Supporting Information

**Rare-earth Metal/Platinum Heterobinuclear Complexes Containing Reactive Ln-alkyl groups (Ln = Y, Lu): Synthesis, Structural Characterization and Reactivity**

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The $^1$H and $^{13}$C NMR spectra were recorded on a JEOL JNM ECA600, JNM ECP500 or JNM AL-300. The $^{31}$P NMR spectra were recorded on a JNM AL400. $^1$H and $^{13}$C spectra were referenced to the residual solvent resonances. $^{31}$P NMR spectra were recorded based on an external 85% H$_3$PO$_4$ standard.
1. Spectral data for (C₆Me₅SiMe₂CH₂PPh₂)Y(CH₂SiMe₃)₂(OCH₃)₃PtMe₂ (3a)

H NMR (500.16MHz, toluene-d₈, 50°C): δ -0.76 (br, 2H, YCH₂), -0.28 (br, 1H+3H, µ-CH₂ + SiMe₂), 0.00 (s, 9H, SiMe₂), 0.19 (br s, 3H, SiMe₂), 0.36 (s, 9H, SiMe₃), 0.47 (1H, µ-CH₃)*, 0.58 (br, 3H, PtMe), 0.99 (d, 3H, 3J_HP = 5.50Hz, 2J_HH = 49.97 Hz, PtMe), 1.44 (brs, 4H, β-THF), 1.9-2.2 (br, 9H + 2H, Cp’Me + CH₂), 2.31 (s, 3H, Cp’Me), 3.89 (br, 4H, α-THF), 7.1 (m, 6H, m+p-Pb), 7.65 (t, 4H, 3J_HH = 3J_HB = 8.48Hz, o-Ph). COSY (toluene-d₈, 50°C): -0.74 – 4.0. 1H NMR (600.17MHz, toluene-d₆, -10°C): δ -1.35 (dt, 1H, 2J_HH = 3.42Hz, 2J_HH = 6.8Hz, µ-CH₂), -1.09 (dd, 1H, 2J_HH = 3.10 Hz, 2J_HH = 11.0Hz, η²-CH₂), -0.96 (dd, 1H, 2J_HH = 3.09Hz, 2J_HH = 10.30Hz, η¹-CH₂), -0.57 (s, 3H, SiMe₂_major), -0.49 (dd, 1H, 2J_HH = 3.43 Hz, 2J_HH = 10.65Hz, η¹-CH₂), -0.47 (dd, 1H, 2J_HH = 3.47Hz, 2J_HH = 10.31Hz, η¹-CH₂), -0.10 (dd, 1H, 2J_HH = 3.78Hz, 2J_HH = 10.65Hz, µ-CH₂), -0.06 (s, 3H, SiMe₂_minor), 0.00 (s, 9H, SiMe₃_major), 0.10 (s, 9H, SiMe₃_major), 0.16 (s, 3H, SiMe₂_minor), 0.34 (s, 3H, SiMe₂_major), 0.4 (3H, PtMe)**, 0.43 (s, 9H, SiMe₃_minor), 0.44 (1H, µ-CH₂)*, 0.48 (s, 9H, SiMe₃_major), 0.84 (1H, µ-CH₂)***, 0.86 (d, 3H, 3J_HH = 4.81Hz, PtMe), 1.03 (d, 3H, 3J_HH = 5.46Hz, PtMe), 1.08 (d, 3H, 3J_HH = 5.16Hz, PtMe), 1.28 (m, 4H, β-THF), 1.37 (m, 4H, β-THF), 1.66 (s, 3H, Cp’Me_minor), 1.76 (s, 3H, Cp’Me_major), 1.88 (m, 1H, CH₂), 1.91 (s, 3H, Cp’Me_major), 2.01 (m, 1H + 2H, CH₂), 2.18 (s, 6H, Cp’Me_minor), 2.26 (s, 3H, Cp’Me_major), 2.38 (s, 3H, Cp’Me_major), 3.51 (m, 2H, α-THF), 3.72 (m, 2H, α-THF), 3.87 (m, 2H, α-THF), 4.06 (m, 2H, α-THF), 7.04 (brm, 4H, m+p-Pb), 7.13 (brm, 8H, m+p-Pb), 7.32 (t, 2H, 2J_HH = 8.25Hz, o-Ph), 7.59 (t, 2H, 2J_HH = 8.43Hz, o-Ph), 7.66 (t, 2H, 2J_HH = 8.25Hz, o-Ph), 7.86 (t, 2H, 2J_HH = 8.61Hz, o-Ph). Two isomers were observed in the ratio of 68% to 32%. 13C NMR (150.91MHz, C₆D₆, -10°C): δ 1.11 (s, SiMe₂), 2.9 (s, SiMe₂), 3.0 (d, 2J_CP-cis = 7.63 Hz, PtMe), 3.4 (SiMe₃ + SiMe₂****, ****), 4.1 (s, SiMe₂), 4.2 (s, SiMe₂), 4.5 (d, 2J_CP = 10.17Hz, µ-CH₂), 4.7 (s, SiMe₂), 5.2 (s, SiMe₃), 9.5 (br, PtMe), 10.0 (d, 2J_CP-trans = 104.27 Hz, PtMe), 10.6 (d, 2J_CP-trans = 106.79Hz, PtMe), 11.0 (s, Cp’Me), 11.6 (s, Cp’Me), 13.0 (s, Cp’Me), 13.3 (s, Cp’Me), 14.8 (Cp’Me2), 15.4 (s, Cp’Me), 16.3 (d, 1J_CP = 15.26Hz, CH₂), 16.9 (d, 1J_CP = 17.81Hz, CH₂), 17.3 (s, Cp’Me), 17.7 (brs, µ-CH₂), 24.6 (brs, β-THF), 24.9 (brs, β-THF), 32.0 (d, 1J_VC = 43.24Hz, η²-CH₂), 34.5 (d, 1J_VC = 40.69Hz, η¹-CH₂), 70.9 (brs, α-THF), 71.6 (brs, α-THF), 109.0 (s, Cp’-ring), 109.2 (s, Cp’-ring), 123.6 (s, Cp’-ring), 124.1 (s, Cp’-ring), 124.6 (s, Cp’-ring), 124.8 (Cp’-ring)****, 126.2 (s, Cp’-ring), 126.9 (s, Cp’-ring), 129.9 (s, p-Pb), 130.1 (s, p-Pb), 132.6 (d, 2J_CP = 12.71Hz, o-Ph), 133.5 (2J_CP = 7.63 Hz, o-Ph), 133.9 (2J_CP = 12.70Hz, o-Ph), 135.2 (d, 2J_CP = 12.71Hz, o-Ph). The carbon signals for m-Pb and one p-Pb are obscured in toluene-d₈ signals. Two Cp’-ring carbon signals are obscured in other signals. The carbon signals for ipso-Ph were not observed. * the signal was determined by COSY. ** the signal was determined by NOESY. *** the signal was determined by HSQC.

**** the signal was determined by HMBC. COSY (toluene-d₈, -10°C) -1.35 – 0.84, -1.09 – -0.49, -0.96 – -0.47, -0.10 – 0.44, 1.88 – 2.01, 7.04 – 7.32,7.66, 7.13 – 7.59,7.86. HSQC (toluene-d₈, -10°C) δH-δC: -1.35,0.84 - 17.7, -1.09,-0.49 – 32.0, -0.57 – 1.1, -0.96,-0.47 – 34.5, -0.06 – 2.9, 0.00 – 4.1, 0.10 – 3.4, 0.4 – 9.5, 0.43 – 4.7, 0.48 – 5.2, 0.86 – 3.0, 1.03 – 10.0, 1.08 – 10.6, 1.28 – 24.9, 1.37 – 24.6, 1.66 – 11.0, 1.76 – 11.6, 1.88,2.01 – 16.3, 1.91,2.28 – 14.8, 2.18 – 13.0,15.4, 2.26 – 13.3, 2.28 – 14.8, 2.38 – 17.3, 3.51,3.87 – 71.6, 3.72,4.06 – 70.9, 7.04 – 129.9,130.1, 7.32 – 133.5, 7.59 – 133.9, 7.66 – 135.2, 7.86 – 132.6. HMBC
31P NMR (160.1MHz, C6D6, RT): $\delta$ 8.66 ($^1J_{PP} = 2084.3$ Hz), 12.06 ($^1J_{PP} = 2128.4$ Hz) The integral intensity of $\delta$8.66 to $\delta$12.06 is 66%/34%.

Figure S1. $^1$H NMR spectrum (300.40MHz) of 3a at various temperature in toluene-$d_8$ (*). The signals marked with $\$ and signals marked with # is residual Et$_2$O and hexane proton signals, respectively.
2. Spectral data for (C₅Me₅SiMe₅CH₂PPh₂)₂(OC₅H₄)PtMe₂ (3b)

1H NMR (500.16MHz, toluene-d₆, 50°C): δ -0.10 (br, 1H, η⁴-CH₂), -0.87 (brd, 1H, ²J_HH = 9.15Hz, η¹-CH₂), -0.50 (br, 1H, μ-CH₂), -0.16 (s, 3H, SiMe₂), -0.02 (s, 9H, SiMe₃), 0.14 (s, 3H, SiMe₂), 0.35 (s, 9H, SiMe₃), 0.62 (1H, μ-CH₂)², 0.67 (d, 3H, ³J_HP = 4.75 Hz, ²J_HP = 44.47 Hz, PtMe), 1.09 (d, 3H, ³J_HP = 5.05Hz, ²J_HP = 49.92 Hz, PtMe), 1.44 (brs, 4H, β-THF), 1.92 (br, 3H, Cp’Me), 1.96 (s, 3H, Cp’Me), 2.05 (s, 3H, Cp’Me), 2.34 (s, 3H, Cp’Me), 3.90 (brs, 4H, α-THF), 7.06 (m, 2H, p-Ph), 7.12 (brm, 4H, m-Ph), 7.56 (brs, 2H, o-Ph), 7.67 (t, 2H, ³J_HH = ²J_HP = 8.48Hz, o-Ph). The CH₂ signal was obscured in broad Cp’Me signals. COSY (toluene-d₆, 50°C) -0.10 – -0.87, -0.50 – 0.62. ³H NMR (600.17MHz, toluene-d₆, -10°C): δ -1.27 (d, 1H, ²J_HH = 11.70Hz, η¹-CH₂), -1.06 (d, 1H, ²J_HH = 10.62Hz, η¹-CH₂), -0.91 (t, 1H, ³J_HH = ³J_HP = 6.51Hz, μ-CH₂), -0.66 (d, 2H, ²J_HH = 11.34Hz, η¹-CH₂), -0.56 (d, 3H, SiMe₂), -0.09 (brm, 1H, μ-CH₂), -0.09 (s, 6H, SiMe₆), -0.02 (s, 6H, SiMe₂), 0.10 (s, 9H, SiMe₃), 0.15 (s, 3H, SiMe₂), 0.37 (s, 3H, SiMe₂), 0.42 (s, 9H, SiMe₃), 0.49 (s, 9H, SiMe₃), 0.58 (br, 1H, μ-CH₂), 0.62 (d, 3H, ³J_HP-cis = 4.80Hz, PtMe), 0.87 (br, 1H, μ-CH₂), 0.92 (d, 3H, ³J_HP-cis = 4.80Hz, PtMe), 1.07 (d, 3H, ³J_HP-trans = 5.46Hz, PtMe), 1.24 (d, 3H, ³J_HP-trans = 4.44Hz, PtMe), 1.27 (brm, 4H, β-THF), 1.38 (brm, 4H, β-THF), 1.66 (s, 3H, Cp’Me), 1.76 (s, 3H, Cp’Me), 1.91 (s, 3H, Cp’Me), 1.9 (m, 1H, CH₂), 2.1 (m, 2H, CH₂), 2.13 (s, 3H, Cp’Me), 2.19 (s, 3H, Cp’Me), 2.2 (1H, CH₃)², 2.24 (s, 3H, Cp’Me), 2.36 (s, 3H, Cp’Me), 2.41 (s, 3H, Cp’Me), 3.52 (brs, 2H, α-THF), 3.74 (brs, 2H, α-THF), 3.89 (brs, 2H, α-THF), 4.14 (brs, 2H, α-THF), 7.05 (brm, 2H + 2H, p-Ph), 7.28 (t, 4H + 4H, ³J_HH = ³J_HP = 8.07Hz, o-Ph), 7.61 (t, 4H, ³J_HH = ²J_HP = 7.92Hz, o-Ph), 7.68 (t, 4H, ³J_HH = ³J_HP = 8.43Hz, o-Ph). One o-Ph and m-Ph signals are obscured in residual toluene-d₆ signals. Two isomers were observed in the ratio of 53% to 47%.

13C NMR (150.91MHz, toluene-d₆, -10°C): δ 1.2 (s, SiMe₂), 3.1 (d, ³J_CP = 2.5Hz, SiMe₂), 3.4 (d, ²J_CP-cis = 6.4Hz, PtMe), 3.5 (s, SiMe₂), 3.7 (s, SiMe₂), 4.1 (s, SiMe₂), 4.4 (d, ³J_CP = 10.17Hz, μ-CH₂), 4.4 (s, SiMe₂), 4.8 (s, SiMe₂), 5.4 (s, SiMe₂), 8.9 (d, ²J_CP-trans = 100.45Hz, PtMe), 10.4 (d, ²J_CP-cis = 5.09 Hz, PtMe), 10.6 (d, ²J_CP-trans = 102.69 Hz, PtMe), 11.0 (s, Cp’Me), 11.6 (s, Cp’Me), 13.0 (s, Cp’Me), 13.3 (s, Cp’Me), 14.9 (s, Cp’Me), 15.0 (s, Cp’Me), 15.2 (s, Cp’Me), 16.2 (d, ³J_CP = 16.54Hz, CH₃), 16.4 (br, μ-CH₂), 16.9 (d, ³J_CP = 13.99Hz, CH₂), 17.3 (s, Cp’Me), 24.6 (brs, β-THF), 25.1 (brs, β-THF), 33.0 (s, η⁴-CH₂), 36.1 (s, η⁴-CH₂), 71.2 (brs, α-THF), 72.3 (brs, α-THF), 108.7 (s, Cp’-ring), 109.1 (s, Cp’-ring), 122.2 (s, Cp’-ring), 123.4 (s, Cp’-ring), 124.2 (s, Cp’-ring), 124.4 (s, Cp’-ring), 126.9 (s, Cp’-ring), 129.8 (s, p-Ph), 129.9 (s, p-Ph), 132.6 (d, ²J_CP = 12.72 Hz, o-Ph), 133.3 (d, ²J_CP = 8.90Hz, o-Ph), 134.2 (d, ²J_CP = 11.45 Hz, o-Ph), 135.2 (d, ²J_CP = 11.45Hz, o-Ph). Three Cp’-ring carbons are obscured in other signals. Four m-Ph and one p-Ph signals are obscured in residual toluene-d₆ signals. COSY (toluene-d₆, -10°C) δ₁₉-δ₁₄ -1.27,-1.06 – -0.66, -0.91 – 0.87, -0.09 – 0.58, 1.9 – 2.1, 2.1 – 2.2. HSQC (toluene-d₆, -10°C) δ₁₉ – δ₁₄ -1.27,-1.06 – 33.0, -0.91 – 16.4, -0.66 – 33.0,36.1, -0.56 – 1.2, -0.09 – 3.1, -0.02 – 4.1, 0.10 – 3.7, 0.15 – 3.5, 0.37 – 4.4, 0.42 – 4.8, 0.49 – 5.4, 0.62 – 10.4, 0.92 – 3.4, 1.07 – 8.9, 1.24 – 10.6, 1.27 – 25.1, 1.38 – 24.6, 1.66 – 11.0, 1.76 – 11.6, 1.91 – 15.0, 1.9,2.1 – 16.2, 2.1,2.2 – 16.9, 2.13 – 13.0, 2.19 – 15.2, 2.24 – 13.3, 2.36 – 14.9, 2.41 – 17.3, 7.05 – 129.8,129.9,130.3, 3.52,3.89 – 71.2, 3.74,4.14 – 72.3, 7.28 – 133.3, 7.61 – 134.2, 7.68 – 135.2, 7.86 – 132.6. HMBC (toluene-d₆, -10°C) δ₁₉ – δ₁₄ -1.27,-0.66 – 4.8, -1.06,-0.66 – 5.4, 0.10 – 16.4, 0.92 – 8.9, 1.07 – 3.4,16.4, 1.24 – 4.6,10.4. ¹³P NMR (160.10MHz, C₅D₆, RT): δ 12.30 (¹J_PP = 2172.2Hz), 8.00 (¹J_PP =
The integral ratio of $\delta 12.3$ to $\delta 8.00$ is 55/45. * determined by COSY

Figure S2. $^1$H NMR spectrum (300.40 MHz) of 3b at various temperature in toluene-$d_8$ (*). The signals marked with $\$$ and signals marked with # is residual Et$_2$O and hexane proton signals, respectively.
3. Full spectral data for (C₆Me₃C₂H₄PPh₂)Y(CH₂SiMe₃)₂(OC₆H₅)PtMe₂ (4a)

¹H NMR (500.16MHz, toluene-d₈, 65°C): δ -0.79 (br, 2H, ν₁-CH₂), -0.50 (br, 1H, µ-CH₂), -0.02 (s, 9H, SiMe₃), 0.15 (1H, µ-CH₂)*, 0.32 (s, 9H, SiMe₃), 0.50 (brm, 3H, PtMe), 0.91 (d, 3H, ²JHₓ = 5.45 Hz, ²JHH = 48.12Hz, PtMe), 1.47 (brs, β-THF), 1.86 (brs, 3H, Cp’Me), 1.97 (br, 3H, Cp’Me), 2.01 (br, 3H, Cp’Me), 2.18 (s, 3H, Cp’Me), 2.44 (br, 1H, CH₂), 2.68 (brm, 2H, CH₂), 2.86 (br 1H, CH₂), 3.86 (brs, 4H, α-THF), 7.0-7.2 (m, 6H, m+p-Pb), 7.56 (br, 2H, o-Pb), 7.61 (brm, 2H, o-Pb). COSY (toluene-d₈, 65°C) -0.50 - 0.15. ¹H NMR (600.17MHz, toluene-d₈, -20°C): δ -1.02 (dd, 1H, ²JYY = 2.61Hz, ²JHH = 10.62 Hz, ν₁-CH₂), -0.92 (dd, 1H, ²JYH = 2.92Hz, ²JHH = 10.30Hz, ν₁-CH₂), -0.87 (td, 1H, ²JYH = 2.75Hz, ²JHH = 7.05Hz, µ-CH₂), -0.55 (dd, 1H, ²JYH = 3.44Hz, ²JHH = 10.65Hz, ν₁-CH₂), -0.45 (dd, 1H, ²JYH = 2.40Hz, ²JHH = 10.31Hz, ν₁-CH₂), 0.06 (s, 9H, SiMe₃), 0.08 (s, 9H, SiMe₃), 0.20 (dd, 3H, ²JHP = 5.5Hz, ²JVH = 2.58Hz, PtMe), 0.44 (s, 9H, SiMe₃), 0.51 (s, 9H, SiMe₃), 0.52 (1H, µ-CH₂), the coupling constant value is obscured in a signal at δ 0.51, 0.90 (d, 3H, ²JHP = 5.5Hz, ²JHH = 54.6Hz, PtMe), 0.98 (d, 3H, ²JHP = 6.19Hz, ²JHH = 54.6Hz, PtMe), 1.02 (d, 3H, ²JHP = 5.5 Hz, ²JHH = 55.7Hz, PtMe), 1.27 (brm, 4H, β-THF), 1.34 (brm, 4H, β-THF), 1.72 (s, 3H, Cp’Me), 1.76 (brs, 3H, Cp’Me), 1.78 (brs, 3H, Cp’Me), 1.97 (s, 3H, Cp’Me), 2.19 (s, 3H, Cp’Me), 2.2 (1H + 2H, CH₂)*, 2.25 (w, 3H, Cp’Me), 2.30 (s, 3H, Cp’Me), 2.31 (s, 3H, Cp’Me), 2.45 (m, 1H, CH₂), 2.63 (m, 1H, CH₂), 2.7 (br, 1H, CH₂), 2.77 (m, 1H, CH₂), 2.86 (t, 1H, ³JHH = 13.72 Hz, CH₂), 3.50 (m, 2H, α-THF), 3.71 (m, 2H, α-THF), 3.80 (m, 2H, α-THF), 4.04 (m, 2H, α-THF), 6.95-7.2 (brm, 12H, m+p-Pb), 7.43 (br, 2H, o-Pb), 7.56 (t, 2H, ³JHH = 8.92Hz, o-Pb), 7.66 (t, 2H, ³JHH = 8.70Hz, o-Pb), 7.69 (t, 2H, ³JHH = 9.12Hz, o-Pb). Two µ-CH₂ proton were not observed. Two isomers were observed in the ratio of 54% to 46%. ¹³C NMR (150.91MHz, toluene-d₈, -20°C): δ 2.0 (d, ²JCPCis = 6.88Hz, PtMe), 3.3 (s, SiMe₃), 3.9 (s, SiMe₃), 4.8 (s, SiMe₃), 5.3 (s, SiMe₃), 5.4 (brs, µ-CH₂), 9.2 (d, PtMe, ²JCPtrans = 103.15Hz), 9.4 (br, PtMe), 10.6 (s, Cp’Me), 11.2 (d, ²JCPtrans = 103.87Hz, PtMe), 11.5 (s, Cp’Me), 11.5 (s, Cp’Me), 11.9 (br, Cp’Me), 12.9 (Cp’Me)**, 12.9 (s, Cp’Me), 13.0 (s, Cp’Me2), 16.6 (d, ²JCPcis = 5.5Hz, µ-CH₂), 20.0 (CH₂)**, 22.0 (br, CH₂), 24.6 (s, β-THF), 24.8 (s, β-THF), 25.5 (CH₂)**, 25.6 (d, ¹JCp = 29.04Hz, CH₂), 32.0 (d, ¹JYC = 45.62Hz, ν₂-CH₂), 32.8 (d, ¹JYC = 44.23Hz, ν₂-CH₂), 71.0 (brs, α-THF), 71.7 (brs, α-THF), 96.1 (s, Cp’-ring), 99.6 (s, Cp’-ring), 115.2 (Cp’-ring)***, 117.2 (s, Cp’-ring), 118.1 (s, Cp’-ring), 118.9 (s, Cp’-ring), 119.4 (s, Cp’-ring), 119.9 (br, Cp’-ring), 121.5 (s, Cp’-ring), 129.9 (s, p-Pb), 130.0 (s, p-Pb), 130.6 (s, p-Pb), 132.7 (s, ²JCP = 9.67 Hz, o-Pb), 133.4 (br, o-Pb), 134.6 (d, ²JCP = 11.06Hz, o-Pb), 135.3 (d, ²JCP = 11.04Hz, o-Pb). * the signal was determined by COSY, ** the signal was determined by HSQC. Carbon signals for ipso-Pb were not observed. Carbon signals for ipso-Pb were not observed. COSY (toluened₆, -20°C) -1.02 - 0.55, -0.92 - 0.45, -0.87 - 0.52, 2.2 - 2.63, 2.45 - 2.86, 3.50 - 3.80, 3.71 - 4.04. HSQC (toluene-d₆, -20°C) δ₁H-δ₁C -1.02 - 0.55 - 32.0, -0.92 - 0.45 - 32.8, -0.87,0.52 - 16.6, 0.06 - 3.3, 0.51 - 5.3, 0.90 - 2.0, 0.98 - 9.2, 1.02 - 11.2, 1.27 - 24.8, 1.34 - 24.6, 1.72 - 10.6, 1.76,1.78 - 11.5, 1.97 - 11.9, 2.19 - 12.9, 2.2, 2.6 - 20.3, 2.25 - 12.9, 2.30,2.31 - 13.0, 2.45,2.86 - 25.6, 2.77 - 25.5, 3.50,3.80 - 71.0, 3.71,4.04 - 71.7, (6.95-7.2) - 129,9,130.00,130.6, 7.56 - 135.3, 5.66 - 132.7, 7.69 - 134.6. HMBC (toluened₆, -20°C) δ₁H-δ₁C -0.87,0.5 - 3.3, 0.06 - 16.6, 0.08 - 5.4, 0.44 - 32.0, 0.51 - 32.8, 0.90,0.98 - 16.6, 1.02 - 5.4, 1.72-115.2,118.9,119.9. ³¹P NMR (160.10MHz, C₆D₆,
RT): $\delta$ 10.76 (s, $^1J_{PPt} = 2078.4$ Hz), 10.31 (s, $^1J_{PPt} = 1931.9$ Hz). The integral intensity ratio of $\delta$ 10.76 to $\delta$ 10.31 is 42%/58%.

**Figure S3.** $^1$H NMR spectrum (300.40MHz) of 4a at various temperature in toluene-$d_8$ (*). The signals marked with $\$$ and signals marked with # is residual Et$_2$O and hexane proton signals, respectively. The signal marked with $\&$ is based on unidentified impurity.
4. Full spectral data for (C_2Me_3C_6H_2PPh_2)Lu(CH_2SiMe_3)_2(OC_3H_8)PtMe_2 (4b)

1H NMR (399.65MHz, C_6D_6, 60°C): δ -0.96 (br, 1H, η^1-CH_2), -0.88 (br, 1H, η^1-CH_2), -0.23 (br, 1H, μ-CH_2), -0.04 (s, 9H, SiMe_3), 0.32 (s, 9H, SiMe_3), 0.57 (brm, 3H, PtMe), 0.84 (LuCH_2)*, 1.00 (d, 3H, 2^J_{HH} = 5.95 Hz, 2^J_{HH} = 52.66 Hz, PtMe), 1.43 (brs, 4H, β-THF), 1.88 (s, 3H, Cp’Me), 1.96 (s, 3H, Cp’Me), 2.02 (s, 3H, Cp’Me), 2.20 (s, 3H, Cp’Me), 2.5-3.0 (m, 4H, CH_2), 3.91 (brs, 4H, α-THF), 7.09 (m, 2H, p-Ph), 7.14 (m, 4H, m-Ph), 7.53 (br, 2H, o-Ph), 7.63 (t, 2H, 3^J_{HH} = 3^J_{HH} = 8.70Hz, o-Ph). COSY (toluene-d_6, 50°C) -0.96 -- 0.88, -0.23 -- 0.84. 1H NMR (600.17MHz, toluene-d_6, -20°C): δ -1.17 (d, 1H, 2^J_{HH} = 10.98Hz, η^1-CH_2), -1.03 (d, 1H, 2^J_{HH} = 11.04Hz, η^2-CH_2), -0.69 (d, 1H, 2^J_{HH} = 10.98Hz, η^2-CH_2), -0.61 (d, 1H, 2^J_{HH} = 10.32Hz, η^1-CH_2), -0.50 (t, 1H, 2^J_{HH} = 6.8Hz, μ-CH_2), 0.06 (s, 9H, SiMe_3), 0.07 (s, 9H, SiMe_3), 0.07 (1H, μ-CH_2)**, 0.44 (s, 9H, SiMe_3), 0.46 (d, 3H, 2^J_{HH} = 4.80Hz, PtMe), 0.52 (s, 9H, SiMe_3), 0.56 (m, 1H, μ-CH_2), 0.97 (d, 3H, 3^J_{HH} = 5.52 Hz, PtMe), 1.00 (d, 3H, 2^J_{HH} = 6.18 Hz, PtMe), 1.05 (1H, μ-CH_2)**, 1.23 (brm, 4H, β-THF), 1.34 (brm, 4H, β-THF), 1.15 (d, 3H, 2^J_{HH} = 4.86 Hz, PtMe), 1.72 (s, 3H, Cp’Me), 1.76 (s, 3H, Cp’Me), 1.82 (s, 3H, Cp’Me), 1.97 (s, 3H, Cp’Me), 2.14 (m, 1H, CH_2), 2.22 (m, 2H, CH_2), 2.22 (s, 6H, Cp’Me), 2.29 (s, 3H, Cp’Me), 2.33 (s, 3H, Cp’Me), 2.44 (m, 1H, CH_2), 2.64 (m, 1H, CH_2), 2.76 (d, 2H, 3^J_{HH} = 17.89Hz, CH_2), 2.85 (t, 1H, 2^J_{HH} = 11.7Hz, CH_2), 3.50 (m, 2H, α-THF), 3.71 (m, 2H, α-THF), 3.87 (brm, 2H, α-THF), 4.12 (brm, 2H, α-THF), 7.03 (m, 2H, p-Ph), 7.0-7.2 (m, 8H, m-Ph), 7.10 (m, 2H, p-Ph), 7.34 (br, 2H, o-Ph), 7.59 (t, 2H, 2^J_{HH} = 8.35Hz, o-Ph), 7.66 (t, 2H, 2^J_{HH} = 8.25Hz, o-Ph), 7.69 (m, 2H, o-Ph). Two isomers were observed in the ratio of 55% to 45% in the 1^H NMR spectrum at -20°C. 13C NMR (150.91MHz, toluene-d_6, -20°C): δ 2.2 (d, 2^J_{CP,cis} = 6.91Hz, PtMe), 3.6 (s, SiMe_3), 3.8 (s, SiMe_3), 4.9 (s, SiMe_3), 5.4 (s, SiMe_3), 5.7 (br, μ-CH_2), 8.3 (d, 2^J_{CP,trig} = 102.96Hz, PtMe), 10.3 (br, PtMe), 10.4 (d, 2^J_{CP,trig} = 100.19Hz, PtMe), 10.6 (s, Cp’Me), 11.5 (s, Cp’Me), 11.6 (s, Cp’Me), 13.0 (s, Cp’Mex), 12.9 (s, Cp’Me), 11.8 (s, Cp’Me), 15.2 (μ-CH_2), 20.5 (CH_2)**, 22.2 (br, CH_2), 24.6 (s, β-THF), 25.0 (s, β-THF), 25.7 (d, 1^J_{CP} = 35.93Hz, CH_2), 28.3 (s, CH_2), 33.7 (brs, η^2-CH_2), 34.9 (s, η^2-CH_2), 71.5 (brs, α-THF), 72.4 (brs, α-THF), 96.1 (s, Cp’-ring), 99.6 (s, Cp’-ring), 116.7 (s, Cp’-ring), 117.3 (s, Cp’-ring), 117.5 (s, Cp’-ring), 118.2 (s, Cp’-ring), 118.2 (s, Cp’-ring), 119.0 (s, Cp’-ring), 119.7 (s, Cp’-ring), 121.3 (s, Cp’-ring), 129.9 (s, p-Ph), 130.6 (s, p-Ph), 132.7 (d, 2^J_{CP} = 10.32 Hz, o-Ph), 133.2 (br, o-Ph), 134.5 (br, o-Ph), 135.4 (d, 2^J_{CP} = 10.35Hz, o-Ph). Carbon signals for two p-Ph and four m-Ph were obscured in toluene-d_6. The carbon signals for ipso-Ph were not observed. COSY (toluene-d_6, -20°C) -1.17 -- 0.69, -1.03 -- 0.61, -0.50 -- 0.56. HSQC (toluene-d_6, -20°C) δ_C - δ_H: -1.17, 33.7; 1.03, -0.61; -0.50, -0.56; 15.2, 0.06; 3.9, 0.44; 4.9, 0.46; 10.3, 0.52; 5.4, 0.97; 2.2, 1.00; 8.3, 1.15; 10.4, 1.23; 24.6, 1.34; 25.0, 1.72; 10.6, 1.76; 11.6, 1.82; 11.5, 1.97; 11.8, 2.14; 26.5, 2.22; 28.3, 2.22; 29.0, 13.0, 2.33; 12.9, 2.44; 8.55; 25.7; 2.76; 22.2, 3.50; 3.87; 71.5, 3.71; 14.12; 72.4, 7.03; 129.9, 7.10; 130.6, 7.34; 133.2, 7.59; 135.4, 7.66; 132.7, 7.69; 134.5. HMBC (toluene-d_6, -10°C) δ_C - δ_H: -1.17; -0.69; -0.50; -0.56; 3.6, 0.07; 1.05; 3.9, 0.46; 10.4, 0.61; 1.03; 6.10; 2.2, 15.2, 1.15; 5.8, 10.3. 13P NMR (160.10MHz, C_6D_6, RT): δ 8.22 (br, 1^J_{PP} = 2037.4 Hz), 11.85 (br, 1^J_{PP} = 2148.9 Hz). The integral intensity ratio of δ 8.22 to δ 11.85 is 56%/44%. *The signal was determined by COSY. **The signal was determined by HSQC.
**Figure S4.** $^1$H NMR spectrum (300.40MHz) of 4a at various temperature in toluene-$d_8$ (*). The signals marked with # is residual hexane proton signals. The signal marked with & is based on unidentified impurity.

**Figure S5.** (a) GPC profiles of a polyisoprene (Table 2. run1). (b) GPC profiles of a polyisoprene (Table 2. run2).