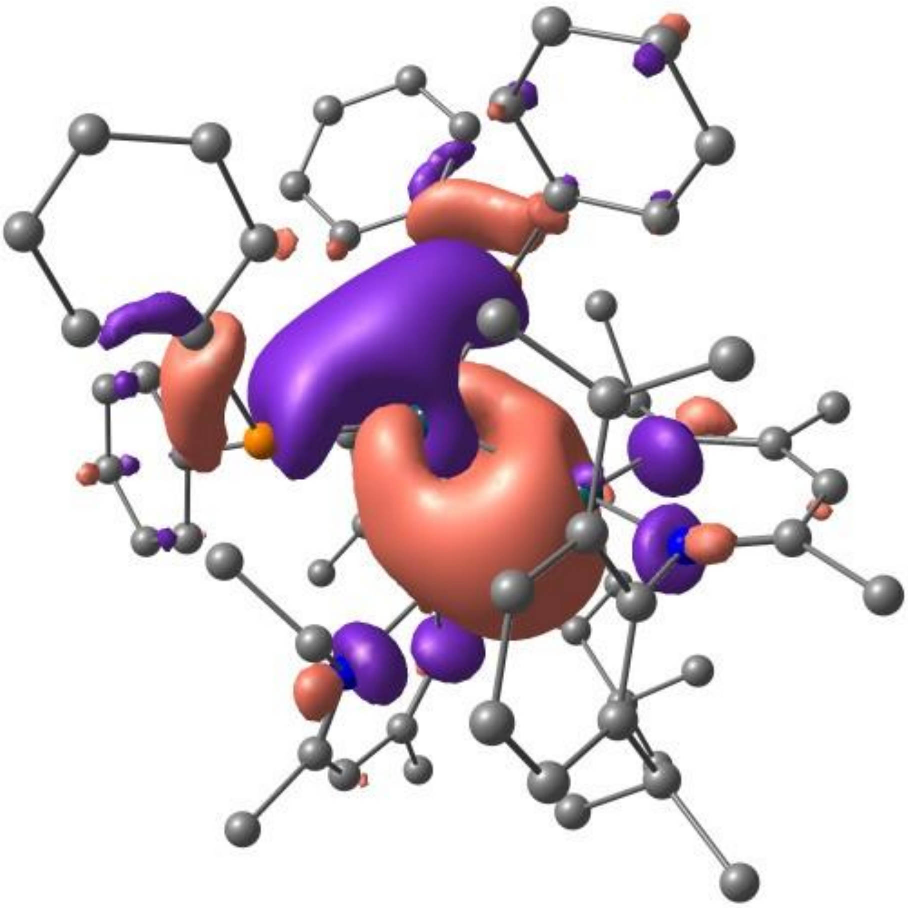


Fig. S53. HOMO of complex **4a**.

Cartesian coordinates of all optimized structures :

Complex 4a

46	13.065433000	5.612343000	5.838916000
30	15.136872000	4.256963000	5.703649000
30	13.542347000	3.841982000	7.502762000
7	12.615816000	2.090113000	7.663252000
7	13.177924000	4.408203000	9.359922000
1	14.590682000	2.572679000	2.345874000
7	16.976437000	4.883715000	6.149989000
15	11.839234000	6.699142000	7.451162000

15	13.129512000	5.909882000	3.559506000
6	11.510676000	6.374198000	2.792456000
6	10.406440000	6.508514000	3.637869000
6	9.143311000	6.780223000	3.118708000
6	8.981764000	6.939044000	1.744434000
6	10.083762000	6.835974000	0.893823000
6	11.344084000	6.550778000	1.413733000
7	15.562524000	3.719807000	3.846836000
6	14.376530000	3.348554000	3.092960000
6	13.685373000	4.524548000	2.394626000
6	12.396997000	6.767525000	9.260698000
6	13.529379000	5.795618000	9.609090000
6	10.118313000	6.053077000	7.592925000
6	9.071033000	6.642168000	6.875843000
6	7.805173000	6.061364000	6.869013000
6	7.568614000	4.886216000	7.582221000
6	8.608456000	4.297408000	8.301633000
6	9.877448000	4.870899000	8.303253000
6	11.565487000	8.505005000	7.126288000
6	12.155409000	9.055260000	5.987103000
6	12.089485000	10.426676000	5.746496000
6	11.409405000	11.256209000	6.635546000
6	10.783808000	10.708492000	7.758848000
6	10.862989000	9.339939000	8.004556000
6	14.224388000	7.304010000	3.045611000
6	13.715898000	8.576886000	2.763540000
6	14.580401000	9.642156000	2.515755000
6	15.961397000	9.450193000	2.537496000
6	16.472777000	8.181693000	2.810836000
6	15.612237000	7.120052000	3.072489000

6	12.549628000	3.665661000	10.259977000
6	12.032867000	2.382724000	9.984713000
6	12.022392000	1.667704000	8.769751000
6	11.239961000	0.376778000	8.741524000
6	12.594728000	1.363430000	6.443926000
6	11.495238000	1.461059000	5.570055000
6	11.574088000	0.836447000	4.321968000
6	12.713994000	0.142062000	3.934467000
6	13.803258000	0.072123000	4.797100000
6	13.766259000	0.678898000	6.053608000
6	17.984332000	4.853957000	5.288950000
6	19.318542000	5.438341000	5.688896000
6	17.074398000	5.516951000	7.416751000
6	16.987792000	6.920636000	7.516750000
6	16.992801000	7.505656000	8.785709000
6	17.070374000	6.731369000	9.936460000
6	17.120734000	5.345869000	9.827137000
6	17.111629000	4.717479000	8.580350000
6	10.281253000	2.291100000	5.923051000
6	10.279902000	3.586168000	5.111931000
6	14.947469000	0.586289000	6.995567000
6	16.289735000	0.570308000	6.273616000
6	16.793559000	7.791308000	6.294318000
6	15.337026000	8.249755000	6.218729000
6	17.179453000	3.208740000	8.473723000
6	16.473214000	2.489280000	9.621662000
6	16.748244000	3.878503000	3.280973000
6	17.883009000	4.352150000	3.975638000
6	12.332128000	4.196304000	11.659151000
6	8.965040000	1.530618000	5.749944000

6	14.811179000	-0.628276000	7.920751000
6	16.937356000	3.617292000	1.803579000
6	17.751740000	8.982678000	6.242799000
6	18.633556000	2.741482000	8.341139000
1	13.287644000	4.439737000	12.135785000
1	11.817108000	3.463022000	12.280977000
1	11.733501000	5.112940000	11.646376000
1	11.537706000	1.890525000	10.813634000
1	10.238782000	0.564881000	8.338086000
1	11.127738000	-0.041346000	9.743696000
1	11.711056000	-0.361968000	8.089686000
1	10.730965000	0.910423000	3.640332000
1	12.759248000	-0.335523000	2.959657000
1	14.703638000	-0.444706000	4.485895000
1	10.365146000	2.578462000	6.973135000
1	8.773094000	1.289353000	4.698864000
1	8.132534000	2.147589000	6.102884000
1	8.963025000	0.590418000	6.311500000
1	11.199239000	4.160645000	5.302620000
1	9.427317000	4.214280000	5.384000000
1	10.231469000	3.383582000	4.036249000
1	14.914659000	1.480064000	7.628021000
1	13.909837000	-0.564835000	8.535511000
1	15.672454000	-0.701617000	8.593942000
1	14.760991000	-1.552440000	7.334257000
1	16.436303000	-0.340943000	5.687203000
1	17.108023000	0.615705000	6.997651000
1	16.387781000	1.421467000	5.593858000
1	14.397509000	6.032741000	8.985419000
1	13.839301000	5.968322000	10.647284000

1	12.739813000	7.791989000	9.437379000
1	11.517897000	6.594956000	9.889401000
1	9.242616000	7.552247000	6.311853000
1	7.007737000	6.535026000	6.303272000
1	6.581878000	4.432131000	7.577117000
1	8.440331000	3.377910000	8.855477000
1	10.682607000	4.379940000	8.840028000
1	12.683932000	8.392341000	5.308526000
1	12.575393000	10.839054000	4.867358000
1	11.353413000	12.325326000	6.452033000
1	10.236521000	11.351101000	8.442727000
1	10.378202000	8.917357000	8.880584000
1	16.482599000	2.675427000	1.488544000
1	17.996295000	3.588686000	1.543204000
1	16.468608000	4.416745000	1.219408000
1	18.796368000	4.403111000	3.393567000
1	19.325293000	6.517743000	5.502212000
1	20.130414000	4.992240000	5.110823000
1	19.510216000	5.297395000	6.754544000
1	16.921933000	8.586632000	8.868516000
1	17.076740000	7.203271000	10.915038000
1	17.158854000	4.741101000	10.727323000
1	16.977163000	7.178247000	5.409773000
1	17.550423000	9.700391000	7.045350000
1	17.631057000	9.513048000	5.292837000
1	18.796653000	8.668018000	6.334391000
1	14.664481000	7.379430000	6.160302000
1	15.166710000	8.867784000	5.332572000
1	15.056159000	8.828319000	7.105605000
1	16.666880000	2.936019000	7.544765000

1	19.099403000	3.147657000	7.439681000
1	18.688430000	1.649257000	8.283416000
1	19.222457000	3.066482000	9.206206000
1	16.996672000	2.624957000	10.574333000
1	16.441709000	1.413660000	9.426317000
1	15.445386000	2.846027000	9.741181000
1	13.672772000	2.902818000	3.803987000
1	12.776814000	4.157356000	1.906792000
1	14.323612000	4.965335000	1.623471000
1	12.643524000	8.740098000	2.728939000
1	14.170518000	10.624288000	2.295418000
1	16.632632000	10.281123000	2.341118000
1	17.546080000	8.015632000	2.837946000
1	16.025333000	6.150246000	3.327390000
1	10.556633000	6.379312000	4.705093000
1	8.293907000	6.883627000	3.786327000
1	7.999055000	7.158667000	1.338704000
1	9.959376000	6.974752000	-0.176739000
1	12.199675000	6.472049000	0.748155000

Complex 4a’

46	5.007552000	0.973283000	12.196207000
30	2.983391000	0.654679000	13.436581000
30	4.692293000	-1.266039000	12.974768000
15	5.865722000	0.144090000	10.218478000
15	5.277055000	3.042641000	13.182874000
7	5.366709000	-2.560914000	14.275729000
7	4.417533000	-2.543190000	11.483484000
7	1.041410000	0.563513000	13.236501000
7	3.001626000	1.659242000	15.146645000
6	-1.282711000	0.812127000	13.957636000

1	-1.553011000	0.793735000	12.899703000
1	-1.868821000	1.578410000	14.468747000
1	-1.559711000	-0.160382000	14.379520000
6	0.197403000	1.040657000	14.144113000
6	0.598665000	1.722082000	15.307554000
1	-0.212785000	2.056627000	15.943736000
6	1.898227000	2.004059000	15.787303000
6	1.985926000	2.723409000	17.115157000
1	2.423035000	2.071729000	17.879848000
1	0.998525000	3.033806000	17.459400000
1	2.621285000	3.611669000	17.043092000
6	0.645751000	-0.090439000	12.039966000
6	0.710391000	0.635348000	10.828506000
6	0.480937000	-0.046104000	9.631859000
1	0.527568000	0.500096000	8.694794000
6	0.206849000	-1.410683000	9.618517000
1	0.037120000	-1.923670000	8.675890000
6	0.156351000	-2.112996000	10.816205000
1	-0.048127000	-3.180472000	10.806105000
6	0.375323000	-1.472961000	12.039143000
6	0.991518000	2.124476000	10.831839000
1	1.573389000	2.340561000	11.732711000
6	1.823003000	2.593828000	9.639521000
1	2.716567000	1.976344000	9.520583000
1	2.147798000	3.625423000	9.805199000
1	1.253772000	2.570971000	8.702977000
6	-0.316602000	2.918667000	10.927766000
1	-0.975592000	2.682879000	10.084469000
1	-0.109834000	3.993208000	10.909548000
1	-0.857041000	2.693154000	11.851379000

6	0.352292000	-2.276890000	13.323087000
1	0.480243000	-1.575564000	14.151614000
6	1.519683000	-3.265897000	13.375602000
1	1.471386000	-3.979980000	12.546684000
1	1.506191000	-3.834852000	14.310989000
1	2.480215000	-2.749831000	13.299996000
6	-0.984074000	-3.000367000	13.518129000
1	-1.828128000	-2.306922000	13.455521000
1	-1.015101000	-3.492853000	14.496066000
1	-1.135162000	-3.772347000	12.755876000
6	4.332192000	1.918352000	15.667937000
1	4.949682000	1.042004000	15.438845000
1	4.337206000	2.026152000	16.758024000
6	5.004735000	3.149031000	15.049681000
1	6.001766000	3.259125000	15.488120000
1	4.439647000	4.062066000	15.262952000
6	4.144690000	4.343279000	12.536829000
6	2.824244000	4.397453000	13.000246000
1	2.500758000	3.729304000	13.793518000
6	1.916541000	5.287494000	12.432751000
1	0.897455000	5.321114000	12.806508000
6	2.309431000	6.121409000	11.386132000
1	1.598845000	6.812034000	10.941524000
6	3.620737000	6.063673000	10.914415000
1	3.936121000	6.713567000	10.102579000
6	4.535079000	5.181369000	11.485956000
1	5.556653000	5.144373000	11.119458000
6	6.945219000	3.807642000	12.988702000
6	7.255120000	5.088462000	13.460534000
1	6.488855000	5.687103000	13.945992000

6	8.538362000	5.601761000	13.293222000
1	8.774894000	6.597967000	13.656756000
6	9.520062000	4.838240000	12.657832000
1	10.520902000	5.241425000	12.530500000
6	9.215476000	3.562583000	12.187617000
1	9.975087000	2.960482000	11.697322000
6	7.929542000	3.050284000	12.349531000
1	7.668656000	2.056280000	11.994146000
6	6.012099000	1.358860000	8.836446000
6	5.499731000	2.640847000	9.048684000
1	5.051174000	2.867350000	10.012842000
6	5.555883000	3.596499000	8.035906000
1	5.145315000	4.586982000	8.209712000
6	6.132769000	3.276204000	6.808837000
1	6.180468000	4.019974000	6.018277000
6	6.651614000	1.997689000	6.593032000
1	7.104318000	1.748858000	5.637149000
6	6.590059000	1.040324000	7.601910000
1	7.002179000	0.048324000	7.436682000
6	7.569325000	-0.541622000	10.353615000
6	8.689614000	0.255401000	10.090260000
1	8.556042000	1.256421000	9.690725000
6	9.971983000	-0.233372000	10.330465000
1	10.834523000	0.392213000	10.117048000
6	10.151084000	-1.522275000	10.832504000
1	11.151530000	-1.903057000	11.016023000
6	9.037542000	-2.319418000	11.096328000
1	9.163992000	-3.323382000	11.490602000
6	7.753894000	-1.831643000	10.866753000
1	6.892011000	-2.448796000	11.104579000

6	4.917379000	-1.267559000	9.395138000
1	4.411823000	-0.818085000	8.534460000
1	5.644287000	-1.994434000	9.018456000
6	3.865202000	-1.939222000	10.284058000
1	3.148333000	-1.173949000	10.604000000
1	3.302108000	-2.656974000	9.677618000
6	4.633460000	-3.841772000	11.603735000
6	4.331217000	-4.770942000	10.449073000
1	3.254335000	-4.800647000	10.249013000
1	4.662751000	-5.787217000	10.666080000
1	4.823681000	-4.436238000	9.530726000
6	5.129222000	-4.442889000	12.782808000
1	5.255272000	-5.518756000	12.737464000
6	5.450905000	-3.861482000	14.023256000
6	5.874872000	-4.799404000	15.127493000
1	6.502815000	-4.291816000	15.862215000
1	6.410387000	-5.662269000	14.725739000
1	4.989507000	-5.172568000	15.654283000
6	5.718936000	-1.958763000	15.512184000
6	4.786150000	-1.894469000	16.565807000
6	5.109514000	-1.148824000	17.702893000
1	4.394303000	-1.091191000	18.519365000
6	6.320345000	-0.474754000	17.800378000
1	6.554789000	0.102849000	18.690279000
6	7.230553000	-0.539872000	16.749404000
1	8.173524000	-0.007147000	16.823544000
6	6.950817000	-1.269845000	15.592965000
6	7.958231000	-1.350830000	14.463968000
1	7.397183000	-1.533826000	13.542777000
6	8.748510000	-0.060796000	14.252484000

1	8.078425000	0.799507000	14.180976000
1	9.309101000	-0.127357000	13.315286000
1	9.469011000	0.121933000	15.058230000
6	8.902865000	-2.540308000	14.672585000
1	9.441803000	-2.444637000	15.622003000
1	9.639702000	-2.585265000	13.864801000
1	8.357584000	-3.488207000	14.688618000
6	3.439948000	-2.584494000	16.477609000
1	3.419334000	-3.148449000	15.541814000
6	3.231204000	-3.573624000	17.628616000
1	4.051621000	-4.294902000	17.689409000
1	2.295502000	-4.127010000	17.493774000
1	3.172817000	-3.057879000	18.593170000
6	2.300110000	-1.564179000	16.419523000
1	2.282836000	-0.936625000	17.316852000
1	1.330585000	-2.067068000	16.341705000
1	2.411379000	-0.896168000	15.561793000
1	3.613032000	1.361056000	11.467095000
1	6.173002000	0.339968000	13.127433000

TS H2 release from complex 4a' to complex 4a

C	7.519609	-1.759036	15.572728
C	6.211289	-2.288545	15.576157
C	5.380296	-2.174707	16.706721
C	5.906541	-1.592337	17.862617
C	7.212230	-1.117433	17.894549
C	8.004081	-1.191857	16.752266
N	5.685225	-2.786912	14.355666
C	5.535013	-4.081396	14.098726
C	5.950591	-5.083193	15.147426
C	3.918502	-2.576677	16.655313

C	3.037448	-1.324570	16.554967
C	8.364095	-1.804102	14.313954
C	9.104317	-3.140232	14.191649
Zn	5.087582	-1.413076	13.132324
N	4.368560	-2.570248	11.725652
C	4.387298	-3.890045	11.830112
C	4.969023	-4.583894	12.913157
Pd	5.280061	0.917650	12.748529
P	5.227529	3.138812	13.435395
C	6.875155	3.984831	13.465016
C	7.048299	5.248105	14.044544
C	8.298834	5.859134	14.032083
C	9.383618	5.217680	13.430973
C	9.213726	3.964062	12.847963
C	7.963166	3.347418	12.867550
Zn	2.923674	1.027479	13.228081
N	2.605849	1.970427	14.997713
C	3.804451	2.239217	15.771314
C	4.641762	3.391516	15.214362
P	5.577340	0.266645	10.541084
C	4.547051	-1.091351	9.727715
C	3.647877	-1.873339	10.676260
N	1.015260	0.755281	12.829879
C	0.722784	-0.124871	11.756279
C	0.903208	0.329786	10.429244
C	0.671061	-0.569143	9.386016
C	0.285911	-1.883724	9.634755
C	0.151863	-2.325851	10.944591
C	0.374491	-1.464716	12.022632
C	1.343767	1.757025	10.155869

C	0.322186	-2.006517	13.438867
C	-0.954022	-2.804484	13.720106
C	5.566688	1.534792	9.197298
C	5.116774	2.817133	9.504607
C	5.062542	3.800217	8.517404
C	5.453761	3.499239	7.215432
C	5.906876	2.215707	6.901487
C	5.967261	1.237153	7.888945
C	7.286558	-0.421215	10.368089
C	8.363602	0.441307	10.138027
C	9.668227	-0.043729	10.149839
C	9.914330	-1.395479	10.393956
C	8.844633	-2.258627	10.623246
C	7.537517	-1.775309	10.611621
C	4.210368	4.423283	12.554677
C	2.816538	4.416375	12.698958
C	2.025988	5.322974	11.999281
C	2.611661	6.243956	11.131054
C	3.996431	6.255009	10.978366
C	4.791504	5.353046	11.685173
C	0.031839	1.295157	13.553651
C	0.223445	2.088775	14.691962
C	1.414228	2.365361	15.402933
C	1.254521	3.149793	16.687382
C	-1.399755	1.023638	13.153904
C	1.901664	1.967664	8.750390
C	1.565880	-2.856219	13.720110
C	3.732808	-4.739639	10.763116
C	9.330147	-0.628545	14.186017
C	3.501311	-3.451718	17.839409

H	-2.068183	1.777749	13.573419
H	-1.717665	0.045731	13.530301
H	-1.515482	1.001992	12.068134
H	-0.683914	2.482452	15.134450
H	1.500714	2.530808	17.557117
H	0.227717	3.498732	16.804363
H	1.917424	4.020393	16.706673
H	0.797935	-0.238875	8.360807
H	0.106575	-2.563763	8.806639
H	-0.119686	-3.360047	11.138063
H	2.152237	1.983770	10.866998
H	2.707947	1.268260	8.514764
H	2.315342	2.975095	8.667623
H	1.121804	1.867332	7.986663
H	-0.662177	2.510066	9.788540
H	0.537054	3.767449	10.146796
H	-0.100873	2.767960	11.453078
H	0.348554	-1.157404	14.127658
H	1.625274	-3.709199	13.036339
H	1.549528	-3.245140	14.742886
H	2.481091	-2.272421	13.590807
H	-1.852805	-2.230610	13.473949
H	-1.003426	-3.080749	14.778389
H	-0.985981	-3.732543	13.139490
H	4.422661	1.334504	15.749242
H	3.581522	2.445005	16.824054
H	5.551652	3.487402	15.815216
H	4.095279	4.338287	15.265311
H	2.343852	3.704596	13.368460
H	0.949025	5.305596	12.136013

H	1.994208	6.950163	10.583517
H	4.466311	6.973408	10.311710
H	5.868660	5.371804	11.555869
H	6.201587	5.761406	14.492807
H	8.428109	6.837337	14.487038
H	10.358588	5.697085	13.420279
H	10.055142	3.458388	12.382466
H	7.812229	2.354862	12.447145
H	4.795853	3.030187	10.518732
H	4.703929	4.792349	8.772938
H	5.408690	4.261578	6.442595
H	6.217775	1.981301	5.887081
H	6.337583	0.244290	7.648554
H	8.176670	1.495026	9.951757
H	10.496352	0.635627	9.966924
H	10.932925	-1.772332	10.404419
H	9.023458	-3.312465	10.816103
H	6.713474	-2.453349	10.815309
H	3.907104	-0.585545	8.998949
H	5.224674	-1.753312	9.179736
H	2.975359	-1.155773	11.159926
H	3.009916	-2.538490	10.090756
H	2.648719	-4.580777	10.752047
H	3.918748	-5.799222	10.942685
H	4.108560	-4.487407	9.766429
H	4.926542	-5.664765	12.848397
H	6.123887	-6.066100	14.705494
H	5.161618	-5.184497	15.901049
H	6.851364	-4.755262	15.670854
H	5.278594	-1.497335	18.744471

H	7.607878	-0.670648	18.802500
H	9.010404	-0.786171	16.772579
H	7.677547	-1.730845	13.462807
H	8.798451	0.320322	14.299526
H	9.783695	-0.641599	13.190616
H	10.140463	-0.675147	14.922957
H	9.764934	-3.298027	15.051818
H	9.716774	-3.152026	13.284460
H	8.408033	-3.981718	14.139319
H	3.761734	-3.154871	15.740412
H	4.146373	-4.330887	17.933906
H	2.468860	-3.795506	17.715271
H	3.550645	-2.902300	18.785457
H	3.186893	-0.673623	17.423159
H	1.975722	-1.589301	16.507294
H	3.280995	-0.743709	15.661033
H	4.860626	0.149596	14.144816
H	6.850968	0.622245	13.079498

Complex 5a'

30	12.987864000	5.514065000	5.784195000
28	14.979153000	4.244559000	5.559785000
30	13.380559000	3.624124000	7.202170000
7	13.396814000	3.789465000	9.170195000
7	12.840268000	1.729975000	7.165438000
15	15.521144000	2.185321000	5.365195000
1	9.027640000	5.979710000	3.436506000
1	16.582236000	7.865121000	6.498113000
7	11.379600000	5.631087000	4.635755000
6	10.858663000	4.371097000	4.237488000

6	11.284402000	3.781435000	3.030594000
6	10.823955000	2.502788000	2.707207000
6	9.967736000	1.810940000	3.555681000
6	9.583544000	2.387576000	4.761315000
6	10.028519000	3.658977000	5.130229000
15	16.007133000	6.036828000	4.982543000
6	17.861410000	5.983277000	5.085921000
6	18.451743000	4.807597000	5.552469000
6	19.830059000	4.724227000	5.732230000
6	20.632779000	5.819657000	5.423813000
6	20.056086000	6.992160000	4.932157000
6	18.675555000	7.077212000	4.768033000
7	13.245714000	7.459158000	5.952146000
6	14.443914000	7.776395000	6.707863000
6	15.712042000	7.705064000	5.854018000
6	14.219376000	0.795981000	5.324279000
6	12.825867000	1.196477000	5.815742000
6	16.657896000	1.565631000	6.688338000
6	18.042503000	1.527712000	6.490667000
6	18.898876000	1.202336000	7.540189000
6	18.381679000	0.897649000	8.799246000
6	17.001434000	0.919629000	8.998470000
6	16.145128000	1.258052000	7.953877000
6	16.457199000	1.730265000	3.821824000
6	16.712919000	2.743167000	2.897394000
6	17.295561000	2.451567000	1.665244000
6	17.648910000	1.139763000	1.357111000
6	17.430465000	0.123665000	2.291322000
6	16.835681000	0.416693000	3.516195000
6	12.662159000	0.982363000	8.241214000

6	12.803771000	1.478218000	9.555810000
6	13.166478000	2.768863000	9.988154000
6	13.346839000	2.970956000	11.473244000
6	13.786549000	5.070088000	9.648584000
6	15.139476000	5.327661000	9.947207000
6	15.506263000	6.615808000	10.342972000
6	14.565500000	7.634744000	10.432877000
6	13.241233000	7.381760000	10.095913000
6	12.832288000	6.109123000	9.690074000
6	10.894599000	6.779190000	4.175926000
6	9.762990000	6.744713000	3.176849000
6	16.198525000	4.268518000	9.739235000
6	16.899003000	4.517860000	8.403364000
6	11.384105000	5.849797000	9.331332000
6	10.765964000	6.983886000	8.513788000
6	12.305247000	4.466658000	2.149750000
6	13.686046000	3.863971000	2.412151000
6	9.616854000	4.269003000	6.453844000
6	9.522268000	3.244921000	7.584652000
6	15.751431000	6.506444000	3.208110000
6	16.692945000	6.181350000	2.224499000
6	16.415784000	6.405335000	0.877275000
6	15.199250000	6.969231000	0.493735000
6	14.264959000	7.312878000	1.470404000
6	14.534800000	7.077047000	2.815605000
6	12.502703000	8.370041000	5.350025000
6	11.401400000	8.044948000	4.527262000
6	12.311773000	-0.480566000	8.096653000
6	17.211075000	4.176682000	10.881288000
6	10.554319000	5.568555000	10.589005000

6	12.826975000	9.835836000	5.511635000
6	11.959140000	4.422819000	0.661217000
6	8.306873000	5.052113000	6.311536000
1	11.362575000	-0.603251000	7.564122000
1	12.221619000	-0.961967000	9.071245000
1	13.078603000	-1.010264000	7.521956000
1	12.630733000	0.758402000	10.347190000
1	14.415047000	2.981288000	11.717620000
1	12.872542000	2.170932000	12.044273000
1	12.943361000	3.934407000	11.793110000
1	16.547989000	6.821700000	10.572801000
1	14.859072000	8.627877000	10.754719000
1	12.519528000	8.189332000	10.142593000
1	15.700912000	3.299532000	9.660024000
1	17.829980000	5.077646000	10.950119000
1	17.883893000	3.331137000	10.707449000
1	16.718150000	4.035467000	11.849076000
1	16.174651000	4.487073000	7.572618000
1	17.661087000	3.758363000	8.211560000
1	17.378523000	5.502593000	8.388139000
1	11.367608000	4.941830000	8.719887000
1	10.926512000	4.690900000	11.124775000
1	9.505426000	5.385402000	10.330004000
1	10.589599000	6.424364000	11.272600000
1	10.707432000	7.912177000	9.088851000
1	9.747586000	6.720666000	8.212875000
1	11.349833000	7.185279000	7.611698000
1	12.435261000	1.980912000	5.159131000
1	12.150009000	0.339053000	5.710247000
1	14.146277000	0.477670000	4.279850000

1	14.615104000	-0.043164000	5.905506000
1	18.458626000	1.761997000	5.517164000
1	19.970891000	1.188608000	7.364259000
1	19.048678000	0.643818000	9.618203000
1	16.583315000	0.688379000	9.974294000
1	15.076877000	1.302574000	8.135127000
1	16.423468000	3.757624000	3.151202000
1	17.463925000	3.251086000	0.949765000
1	18.103974000	0.906415000	0.398798000
1	17.722905000	-0.897128000	2.061530000
1	16.663912000	-0.377729000	4.237522000
1	12.771017000	10.120776000	6.566005000
1	12.132684000	10.459674000	4.947083000
1	13.843553000	10.052696000	5.167289000
1	10.883048000	8.888352000	4.086324000
1	10.152752000	6.483510000	2.186553000
1	9.267048000	7.714210000	3.103382000
1	11.152647000	2.040978000	1.780515000
1	9.614515000	0.819219000	3.287170000
1	8.936594000	1.835338000	5.435664000
1	12.355926000	5.516485000	2.446654000
1	11.996869000	3.403229000	0.262787000
1	12.682697000	5.020023000	0.097294000
1	10.956620000	4.818906000	0.467671000
1	13.970470000	3.985273000	3.470928000
1	14.449557000	4.355699000	1.803544000
1	13.698231000	2.792244000	2.186046000
1	10.397252000	4.988977000	6.720955000
1	8.413897000	5.882643000	5.609021000
1	7.995432000	5.466673000	7.276560000

1	7.504534000	4.399741000	5.948970000
1	8.690279000	2.547246000	7.438557000
1	9.347768000	3.754682000	8.536698000
1	10.445816000	2.666041000	7.671975000
1	14.522729000	7.040615000	7.515361000
1	14.386507000	8.758746000	7.192604000
1	15.713332000	8.483961000	5.084489000
1	17.649044000	5.758848000	2.515379000
1	17.157553000	6.146331000	0.126402000
1	14.984232000	7.144773000	-0.556356000
1	13.313162000	7.754946000	1.189072000
1	13.785298000	7.322452000	3.559676000
1	17.808664000	3.967008000	5.788119000
1	20.274543000	3.803155000	6.095475000
1	21.708708000	5.754188000	5.553800000
1	20.683710000	7.842724000	4.679658000
1	18.231574000	7.992017000	4.384431000

Complex 5a

28	5.007933000	0.973064000	12.204442000
30	3.019310000	0.738558000	13.289110000
30	4.833109000	-1.158391000	12.979929000
15	5.797229000	0.250718000	10.327053000
15	5.310157000	2.907419000	13.113285000
7	5.394789000	-2.496513000	14.290843000
7	4.384510000	-2.443531000	11.531710000
7	1.074686000	0.555910000	13.164249000
7	3.048044000	1.599213000	15.080061000
6	-1.245001000	0.801724000	13.902174000
1	-1.518648000	0.822898000	12.844993000
1	-1.819746000	1.557703000	14.440753000

1	-1.534146000	-0.180524000	14.291763000
6	0.237590000	1.012611000	14.089323000
6	0.648085000	1.659527000	15.267848000
1	-0.157185000	1.977507000	15.920005000
6	1.953260000	1.905026000	15.752541000
6	2.054921000	2.537530000	17.122517000
1	2.490789000	1.834736000	17.841180000
1	1.071542000	2.831818000	17.491515000
1	2.696450000	3.424065000	17.103367000
6	0.662106000	-0.110776000	11.981260000
6	0.722929000	0.594752000	10.758359000
6	0.476178000	-0.102298000	9.574034000
1	0.519269000	0.429731000	8.628400000
6	0.187868000	-1.463698000	9.585228000
1	0.005494000	-1.990452000	8.652648000
6	0.137311000	-2.145802000	10.795088000
1	-0.079494000	-3.210839000	10.803261000
6	0.371419000	-1.489274000	12.006161000
6	1.018729000	2.080443000	10.735177000
1	1.542034000	2.321504000	11.664422000
6	1.934579000	2.500589000	9.587479000
1	2.830244000	1.876304000	9.557066000
1	2.254295000	3.536824000	9.733643000
1	1.435350000	2.440457000	8.613607000
6	-0.283505000	2.888616000	10.724421000
1	-0.880760000	2.651370000	9.836672000
1	-0.064533000	3.960985000	10.712981000
1	-0.893278000	2.674825000	11.607281000
6	0.352326000	-2.271587000	13.303783000
1	0.456034000	-1.555066000	14.122312000

6	1.545855000	-3.226460000	13.383854000
1	1.530163000	-3.946825000	12.559203000
1	1.532380000	-3.789567000	14.322730000
1	2.491001000	-2.682293000	13.321423000
6	-0.966639000	-3.025310000	13.499901000
1	-1.828493000	-2.357039000	13.409846000
1	-0.996210000	-3.493483000	14.489649000
1	-1.087980000	-3.821182000	12.757205000
6	4.384296000	1.804299000	15.609431000
1	4.970801000	0.907969000	15.377722000
1	4.391273000	1.905634000	16.699449000
6	5.093848000	3.010713000	14.991651000
1	6.106207000	3.071233000	15.403492000
1	4.574813000	3.944536000	15.230685000
6	4.169467000	4.238064000	12.520612000
6	2.848019000	4.269762000	12.984778000
1	2.529310000	3.578721000	13.760003000
6	1.931863000	5.170741000	12.448755000
1	0.912092000	5.179873000	12.822360000
6	2.317431000	6.046085000	11.433928000
1	1.600626000	6.744653000	11.012161000
6	3.631695000	6.022094000	10.968769000
1	3.944794000	6.707918000	10.186033000
6	4.553144000	5.127320000	11.509735000
1	5.576298000	5.120294000	11.146550000
6	6.969070000	3.697154000	12.914049000
6	7.273156000	4.978294000	13.388977000
1	6.503590000	5.573162000	13.873827000
6	8.554708000	5.497005000	13.225867000
1	8.786200000	6.493590000	13.591813000

6	9.541845000	4.738602000	12.592525000
1	10.541377000	5.146148000	12.468706000
6	9.244034000	3.461930000	12.121164000
1	10.007786000	2.862281000	11.634275000
6	7.959216000	2.946030000	12.279432000
1	7.705998000	1.949950000	11.928827000
6	5.968284000	1.462941000	8.941580000
6	5.462469000	2.746652000	9.150327000
1	5.010411000	2.974996000	10.110601000
6	5.522901000	3.702727000	8.138402000
1	5.115956000	4.694806000	8.311921000
6	6.098735000	3.379113000	6.911893000
1	6.150636000	4.122083000	6.120815000
6	6.610291000	2.097322000	6.697336000
1	7.061137000	1.845201000	5.741358000
6	6.543591000	1.140858000	7.706674000
1	6.949725000	0.146435000	7.541297000
6	7.493623000	-0.481211000	10.411891000
6	8.628035000	0.286799000	10.122405000
1	8.510958000	1.289976000	9.723702000
6	9.904547000	-0.229652000	10.335620000
1	10.775416000	0.377522000	10.103397000
6	10.066535000	-1.521572000	10.834970000
1	11.061984000	-1.923409000	11.000122000
6	8.941011000	-2.296011000	11.114267000
1	9.052145000	-3.304694000	11.501328000
6	7.664236000	-1.779713000	10.908841000
1	6.795953000	-2.386762000	11.147899000
6	4.817251000	-1.122414000	9.468103000
1	4.287772000	-0.634849000	8.643532000

1	5.526392000	-1.837739000	9.038934000
6	3.791214000	-1.819364000	10.363083000
1	3.081993000	-1.063761000	10.719672000
1	3.212616000	-2.525477000	9.759068000
6	4.543214000	-3.749473000	11.647929000
6	4.141690000	-4.667496000	10.515024000
1	3.056181000	-4.647375000	10.368017000
1	4.435847000	-5.697125000	10.722755000
1	4.604104000	-4.359721000	9.571996000
6	5.066756000	-4.369824000	12.805547000
1	5.156803000	-5.448741000	12.754777000
6	5.435568000	-3.799763000	14.036306000
6	5.865140000	-4.744735000	15.131618000
1	6.622346000	-4.288265000	15.772848000
1	6.254706000	-5.676235000	14.716524000
1	5.009467000	-4.992143000	15.769612000
6	5.749489000	-1.919741000	15.537784000
6	4.819099000	-1.881185000	16.595254000
6	5.142215000	-1.155028000	17.744688000
1	4.427624000	-1.112476000	18.562537000
6	6.351103000	-0.478022000	17.852335000
1	6.584337000	0.084545000	18.752081000
6	7.260194000	-0.521414000	16.799651000
1	8.202597000	0.011627000	16.881912000
6	6.980087000	-1.230839000	15.630447000
6	7.986636000	-1.284693000	14.498982000
1	7.436919000	-1.524164000	13.584668000
6	8.697645000	0.044320000	14.253037000
1	7.976215000	0.858894000	14.158604000
1	9.264645000	-0.011327000	13.318883000

1	9.401634000	0.293518000	15.055226000
6	8.997745000	-2.413330000	14.729748000
1	9.548517000	-2.256303000	15.664135000
1	9.719966000	-2.447964000	13.908101000
1	8.503156000	-3.387258000	14.789839000
6	3.469673000	-2.563194000	16.488961000
1	3.468018000	-3.153264000	15.569306000
6	3.212081000	-3.515272000	17.660747000
1	4.026334000	-4.236836000	17.778931000
1	2.280719000	-4.070073000	17.504261000
1	3.114316000	-2.971313000	18.606360000
6	2.346767000	-1.530788000	16.363926000
1	2.322483000	-0.868525000	17.235780000
1	1.371262000	-2.021817000	16.286153000
1	2.487528000	-0.901411000	15.481920000
1	3.647830000	1.228613000	11.583836000
1	6.001602000	0.321609000	13.145170000