

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

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A series of Ln/Pt heterobinuclear complexes, (C₅Me₄XCH₂PPh₂)Ln(CH₂SiMe₃)₂(OC₄H₈)PtMe₂ $(3a: Ln = Y, X = SiMe_2; 3b: Ln = Lu, X = SiMe_2; 4a: Ln = Y, X = CH_2; 4b: Ln = Lu, X = CH_2)$, were prepared by the reaction of $(C_5Me_4XCH_2PPh_2)Ln(CH_2SiMe_3)_2(OC_4H_8)$ with PtMe₂(COD) (COD = 1,5-cyclooctadiene). Single-crystal X-ray diffraction studies revealed that these complexes possess a binuclear framework, in which the two metal centers are bridged by a μ -CH₂SiMe₃ ligand in addition to the coordination of the phoshpine side arm of the cyclopentadienyl ligand to the Pt atom. Variabletemperature NMR spectroscopic studies revealed the fluxional behavior of the μ -CH₂SiMe₃ ligand in solution. These complexes underwent intramolecular C-H bond cleavage at the SiMe₃ group of the μ -CH₂SiMe₃ ligand at elevated temperatures. In the thermolysis of **3b**, a silul-bridged bidentate alkyl Lu/Pt complex, $(C_5Me_4SiMe_2CH_2PPh_2)Lu(\mu-CH_2SiMe_2CH_2)(OC_4H_8)PtMe_2$ (6), was isolated and structurally characterized. The reaction of the Y/Pt complex 3a, which bears the silvlene-linked Cpphosphine ligand, with $[Ph_3C][B(C_6F_5)_4]$ or H_2 led to fragmentation (C-Si bond cleavage) of the ligand to give several unidentified products including Me₂Si(CH₂PPh₂)PtMe₂ (5). In combination with $[Ph_3C][B(C_6F_5)_4]/Al^1Bu_3$, the Y/Pt complex 4a, which bears the ethylene-linked Cp-phosphine ligand, showed moderate activity for the polymerization of isoprene to yield polyisoprene with isotactic-rich 3,4-microstructures.

Introduction

Mixed metal complexes containing two different metals, such as an electron-rich late transition metal (TM) and an electron-positive rare-earth (group 3 and lanthanide) metal (Ln), have drawn considerable attention because they are expected to exhibit unique reactivity that could result from the cooperative multimetallic synergy effect of two different metals. So far, a number of Ln/TM heteronuclear complexes have been reported, $^{1-3}$ including the isocarbonyl-bridged

Ln-OC-TM heteronuclear complexes,² hydrido-bridged Ln-H-TM-type complexes,³ and Ln/TM mixed complexes with a direct Ln-TM bond.^{2a,4} Most of these complexes were synthesized by using bis(cyclopentadienyl)-ligated lanthanide precursors,^{3a,b,d,e,4a} and their reaction chemistry has remained almost unexplored.

During our studies on the mono(cyclopentadienyl)ligated rare-earth-metal complexes as catalysts for olefin

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Chart 1. Phosphino Alkyl-Substituted Cyclopentadienyl, L1 and L2



polymerization⁵ and other chemical transformations,⁶⁻⁸ we became interested in the use of these complexes as building blocks for the construction of the Ln/TM heteronuclear complexes. We recently reported the synthesis of the d-f heterobinuclear Ln/TM hydrido complexes as the first example of a Ln/TM heteronuclear complex containing a mono-Cp* Ln unit (Cp* = C_5Me_5), such as (C_5Me_5)Lu- $(OC_4H_8)(\mu-H)_2(\mu-\eta^1:\eta^1-\hat{R}PR'R'')Ru(C_5Me_5)(R=C_6H_4, R'=$ $R'' = Ph; R = CH_2, R' = Me, Ph, R'' = Me, Ph).^9$ However, the synthesis of these complexes was achieved at the sacrifice of the reactive Lu-CH₂SiMe₃ groups by alkane (SiMe₄) elimination reaction between (C5Me5)Lu(CH2SiMe3)2- (OC_4H_8) and $(C_5Me_5)Ru(PR_3)H_3$ (R = Me, Ph).^{9a} To synthesize a Ln/TM complex that could possess the reactive Ln-alkyl groups, we envisioned that a half-sandwich rareearth-metal dialkyl complex having a phosphine unit at the side arm of the cyclopentadienyl ligand (e.g., [C₅Me₄- $SiMe_2CH_2PPh_2$ ⁻ (L1) and $[C_5Me_4C_2H_4PPh_2]$ ⁻ (L2)) would serve as a useful building block, because the phosphine unit could form a strong bond with a late transition metal and thus bring the two metal centers to a reasonable vicinity without losing a Ln-C bond. Herein, we report a Ln/Pt heterobinuclear complex containing a mono-Cp'-ligated Lnalkyl unit (Cp' = η^5 -C₅Me₄XCH₂PPh₂, X = SiMe₂,CH₂) by use of a phosphine-side-arm-containing half-sandwich rareearth-metal dialkyl complex as a starting material. Some fundamental reactivity of the Ln/Pt heterobinuclear complex, including intramolecular C-H bond cleavage of a SiMe₃ group, is also described.

Results and Discussion

Mono-Cp' yttrium/lutetium dialkyl complexes supported by L1 or L2, $(C_5Me_4XCH_2PPh_2)Ln(CH_2SiMe_3)_2(OC_4H_8)$ (1a: Ln = Y, X = SiMe_2; 1b: Ln = Lu, X = SiMe_2; 2a: Ln = Y, X = CH_2; 2b: Ln = Lu, X = CH_2), were prepared by the reaction of Ln(CH_2SiMe_3)_3(OC_4H_8)_2 (Ln = Y or Lu) with an equimolar amount of $(C_5Me_4XCH_2PPh_2)H$ (X = SiMe_2, X = CH_2) (Scheme 1). Complexes 1a, 1b, 2a, and 2b were obtained as oily products but could be identified by the ¹H, ¹³C, and ³¹P NMR spectra. In the ¹H NMR spectra of 1a and 2a, the two CH_2SiMe_3 groups exhibited one CH_2 signal and one SiMe_3 signal at δ –0.49 and 0.28 for 1a and δ –0.75 and 0.26 for **2a**, respectively. In a similar manner, the signals of the CH₂SiMe₃ groups appeared at δ -0.75 (CH₂) and 0.26 (SiMe₃) for **1b** and δ -0.81 (CH₂) and 0.26 (SiMe₃) for **2b**, respectively. Consistently, the ¹³C NMR spectra of **1a**, **1b**, **2a**, and **2b** each showed one set of a CH₂ signal and a SiMe₃ signal for the two CH₂SiMe₃ groups. In the ³¹P NMR spectra of the yttrium complexes **1a** and **2a**, one doublet was observed with a ¹J_{YP} coupling constant of 50.0 Hz (**1a**) and 23.5 Hz (**2a**).¹⁰ These observations strongly indicate that the phosphine unit is coordinated to the metal center in solution.

Complexes **1a** and **1b** reacted with PtMe₂(COD) (COD = 1,5-cyclooctadiene) at ambient temperature to give the corresponding Ln/Pt heterobinuclear complexes (C₅Me₄SiMe₂-CH₂PPh₂)Ln(CH₂SiMe₃)₂(OC₄H₈)PtMe₂ (**3a**: Ln = Y; **3b**: Ln = Lu), through replacement of the COD ligand on the Pt center with the phosphine unit in **1a**,**b** (Scheme 1). In these reactions, several unidentified byproducts were also formed. The isolation of **3a** and **3b** was successfully accomplished by a successive crystallization from Et₂O/hexane solution at -35 °C with a yield of 37% and 35%, respectively. One of the byproducts, a mononuclear platinum complex with a bidentate phosphine ligand, PtMe₂{Me₂Si(CH₂PPh₂)₂} (**5**), was isolated as a white solid, which is barely soluble in Et₂O or in hexane.

Complexes **3a** and **3b** are stable at room temperature. Any decomposition of **3a** or **3b** to yield **5** was not observed even at high temperatures. Hence, it is plausible that fragmentation of the $C_5Me_4SiMe_2CH_2PPh_2$ ligand occurs concurrently with the formation of **3a** and **3b** to afford **5** as a result of Si-C bond cleavage. The similar Si-C bond cleavage in Cp ligands was also reported previously.¹¹

The reactions of **2a** and **2b** with $PtMe_2(COD)$ proceeded in the similar manner to produce the heterobinuclear complexes (C₅Me₄C₂H₄PPh₂)Ln(CH₂SiMe₃)₂(OC₄H₈)PtMe₂ (**4a**: Ln = Y; **4b**: Ln = Lu) (Scheme 1). In these reactions, unidentified byproducts were also formed, and complexes **4a** and **4b** were isolated in 20% and 21% yields, respectively.

The solid-state structures of **3a**, **3b**, and **4a** were determined by single-crystal X-ray structural analyses. The OR-TEP diagrams of **3a** and **4a** are depicted in Figures 1 and 2, respectively. Selected bond distances and bond angles of **3a**, **3b**, and **4a** are summarized in Table 1. Complex **3b** adopts the same conformation as that of **3a** and **4a**, and the ORTEP diagram is omitted. In both structures of **3a** and **3b**, the hydrogen atoms on C5 were located in the difference Fourier map and refined with isothermal parameters.

In the structures of **3a**, **3b**, and **4a**, the rare-earth-metal center is bonded to a cyclopentadienyl group, two methylene carbon atoms (C1 and C5), and one oxygen atom of tetrahydrofuran. The platinum is tightly fixed in the dinuclear framework via a pendant phosphine ligand to construct a metallacycle composed of P1, Pt1, Ln1, C11, and a ligand alkyl chain. Around the Pt1 center, P1, C5, C9, and C10 were arranged in a distorted square-planar fashion. One of the two trimethylsilylmethyl groups is bonded to the rare-earth-metal atom in a terminal fashion, while the other bridges the platinum and the rare-earth-metal atom.

The bond distances in **3a**, **3b**, and **4b** between Ln1 and Pt1 (ca. 2.8 Å) are smaller than the sum of the covalent radii of

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⁽¹⁰⁾ The difference in the ${}^{1}J_{YP}$ coupling constant between **1a** and **2a** might be due to the difference in Y–P bond strength between these two complexes.

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Scheme 1. Preparation of 3a, 3b, 4a, and 4b





Figure 1. Molecular structure of **3a** (ellipsoids drawn at the 50% probability level; hydrogen atoms except methylene protons on C5 are omitted for clarity).



Figure 2. Molecular structure of **4a** (ellipsoids drawn at the 50% probability level; hydrogen atoms, disordered tetrahydrofuran carbons, and disordered trimethyl group on SI2 are omitted for clarity).

Ln1 (Y: 1.62 Å, Lu: 1.56 Å) and Pt (1.29 Å).¹² These short Ln1–Pt1 bond distances might be indicative of a metal–metal bonding interaction. However, because the Pt center is Pt(II) with 16 electrons in this formalism, it seems that no electrons are available for a metal–metal bonding interaction.

The Ln-C bond distances vary depending on the coordination mode. The Ln-C1 distances, ca. 2.4 Å, are in the typical range of a Ln-C single bond.¹³ Meanwhile, the

Table 1. Selected Bond Angles (Å), Bond Angles (deg), and aDihedral Angle (deg) of 3a, 3b, and 4a

3a (Ln1 = Y1)	$\mathbf{3b} (Ln1 = Lu1)$	4a (Ln1 = Y1)
2.8333(5)	2.8214	2.7870(11)
2.417(4)	2.377(10)	2.409(9)
2.575(4)	2.542(9)	2.641(4)
2.162(4)	2.137(11)	2.195(6)
2.102(4)	2.0646(12)	2.077(7)
2.092(4)	2.049(10)	2.046(9)
131.21(18)	132.9(5)	128.2(4)
166.8(3)	166.9(5)	171.9(3)
72.87(12)	73.6(3)	69.70(13)
6.6	-11.9	5.8
	3a (Ln1 = Y1) 2.8333(5) 2.417(4) 2.575(4) 2.162(4) 2.092(4) 131.21(18) 166.8(3) 72.87(12) 6.6	3a (Ln1 = Y1) $3b (Ln1 = Lu1)$ $2.8333(5)$ 2.8214 $2.417(4)$ $2.377(10)$ $2.575(4)$ $2.542(9)$ $2.162(4)$ $2.137(11)$ $2.102(4)$ $2.0646(12)$ $2.092(4)$ $2.049(10)$ $131.21(18)$ $132.9(5)$ $166.8(3)$ $166.9(5)$ $72.87(12)$ $73.6(3)$ 6.6 -11.9

Ln-C5 distances, 2.575(4) Å for **3a**, 2.542(9) Å for **3b**, and 2.641(4) A for 4a, are significantly elongated as a result of μ -bridging coordination between Ln and Pt. These values correspond with μ -bridging groups, Y-Me-Y motifs with Y-C distances of 2.51-2.61 Å¹⁴ and Y-CH₂R-M motifs $(R = SiMe_2NSiMe_3, {}^{i}Pr, {}^{n}Pr, M = Y, Al)$ with Y–C distances of 2.54–2.79 Å. 15 The Ln–C5–Si2 bond angles, 166– 172°, which are much larger than those of Ln1-C1-Si1 by ca. 30-45°, are similar to those of a previously reported μ -CH₂SiMe₃ group.¹⁶ The Pt1–C5 bond lengths are slightly longer than Pt1-C9 and Pt1-C10 bond lengths, on the basis of the different coordination fashion: C5 as a neutral L-type ligand and C9 and C10 as a 1e anionic X-type ligand. However, the difference in these bond distances is guite trivial, and all these values are almost within the range of values quoted in the literature for various bidentate phosphine-supported PtMe₂ complexes, with Pt(II)-C bond lengths of 2.0-2.2 Å.¹⁷

The structure of **5** was also determined by a single-crystal X-ray analysis (Figure 3). There is a C_2 rotation axis on the

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Figure 3. Molecular structure of **5** (ellipsoids drawn at the 50% probability level; hydrogen atoms are omitted for clarity) Selected bond lengths (Å) and angles (deg): Pt1–C1 2.093(6), Pt1–P1 2.2844(15), Si1–C2–P1 117.3(3), C2–P1–Pt1 116.4(2).

line determined by Si and Pt1. The Pt atom adopts a squareplanar geometry formed by two phosphine ligands and two methyl groups. All bond distances and angles in **5** are quite similar to structurally similar Pt complexes reported in previous reports.¹⁷ Complex **5** was also identified by NMR and elemental analysis.

Complexes 3a, 3b, 4a, and 4b were further characterized by ¹H, ¹³C, and ³¹P NMR and elemental analyses. Complexes 3a, 3b, 4a, and 4b exhibit fluxional behavior in solution, and the shape of the NMR spectral signals changed significantly according to the temperature. In Figure 4, the Cp'Me proton signals (1.5-2.5 ppm) and SiMe₃ and Cp'SiMe₂ proton signals (-0.5 to -0.6 ppm) of **3a** in the temperature range 60 to -10 °C are shown. At 60 °C, four nonequivalent signals assigned to Cp'Me were observed at δ 1.94, 1.99, 2.02, and 2.30 (\blacklozenge) with the integral ratio of 3H, indicating the lack of symmetry in the structure of 3a. There are two resonances both for SiMe₃ groups at δ -0.01 and 0.33 (\bullet) and for a Cp'SiMe₂ group at δ -0.24 and 0.19 (**A**). With a decrease of temperature, significant broadening of the signals was observed, and three Cp'Me signals coalesced at 30 °C. At 5 °C, the Cp'Me signals split into two sets of four Cp'Me signals, δ 1.77, 1.91, 2.25, and 2.37 (\blacklozenge) and 1.67, 2.17 (\times 2), and 2.28 (\diamondsuit), with a ratio of 68% to 32%, respectively. In accordance with this observation, two sets of SiMe₃ groups were found at $\delta 0.09$ and 0.46 (\bullet) and at δ -0.01 and 0.41(\bigcirc), and two sets of SiMe₂ groups were found at δ -0.56 and 0.36 (**A**) and δ -0.04 and 0.15 (△).

The ¹H NMR spectra of **3b**, **4a**, and **4b** also changed in a similar manner according to the temperature change and exhibit two sets of signals for trimethylsilylmethylene groups and $Cp'Me_4$ groups at low temperature, i.e., four $SiMe_3$ signals, four $Cp'SiMe_2$ signals, and eight Cp'Me signals.¹⁸ These spectral data are indicative of the presence of an isomerization process between the two isomers at ambient temperature. At elevated temperature, the isomerization rate is faster and signals were observed at an averaged location of these two isomers.

Consistent with the signal changes of Cp'Me, Cp'SiMe₃, and SiMe₃ groups, the signals for metal-coordinating alkyl groups, LnCH₂ and PtMe in **3a**, **3b**, **4a**, and **4b**, also changed according to the temperature; that is, the signals at



Figure 4. Variable-temperature ¹H NMR spectra (300 MHz) of **3a** showing (a) the Cp'*Me* region and (b) the Cp'Si*Me*₂ and Si*Me*₃ group region in toluene- d_8 (**). The signal marked with (*) is TMS, the signals marked with \$ and # are SiMe₂CH₂PPh₂ and μ -CH₂, respectively.

ambient temperature split into two different signal sets at low temperature. The LnCH2 and PtMe signals were observed as a multiplet on the basis of a multiple coupling system, and full assignment of these signals was performed by twodimensional (COSY, HSQC, HMBC, NOESY) NMR measurements.¹⁸ At elevated temperature, two LnCH₂ groups, one terminal η^1 -CH₂ and one bridging μ -CH₂, were observed as a broad signal in the ¹H NMR spectrum. Two methylene protons of the terminal alkyl group, η^1 -CH₂, were found in a characteristic high-field region at δ -1.0 to -0.7, whereas bridging methylene signals, μ -CH₂, were slightly shifted to low field and observed around $\delta - 0.2$ to -0.6 and $\delta 0.1 - 0.9$ in a diastereotopic fashion with the integral intensity of 1H, respectively. Two different signals were also observed for PtMe, one broad signal around $\delta 0.50-0.75$ and one doublet around δ 1.0 with a coupling to the phosphorus nucleus ($J_{\rm PH} \approx$ 5–6 Hz), accompanied with a ¹⁹⁵Pt satellite signal, $J_{\rm PtH} \approx$ 50-60 Hz.

At low temperatures (-10 to -20 °C), each isomer exhibits two LnCH₂ signals and two PtMe signals. Two sets of terminal alkyl methylene signals (η^{1} -CH₂) were observed in a diastereotopic fashion at δ -1.4 to -0.4 with a normal geminal coupling constant of ${}^{2}J_{\rm HH} \approx 10-11$ Hz in the ¹H NMR spectrum. In the spectrum of **3a** and **4a**, the η^{1} -CH₂ signals were observed as a doublet of doublets as a result of both a geminal coupling and a coupling to yttrium, ${}^{2}J_{\rm YH} \approx$ 3-4 Hz. Four bridging alkyl signals, μ -CH₂, were observed around δ -1.4 to 1.1 as a diastereotopic multiplet based on a coupling to phosphorus, platinum, and yttrium. In the ¹³C NMR spectrum, η^{1} -CH₂ was observed in the normal range of rare-earth-metal-coordinating methylene signals, around δ 32-36. The μ -CH₂ signals were observed upfield compared

⁽¹⁸⁾ Results of variable-temperature experiments as well as 1 H and 13 C NMR spectral data of **3a**, **3b**, **4a**, and **4b** are supplied as Supporting Information, which is available via the Internet at http://pubs.acs.org.

with a terminal alkyl methylene group, one around $\delta 15-18$ and the other around $\delta 4-6$ as a result of coordination to platinum. There are two PtMe environments for each isomer, *cis* and *trans* to the phosphorus atom. The ¹³C NMR spectrum exhibits a coupling of the PtMe carbons to the ³¹P nucleus, ²J_{PC-cis} = 5-8 Hz or ²J_{PC-trans} = 100-107 Hz, although the satellite peaks coupled to ¹⁹⁵Pt were obscured for most cases.

The fact that two PtMe groups, η^1 -CH₂ and η^2 -CH₂, were observed separately through the whole temperature range 60 to -20 °C excluded the site exchange process either between η^1 -CH₂ and μ -CH₂ or between two PtMe groups. Therefore, we propose two possible ligand exchange processes, which can explain the observed fluxional behavior in the NMR spectrum: (a) a site exchange of μ -CH₂SiMe₃ around the Pt-Y bond and (b) a site exchange between μ -CH₂SiMe₃ and PtMe (Scheme 2). However, full assignment of the PtMe and CH₂ signals is not straightforward because the signal shapes are obscured due to the multicoupling system and overlaps of several signals. Therefore, the isomerization mechanism still remains inconclusive.

There is a possibility of ligand-site exchange around an yttrium, which is accompanied by dissociation of a tetrahydrofuran molecule. However, it was found that the isomerization proceeded both in tetrahydrofuran- d_8 and in toluene- d_8 at room temperature. These results strongly indicate that dissociation of tetrahydrofuran is not essential for the isomerization.

During high-temperature NMR measurements of 3a, 3b, 4a, and 4b, gradual decline in the signal intensity was observed. Hence, the signal change of 3b was monitored at 90 °C by means of ¹H NMR spectroscopy to reveal intramolecular skeletal rearrangement. After 1.5 h, complex 3b was completely consumed and a Lu/Pt complex with a silylbridged bidentate alkyl group, (C5Me4SiMe2CH2PPh2)Lu- $(\mu$ -CH₂SiMe₂CH₂)(OC₄H₈)PtMe₂(**6**), was formed quantitatively with release of SiMe₄ (eq 1). In this reaction, a C-H bond at the SiMe₃ group of the µ-CH₂SiMe₃ unit was cleaved by σ -bond metathesis with the terminal Ln-CH₂SiMe₃ group. In the case of **3a**, **4a**, and **4b**, similar reactions were also observed at elevated temperatures (50-90 °C). However, isolation of the resultants in a pure state was not successful because of their thermal instability and decomposition into unidentified products.



Complex 6 was identified by ¹H, ¹³C, and ³¹P NMR and elemental analyses. In the ¹H NMR spectrum, the η^{1} -CH₂ unit exhibited two diastereotopic doublets at δ –0.45 and 0.24 with a coupling of ¹J_{HH} = 12.8 Hz. One diastereotopic μ -CH₂ signal was observed at δ –0.14 as a doublet of doublets based on coupling to both ³¹P nucleus and the other geminal proton, ²J_{PH} = 8.7 Hz and ²J_{HH} = 14.7 Hz, whereas the other μ -CH₂ signal was observed as a broad signal. The observed geminal coupling constants exhibit larger values than those observed in **3** and **4**. A similar geminal coupling constant value, ²J_{HH} = ca. 13 Hz, was also observed in some

Scheme 2. Possible Isomerization Mechanism



distorted heterobinuclear μ -methylene complexes.¹⁹ In the ¹³C NMR spectrum, the η^{1} -CH₂ unit in the terminal CH₂SiMe₃ group was observed as a singlet at δ 33.3. The μ -CH₂ carbon was observed at higher field at δ 6.2 as a doublet with ²J_{PC} = 3.3 Hz. There are two doublets for PtMe at δ 0.75 (³J_{PH} = 5.5 Hz) and at δ 1.04 (³J_{PH} = 6.0 Hz) in the ¹H NMR spectrum, with satellite signals to ¹⁹⁵Pt (²J_{PtH} \approx 55–58 Hz). The corresponding carbon signals were observed at δ 1.2 and δ 7.9 with a coupling to the phosphorus nucleus.

The structure of **6** was determined by a X-ray analysis by use of a single crystal obtained from a cold Et_2O solution. An ORTEP depiction of **6** is shown in Figure 5, together with selected bond lengths and bond angles.

Around Pt1, four atoms, P1, C1, C5, and C6, were set in a square-planar arrangement. The Lu atom is bonded to a Cp group, two methylene carbons, and one tetrahydrofuran molecule in a pseudo-piano-stool configuration. The silylbridged bidentate alkyl CH₂SiMe₂CH₂ unit is coordinated to two metal centers in a μ - η^1 : η^2 fashion, with a short Lu1-C2 bond distance of 2.345(8) Å. As a result of a tight coordination of a μ - η^1 : η^2 -CH₂SiMe₂CH₂, the Lu1-Pt1 bond distance of 2.7668(5) Å is significantly shorter than that in **3b**. Bond angles around the methylene carbon atoms, Lu1-C1-Si1 85.1(3)° and Lu1-C2-Si1 92.8(3)°, are also greatly distorted. These distorted bond angles around the methylene carbon atom were also found in the above-mentioned methylene-bridged heterobinuclear systems as well as the alkylbridged Y-Li heteronuclear complex.^{19,20}

In attempts to prepare a cationic Ln/Pt species, the reactions of **3a** and **4a** with 1 equiv of $[Ph_3C][B(C_6F_5)_4]$ were carried out.^{5,21} In the case of **3a**, a very complicated product mixture was obtained. The fragmentation (C–Si bond cleavage) of the C₅Me₄SiMe₂CH₂PPh₂ ligand might take place as indicated by the ³¹P NMR. In the case of **4a**, which has a stronger ethylene linker between the Cp group and the phosphine group in the ligand, the corresponding cationic species seemed to be generated together with some unidentified byproduct. However, a full assignment of the cationic species was not achieved because of the complexity of the NMR spectra.

In combination with $[Ph_3C][B(C_6F_5)_4]$ and Al^iBu_3 (5 equiv), complex **4a** was active for the polymerization of isoprene

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Figure 5. Molecular structure of 6 (ellipsoids drawn at the 50% probability level; hydrogen atoms except refined methylene protons on C1 and C2 are omitted for clarity) Selected bond lengths (Å) and angles (deg): Lu1–Pt 2.7668(5), Lu1–C1 2.541(7), Lu1–C2 2.345(8), Pt1–C1 2.225(8), Pt1–C5 2.124(8), Pt1–C6 2.109(7), Pt1–P1 2.2786(19), Lu1–C1–Pt1 70.6(2), C1–Lu1–C2 75.3(3), Lu1–C1–Si1 85.1(3), Lu1–C2–Si1 92.8(3), C1–Si1–C2 106.8(3).

 $(0.95 \text{ g} \text{ (mol } \text{Y}-\text{Pt})^{-1} \text{ h}^{-1})$ in C₆H₅Cl at room temperature. The weight average molecular weight of the resulting polyisoprene is $M_{\rm w} = 4.9 \times 10^5$ with a molecular weight distribution of $M_{\rm w}/M_{\rm n} = 2.1$. The ¹H and ¹³C NMR analyses showed that the resulting polyisoprene possessed isotactic-rich 3,4microstructures (3,4-selectivity: 94%, mm 89%, mmmm 51%).5c,21c Complex 4a alone showed no activity for the polymerization of isoprene. Under the same conditions, complex 3a was also active for the polymerization of isoprene $(0.15 \text{ g} (\text{mol } \text{Y}-\text{Pt})^{-1} \text{h}^{-1})$, but the resulting polymer showed a bimodal GPC profile, indicative of the presence of more than one active species. These results are in agreement with the observations described above in the reactions of 3a and 4a with $[Ph_3C][B(C_6F_5)_4]$. The limited activity of the present catalyst systems for the polymerization of isoprene might be due to the low activity (strong bridge) of the bridged CH₂SiMe₃ group in the resulting cationic species.²²

Hydrogenolysis of 3a and 4a with H₂ did not afford a characterizable hydrido product.²³ In the case of 3a, complex 5 was formed together with other unidentified products as a result of C–Si bond cleavage.

Conclusion

By use of the half-sandwich rare-earth-metal dialkyl complexes bearing Cp ligands with a phosphine side arm, such as **1a,b** and **2a,b**, to react with a late transition metal complex, PtMe₂(COD), we have prepared the corresponding Ln/ Pt complexes **3a,b** and **4a,b** through coordination of the phosphine unit to the late transition metal center, without loss of a rare-earth-metal alkyl group. These heterobimetallic alkyl complexes seem rather reactive and undergo intramolecular C–H bond activation at high temperatures. The reaction of the Y/Pt complex **3a**, which bears the silylenelinked Cp-phosphine ligand, with [Ph₃C][B(C₆F₅)₄] or H₂ has led to fragmentation of the ligand, suggesting that the resulting cationic species or hydrido species of the Y/Pt heterobinuclear skeleton might be extremely reactive. In combination with $[Ph_3C][B(C_6F_5)_4]/Al^iBu_3$, the Y/Pt complex 4a, which bears the ethylene-linked Cp-phosphine ligand, is active for the polymerization of isoprene to yield polyisoprene with isotactic-rich 3,4-microstructures.

Experimental Section

General Procedures. All procedures were performed under a dry and oxygen-free nitrogen or argon atmosphere using Schlenk techniques or a glovebox. Solvents (toluene, hexane, tetrahydrofuran, Et₂O) were purified with the SPS-800 solvent purification system (MBraun) prior to use. C₆H₅Cl was purified with the Ultimate solvent system (GlassCountour). Isoprene was purchased from Junsei Chemical Co., Ltd. and dried over CaH_2 and distilled. $LnCl_3$ (Ln = Y, Lu) were purchased from Strem and used without further purification. LiCH₂SiMe₃ was bought from Aldrich. PtMe2(COD) was purchased from Aldrich or AZmax Co., Ltd. and used without further purification. $[Ph_3C][B(C_6F_5)_4]$ was purchased from Tosohchem Corporation. Toluene-d₈, THF-d₈, and C₆D₆ were dried over sodium/benzophenone ketyl and distilled. $Ln(CH_2SiMe_3)_3(THF)_2^{24}$ and $(C_5Me_4C_2H_4PPh_2)H^{25}$ were prepared according to literature procedures. (C5Me4SiMe2CH2PPh2)H was prepared following the same procedure for the synthesis of $(C_5H_5SiMe_2CH_2-PPh_2)H$.²⁶ ¹H and ¹³C NMR spectra were recorded using the residual solvent signal as a standard on a JEOL JNM ECA600, JNM ECP500, JNM AL400, and JNM AL-300. ³¹P NMR spectra were recorded on the basis of an external 85% H₃PO₄ standard. The weight average molecular weight (M_w) , the number-averaged molecular weight (M_n) , and the molecular weight distribution (M_w/M_n) of the polymers were measured by means of gel permeation chromatography on a TOSOH HLC-8220 GPC (column: Super HZM-H \times 3) at RT using THF as an eluent against polystyrene standards. Elemental analyses were performed by a Mico Corder JM10. Complexes 1a, 1b, 2a, and 2b were obtained as oils, and no elemental analysis was performed.

Preparation of $(C_5Me_4SiMe_2CH_2PPh_2)Y(CH_2SiMe_3)_2(OC_4H_8)$ (1a). The reaction of $Y(CH_2SiMe_3)_3(OC_4H_8)_2$ (100 mg, 0.20 mmol) with $(C_5Me_4SiMe_2CH_2PPh_2)H$ (77 mg, 0.20 mmol) was performed in toluene (1 mL) at RT for 1 h. The volatiles were removed *in vacuo* to afford 1a as an oil. By means of NMR spectroscopy, quantitative formation of 1a was confirmed.

Spectral data for **1a**: ¹H NMR (395.75 MHz, C₆D₆, RT): δ –0.49 (br s, 4H, YCH₂), 0.19 (s, 6H, SiMe₂), 0.28 (s, 18H, SiMe₃), 1.36 (br s, 4H, α -THF), 1.62 (d, ²*J*_{HP} = 6.73 Hz, CH₂), 2.07 (s, 6H, Cp'Me), 2.45 (s, 6H, Cp'Me), 3.64 (br s, 4H, β -THF), 7.03 (br m, 6H, *m*+*p*-Ph), 7.44 (t, 4H, ³*J*_{HH} = ³*J*_{HP} = 8.3 Hz, *o*-Ph). ¹³C NMR (99.45 MHz, C₆D₆, RT): δ 2.3 (d, ³*J*_{CP} = 4.92 Hz, SiMe₂), 4.8 (s, SiMe₃), 12.0 (s, Cp'Me), 15.2 (s, Cp'Me), 17.5 (d, ¹*J*_{CP} = 12.35 Hz, CH₂), 25.6 (s, β -THF), 38.1 (d, ¹*J*_{YC} = 40.7 Hz, YCH₂), 68.7 (s, α -THF), 112.1 (s, Cp'-*ring*), 123.9 (s, Cp'-*ring*), 127.1 (s, Cp'-*ring*), 128.8 (d, *m*-Ph, ³*J*_{CP} = 7.43 Hz), 129.7 (s, *p*-Ph), 133.0 (d, ²*J*_{CP} = 16.57 Hz, *o*-Ph), 137.5 (d, ¹*J*_{CP} = 15.6 Hz, *ipso*-Ph). ³¹P NMR (160.10 MHz, C₆D₆, RT): δ –17.02 (d, ¹*J*_{YP} = 50.0 Hz).

Preparation of $(C_5Me_4SiMe_2CH_2PPh_2)Lu(CH_2SiMe_3)_2(OC_4H_8)$ (1b). To the C₆D₆ solution (0.5 mL) containing Lu(CH₂SiMe₃)₃-(OC₄H₈)₂ (50 mg, 0.086 mmol) was added (C₅Me₄SiMe₂CH₂-PPh₂)H (40 mg, 0.10 mmol) at room temperature. The reaction mixture was kept at 50 °C for 1 h. The quantitative formation of 1b

⁽²²⁾ The terminal CH₂SiMe₃ group in **4a** would be removed upon reaction with 1 equiv of $[Ph_3C][B(C_6F_5)_4]$. (23) The hydrogenolysis of **1a**, **1b**, **2a**, and **2b** resulted in the forma-

⁽²³⁾ The hydrogenolysis of **1a**, **1b**, **2a**, and **2b** resulted in the formation of unidentified complexes. Identification of resultants is still underway.

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was confirmed by means of NMR spectroscopy. After removal of the volatiles, complex **1b** was obtained as an oil.

Spectral data for **1b**: ¹H NMR (395.75 MHz, C₆D₆, RT): δ -0.75 (br s, 4H, LuCH₂), 0.01 (s, 6H, SiMe₂), 0.26 (s, 18H, SiMe₃), 1.36 (br s, 4H, β -THF), 1.61 (d, 2H, ²J_{HP} = 3.96 Hz, CH₂), 2.00 (s, 6H, Cp'Me), 2.18 (s, 6H, Cp'Me), 3.57 (br s, 4H, α -THF), 7.04 (m, 6H, *m*+*p*-Ph), 7.40 (t, 4H, ³J_{HH} = ³J_{HP} = 7.32 Hz, *o*-Ph). ¹³C NMR (99.45 MHz, C₆D₆, RT): δ 2.2 (d, ²J_{CP} = 5.77 Hz, SiMe₂), 4.7 (s, SiMe₃), 11.7 (s, Cp'Me), 14.8 (s, Cp'Me), 17.1 (d, ¹J_{CP} = 18.00 Hz, CH₂), 25.3 (s, β -THF), 43.0 (s, LuCH₂), 68.9 (s, α -THF), 112.1 (d, ³J_{CP} = 3.28 Hz, Cp'-*ring*), 123.1 (s, Cp'-*ring*), 126.4 (s, Cp'-*ring*), 128.3 (d, ³J_{CP} = 10.64 Hz, *m*-Ph), 128.9 (s, *p*-Ph), 132.7 (d, ²J_{CP} = 17.20 Hz, *o*-Ph), 138.7 (br, *ipso*-Ph). ³¹P NMR (160.10 MHz, C₆D₆, RT): δ -15.57.

Preparation of $(C_5Me_4C_2H_4PPh_2)Y(CH_2SiMe_3)_2(OC_4H_8)$ (2a). Tris(trimethylsilylmethyl)yttrium complex Y(CH_2SiMe_3)_3(OC_4H_8)_2 (100 mg, 0.20 mmol) was dissolved in THF (0.5 mL). To this solution was added ($C_5Me_4C_2H_4PPh_2$)H (67 mg, 0.20 mmol) at room temperature. The solution was stirred at room temperature for 1 h, and all the volatiles were removed *in vacuo* to give 2a as an oil. Complete consumption of Y(CH_2SiMe_3)_3(OC_4H_8)_2 and formation of 2a as a major product were confirmed by the NMR data.

Spectral data for **2a**: ¹H NMR (300.40 MHz, C₆D₆, RT): δ -0.75 (br s, 4H, YCH₂), 0.26 (s, 18H, SiMe₃), 1.38 (br s, 4H, β -THF), 2.00 (s, 6H, Cp'Me), 2.03 (s, 6H, Cp'Me), 2.43 (m, 2H, CH₂), 2.61 (m, 2H, CH₂), 3.60 (br s, 4H, α -THF), 7.06 (m, 6H, *m*+*p*-Ph), 7.51 (t, 4H, ³*J*_{HH} = ³*J*_{HP} = 8.26 Hz, *o*-Ph). ¹³C NMR (75.45 MHz, C₆D₆, RT): δ 4.8 (s, SiMe₃), 11.6 (s, Cp'Me), 11.9 (s, Cp'Me), 22.1 (d, ²*J*_{CP} = 14.9 Hz, CH₂), 25.6 (br s, β -THF), 31.6 (br s, CH₂), 33.8 (d, ¹*J*_{YC} = 43.1 Hz, YCH₂), 68.9 (br s, α -THF), 117.2 (br, Cp'-*ring*), 117.6 (br, Cp'-*ring*), 122.7 (d, ³*J*_{CP} = 8.33 Hz, Cp'-*ring*), 128.7 (d, ³*J*_{CP} = 6.62 Hz, *m*-Ph), 129.2 (s, *p*-Ph), 133.3 (d, ²*J*_{CP} = 15.8 Hz, *o*-Ph), 137.3(br, *ipso*-Ph). ³¹P NMR (160.10 MHz, C₆D₆, RT): δ -0.562 (d, ¹*J*_{YP} = 23.5 Hz).

Preparation of $(C_5Me_4C_2H_4PPh_2)Lu(CH_2SiMe_3)_2(OC_4H_8)$ (2b). The reaction of Lu(CH_2SiMe_3)_3(OC_4H_8)_2 (200 mg, 0.34 mmol) with $(C_5Me_4C_2H_4PPh_2)H$ (115 mg, 0.34 mmol) was performed in toluene (2 mL) at 50 °C for 8 h. After removing all the volatiles *in vacuo*, complex **2b** was obtained as an oil. Quantitative formation was confirmed by means of NMR spectroscopy.

Spectral data for **2b**: ¹H NMR (399.65 MHz, C_6D_6 , RT): δ -0.81 (br s, 4H, LuCH₂), 0.26 (s, 18H, SiMe₃), 1.21 (br s, 4H, β -THF), 1.93 (s, 6H, Cp'Me), 2.08 (s, 6H, Cp'Me), 2.29 (m, 2H, CH₂), 2.57 (m, 2H, CH₂), 3.45 (br s, 4H, α -THF), 7.09 (m, *m*+*p*-Ph, 6H), 7.38 (t, 4H, ³J_{HH} = ³J_{HP} = 6.99 Hz, *o*-Ph). ¹³C NMR (100.40 MHz, C₆D₆, RT): δ 4.9 (s, SiMe₃), 11.5 (s, Cp'Me), 11.7 (s, Cp'Me), 22.3 (d, ²J_{CP} = 16.8 Hz, CH₂), 25.1 (br s, β -THF), 31.2 (br, CH₂), 41.8 (s, LuCH₂), 70.2 (br s, α -THF), 117.2 (s, Cp'-*ring*), 117.8 (s, Cp'-*ring*), 122.2 (d, ¹J_{CP} = 10.8 Hz, Cp'-*ring*), 128.8 (d, ³J_{CP} = 7.53 Hz, *m*-Ph), 129.8 (s, *p*-Ph), 133.1 (d, ²J_{CP} = 16.6 Hz, *o*-Ph), 136.7 (*ipso*-Ph). ³¹P NMR (160.10 MHz, C₆D₆, RT): δ -10.40 (br).

Preparation of (C5Me4SiMe2CH2PPh2)Y(CH2SiMe3)2(OC4H8)-PtMe₂ (3a). Complex 1a was prepared in situ by the reaction of $Y(CH_2SiMe_3)_3(OC_4H_8)_2$ (100 mg, 0.20 mmol) with (C₅Me₄-SiMe₂CH₂PPh₂)H (77 mg, 0.20 mmol) in toluene following the procedure above. To the toluene solution containing 1a was added a toluene solution of PtMe2(COD) (77 mg, 0.23 mmol). After the reaction mixture was stirred for 1 h, all the volatiles were removed in vacuo. The ³¹P NMR spectrum revealed the formation of 3a (78.8%) and 5 (12.5%). Some unidentified products (8.7%), which exhibited singlets at δ 17.2, 10.2, 2.9 etc., were also formed. The resulting slurry was extracted with Et2O/hexane, and the extracts were cooled at -35 °C to afford a mixture of 3a(84.3%) and 5 (15.7%) as small crystals (first crop: 48 mg; second crop: 48 mg). The mixture of 3a and 5 was extracted with Et_2O and recrystallized at -35 °C to afford pure **3a** (70 mg, 0.075 mmol, 37.0% isolated yield). After the extraction, 5 (ca. 1 mg, 0.0015 mmol) was isolated as insoluble white crystals.

Spectral data for 3a: ¹H NMR (500.16 MHz, toluene-d₈, 50 °C): δ -0.76 (br, 2H, YCH₂), -0.28 (br, 1H + 3H, μ -CH₂ + SiMe₂), 0.00 (s, 9H, SiMe₃), 0.19 (br s, 3H, SiMe₂), 0.36 (s, 9H, SiMe₃), 0.47 (1H, μ -CH₂),²⁷ 0.58 (br, 3H, PtMe), 0.99 (d, 3H, ³J_{HP} = 5.50 Hz, ²J_{HPt} = 49.97 Hz, PtMe), 1.44 (br s, 4H, β -THF), 1.9–2.2 (br, 9H + 2H, Cp'Me + CH₂), 2.31 (s, 3H, Cp'Me), 3.89 (br, 4H, a-THF), 7.1 (m, 6H, m+p-Ph), 7.65 (t, 4H, ${}^{3}J_{\text{HH}} = {}^{3}J_{\text{HP}} = 8.48 \text{ Hz}, o\text{-Ph}$). COSY (toluene- $d_{8}, 50 \text{ °C}$): -0.28 ${}^{3}J_{\text{HH}} = {}^{3}J_{\text{HP}} = 8.48 \text{ Hz}, o-\text{Ph}).$ COS Y (toluene- $a_{8}, 50^{-1}\text{C}$): -0.20to 0.47. ${}^{1}\text{H}$ NMR (600.17 MHz, toluene- $d_{8}, -10^{\circ}\text{C}$): $\delta - 1.35$ (dt, 1H, ${}^{2}J_{\text{YH}} = 3.42 \text{ Hz}, {}^{2}J_{\text{HH}} = {}^{2}J_{\text{HP}} = 6.8 \text{ Hz}, \mu-\text{CH}_{2}$), -1.09(dd, 1H, ${}^{2}J_{\text{YH}} = 3.10 \text{ Hz}, {}^{2}J_{\text{HH}} = 11.0 \text{ Hz}, \eta^{1}\text{-CH}_{2}$), -0.96 (dd, 1H, ${}^{2}J_{\text{YH}} = 3.09 \text{ Hz}, {}^{2}J_{\text{HH}} = 10.30 \text{ Hz}, \eta^{1}\text{-CH}_{2}$), -0.57 (s, 3H, SiMe₂), -0.49 (dd, 1H, ${}^{2}J_{\text{YH}} = 3.43 \text{ Hz}, {}^{2}J_{\text{HH}} = 10.65 \text{ Hz}, \eta^{1}$ -CH₂), -0.10 (dd, 1H, ${}^{2}J_{\text{YH}} = 3.78 \text{ Hz}, {}^{2}J_{\text{HH}} = 10.65 \text{ Hz}, \mu-\text{CH}_{2}$), -0.06 (s, 3H SiMe₂), 0.00 (s, 9H SiMe₃), 0.10 (s, 9H, SiMe₃), -0.06 (s, 3H, SiMe₂), 0.00 (s, 9H, SiMe₃), 0.10 (s, 9H, SiMe₃), 0.16 (s, 3H, SiMe₂), 0.34 (s, 3H, SiMe₂), 0.4 (3H, PtMe),²⁷ 0.43 (s, 9H, SiMe₃), 0.44 (1H, μ -CH₂),²⁷ 0.48 (s, 9H, SiMe₃), 0.84 (1H, μ -CH₂),²⁷ 0.86 (d, 3H, ³J_{HP} = 4.81 Hz, PtMe), 1.03 (d, 3H, ³J_{HP} = 5.46 Hz, PtMe), 1.08 (d, 3H, ³J_{HP} = 5.16 Hz, PtMe), 1.28 (m, 4H, β-THF), 1.37 (m, 4H, β-THF), 1.66 (s, 3H, Cp'Me), 1.76 (s, 3H, Cp'Me), 1.88 (m, 1H, CH₂), 1.91 (s, 3H, Cp'Me), 2.01 (m, 1H + 2H, CH₂), 2.18 (s, 6H, Cp'Me), 2.26 (s, 3H, Cp'Me), 2.28 (s, 3H, Cp'Me), 2.38 (s, 3H, Cp'Me), 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 (br m, 4H, m+p-Ph), 7.13 (br m, 8H, m+p-Ph), 7.32 (t, 2H, ${}^{3}J_{HH} = {}^{3}J_{HP} = 8.25$ Hz, o-Ph), 7.59 (t, 2H, ${}^{3}J_{HH} = {}^{3}J_{HP} = 8.43$ Hz, o-Ph), 7.66 (t, 2H, ${}^{3}J_{HH} = {}^{3}J_{HP} = 8.25$ Hz, o-Ph), 7.86 (t, 2H, ${}^{3}J_{HH} = {}^{3}J_{HP} = 8.61$ Hz, o-Ph). Two isomers were observed in the ratio of 68% to 32%. COSY (toluene-d₈, -10 °C): -1.35 to 0.84, -1.09 to -0.49, -0.96 to -0.47, -0.10 to 0.44, 1.88-2.01, 7.04-7.32, 7.66, 7.13-7.59, 7.86. ³¹P NMR (160.1 MHz, C_6D_6 , RT): $\delta 8.66 ({}^{1}J_{PPt} = 2084.3 \text{ Hz}), 12.06 ({}^{1}J_{PPt} = 2128.4 \text{ Hz}).$ The integration ratio of the signals at δ 8.66 and 12.06 is 66:34. Anal. Calcd for C₃₈H₆₆OPPtSi₃Y: C 48.65, H 7.09. Found: C 48.69, H 6.92.

Spectral data for **5**: ¹H NMR (395.75 MHz, C₆D₆, RT): δ -0.56 (s, 6H, SiMe₂), 1.09 (dd, 6H, ³J_{HP} = 5.94, 7.91 Hz, ²J_{HPt} = 68.46 Hz, PtMe), 1.47 (d, 4H, ³J_{HP} = 10.30 Hz, ³J_{HPt} = 22.56 Hz, CH₂), 7.11 (m, 12H, *m*+*p*-Ph), 7.69 (m, 8H, *o*-Ph). ¹³C NMR (99.45 MHz, C₆D₆, RT): δ 0.8 (s, SiMe₂), 7.1 (dd, PtMe, ²J_{CP} = 92.7 (*trans*), 8.8 (*cis*) Hz), 13.9 (m, CH₂), obscured in C₆D₆ signals (*m*-Ph), 129.7 (s, *p*-Ph), 133.8 (m, *o*-Ph), 136.6 (d, *ipso*-Ph, ¹J_{CP} = 42.86 Hz). ³¹P NMR (160.10 MHz, C₆D₆, RT): δ 8.93 (s, ¹J_{PPt} = 1811.7 Hz). Anal. Calcd for C₃₀H₃₆Si₁P₂Pt₁ (**5**): C 52.86, H 5.32. Found: C 52.47, H 5.22.

Preparation of (C5Me4SiMe2CH2PPh2)Lu(CH2SiMe3)2-(OC₄H₈)PtMe₂ (3b). To the C₆D₆ solution (0.4 mL) containing Lu(CH₂SiMe₃)₃(OC₄H₈)₂ (50 mg, 0.086 mmol) was added (C₅Me₄SiMe₂CH₂PPh₂)H (40 mg, 0.10 mmol) at room temperature. After the reaction mixture was stirred at 50 °C for 1 h, a C_6D_6 (0.1 mL) solution of PtMe₂(COD) (29 mg, 0.087 mmol) was added to the reaction mixture and the reaction mixture was stirred for 1 h. After removal of all the volatiles *in vacuo*, the ³¹P NMR was obtained to reveal the formation of 3b (45.2%), 5 (19.2%), and unidentified complexes (35.6%), which exhibit several singlets at δ 17.4, 14.8, 14.7, 11.9, 10.2, etc. The resulting mixture was extracted with hexane/Et₂O. On cooling the extracts at -35 °C, a mixture of **3b** (77%) and **5** (23%) was obtained (46 mg). The mixture was again extracted with Et_2O , and successive recrystallization at -35 °C afforded pure 3b (31 mg, 0.030 mmol, 35.1%). After extracting, complex 5 was isolated as an insoluble part (ca. 2 mg, 0.0029 mmol).

Spectral data for **3b**: ¹H NMR (500.16 MHz, toluene- d_8 , 50 °C): δ -1.00 (br, 1H, η^1 -CH₂), -0.87 (br d, 1H, ² J_{HH} = 9.15 Hz, η^1 -CH₂), -0.50 (br, 1H, μ -CH₂), -0.16 (s, 3H, SiMe₂),

⁽²⁷⁾ The signal was determined by a two-dimensional NMR spectrum. For more detailed spectroscopic data, see the Supporting Information, http://pubs.acs.org.

-0.02 (s, 9H, SiMe₃), 0.14 (s, 3H, SiMe₂), 0.35 (s, 9H, SiMe₃), 0.62 (1H, μ -CH₂),²⁷ 0.67 (d, 3H, ³ $J_{HP} = 4.75$ Hz, ² $J_{HPt} = 44.47$ Hz, PtMe), 1.09 (d, 3H, ${}^{3}J_{HP} = 5.05$ Hz, ${}^{2}J_{HPt} = 49.92$ Hz, PtMe), 1.44 (br s, 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 (br s, 4H, α-THF), 7.06 (m, 2H, *p*-Ph), 7.12 (br m, 4H, *m*-Ph), 7.56 (br s, 2H, *o*-Ph), 7.67 (t, 2H, ${}^{3}J_{HH} = {}^{3}J_{HP} = 8.48$ Hz, *o*-Ph). The CH₂ signal was obscured by broad Cp'Me signals. COSY (toluene- d_8 , 50 °C): -0.10 to -0.87, -0.50 to 0.62. ¹H NMR (600.17 MHz, toluene- d_8 , -10 °C): δ -1.27 (d, 1H, $^2J_{\text{HH}}$ = 11.70 Hz, η^1 -CH₂), -1.06 (d, 1H, $^2J_{\text{HH}}$ = 10.62 Hz, η^1 -CH₂), -0.91 (t, 1H, $^2J_{\text{HH}}$ = $^3J_{\text{HP}}$ = 6.51 Hz, μ -CH₂), -0.66 (d, 2H, $^2J_{\text{HH}}$ = 11.34 Hz, η^1 -CH₂), -0.56 (s, 3H, SiMe₂), -0.09 (br m, 1H, μ -CH₂), -0.09 (s, 3H, SiMe₂), -0.02 (s, 9H, SiMe₃), 0.097 (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} = 4.80 Hz, PtMe), 0.87 (br, 1H, μ -CH₂), 0.92 (d, 3H, ³J_{HP-cis} = 4.80 Hz, PtMe), 1.07 (d, 3H, ³J_{HP-trans} = 5.46 Hz, PtMe), 1.24 (d, 3H, ³J_H) ${}^{3}J_{\text{HP-trans}} = 4.44 \text{ Hz}, \text{PtMe}), 1.27 (\text{brm}, 4\text{H}, \beta\text{-THF}), 1.38 (\text{br m}, \beta\text{-THF}), 1.38 (\text{br m}, \beta\text{-THF}))$ 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, CH₂),²⁷ 2.24 (s, 3H, Cp'Me), 2.36 (s, 3H, Cp'Me), 2.41 (s, 3H, Cp'Me), 3.52 (br s, 2H, α-THF), 3.74 (br s, 2H, α-THF), 3.89 (br s, 2H, α-THF), 4.14 (br s, 2H, α -THF), 7.05 (br m, 2H + 2H, *p*-Ph), 7.28 (t, 4H + 4H, ³J_{HH} = ³J_{HP} = 8.07 Hz, *o*-Ph), 7.61 (t, 4H, ³J_{HH} = ³J_{HP} = 7.92 Hz, *o*-Ph), 7.68 (t, 4H, ³J_{HH} = ³J_{HP} = 8.43 Hz, *o*-Ph). The *o*-Ph and *m*-Ph signals are obscured in residual toluene- d_8 signals. Two isomers were observed in the ratio of 53% to 47%. COSY (toluene- d_8 , -10 °C): $\delta_{\rm H} - \delta_{\rm H} - 1.27$, -1.06 to -0.66, -0.91 to 0.87, -0.09 to 0.58, 1.9-2.1, 2.1-2.2. ³¹P NMR (160.10 MHz, C_6D_6 , RT): δ 12.30 (${}^1J_{PPt} = 2172.2 \text{ Hz}$), 8.00 (${}^1J_{PPt} = 2002.2$ Hz). The integral ratio of δ 12.3 to δ 8.00 is 55:45. Anal. Calcd for C₃₈H₆₆OPPtSi₃Lu: C 44.56, H 6.50. Found: C 44.86, H 6.49.

Preparation of (C₅Me₄C₂H₄PPh₂)Y(CH₂SiMe₃)₂(OC₄H₈)-PtMe₂ (4a). Complex 2a was prepared *in situ* from the reaction of Y(CH₂SiMe₃)(OC₄H₈)₂ (153 mg, 0.31 mmol) and (C₅Me₄-C₂H₄PPh₂)H (105 mg, 0.314) in tetrahydrofuran (1 mL). To the reaction mixture was added a tetrahydrofuran solution (0.5 mL) containing PtMe₂(COD) (102 mg, 0.31 mmol), and the mixture was further stirred for 12 h at room temperature. After all the volatiles were removed *in vacuo*, the formation of 4a (25% yield) was detected by ³¹P NMR spectroscopy as well as unidentified byproducts (75% yield), which exhibit many signals around δ 14–16. The resulting residue was dissolved in toluene/hexane solution and cooled at -35 °C to produce pale yellow crystalline 4a (55 mg, 0.062 mmol, 19.8%).

Spectral data for 4a: ¹H NMR (500.16 MHz, toluene- d_8 , 65 °C): δ -0.79 (br, 2H, η^1 -CH₂), -0.50 (br, 1H, μ -CH₂), -0.02 (s, 9H, SiMe₃), 0.15 (1H, μ -CH₂), ²⁷ 0.32 (s, 9H, SiMe₃), 0.50 (br m, 3H, PtMe), 0.91 (d, 3H, ³J_{HP} = 5.45 Hz, ²J_{HPt} = 48.12 Hz, PtMe), 1.47 (br s, β-THF), 1.86 (br s, 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 (br m, 2H, CH₂), 2.86 (br, 1H, CH₂), 3.86 (br s, 4H, α-THF), 7.0–7.2 (m, 6H, *m*+*p*-Ph), 7.56 (br, 2H, *o*-Ph), 7.61 (br m, 2H, o-Ph). COSY (toluene-d₈, 65 °C): -0.50 to 0.15. ¹H NMR (600.17 MHz, toluene- d_8 , -20 °C): δ -1.02 (dd, 1H, ${}^{2}J_{\rm YH} = 2.61 \,{\rm Hz}, {}^{2}J_{\rm HH} = 10.62 \,{\rm Hz}, \eta^{1} \cdot {\rm CH}_{2}), -0.92 \,({\rm dd}, {\rm 1H}, {}^{2}J_{\rm YH} =$ $\begin{array}{l} 2.92 \text{ Hz}, \ ^{2}J_{\text{HH}} = 10.30 \text{ Hz}, \ \eta^{1}\text{-CH}_{2}), \ 0.52 (\text{dd}, \text{1H}, \ ^{2}J_{\text{YH}} = 2.75 \\ \text{Hz}, \ ^{2}J_{\text{HH}} = 2J_{\text{PH}} = 7.05 \text{ Hz}, \ \mu\text{-CH}_{2}), \ -0.87 (\text{td}, 1\text{H}, \ ^{2}J_{\text{YH}} = 3.44 \\ \text{Hz}, \ ^{2}J_{\text{HH}} = 10.65 \text{ Hz}, \ \eta^{1}\text{-CH}_{2}), \ -0.45 (\text{dd}, 1\text{H}, \ ^{2}J_{\text{YH}} = 3.44 \\ \text{Hz}, \ ^{2}J_{\text{HH}} = 10.31 \text{ Hz}, \ \eta^{1}\text{-CH}_{2}), \ -0.45 (\text{dd}, 1\text{H}, \ ^{2}J_{\text{YH}} = 2.40 \text{ Hz}, \\ ^{2}J_{\text{HH}} = 10.31 \text{ Hz}, \ \eta^{1}\text{-CH}_{2}), \ 0.06 (\text{s}, \text{9H}, \text{SiMe}_{3}), \ 0.08 (\text{s}, \text{9H}, \\ \text{SiMe}_{3}), \ 0.20 (\text{dd}, 3\text{H}, \ ^{3}J_{\text{HP}} = 5.50 \text{ Hz}, \ ^{2}J_{\text{YH}} = 2.58 \text{ Hz}, \text{ PtMe}), \end{array}$ 0.44 (s, 9H, SiMe₃), 0.51 (s, 9H, SiMe₃), 0.52 (1H, µ-CH₂, the coupling constant value is obscured by a signal at δ 0.51), 0.90 (d, ${}^{3}\text{H}, {}^{3}J_{\text{HP}} = 5.50 \text{ Hz}, {}^{2}J_{\text{HPt}} = 54.6 \text{ Hz}, \text{PtMe}$), 0.98 (d, ${}^{3}\text{H}, {}^{3}J_{\text{HP}} = 6.19 \text{ Hz}, {}^{2}J_{\text{HPt}} = 54.6 \text{ Hz}, \text{PtMe}$), 1.02 (d, ${}^{3}\text{H}, {}^{3}J_{\text{HP}} = 5.50 \text{ Hz}$, ${}^{2}J_{\rm HPt} = 55.7$ Hz, PtMe), 1.27 (br m, 4H, β -THF), 1.34 (br m, 4H, β-THF), 1.72 (s, 3H, Cp'Me), 1.76 (br s, 3H, Cp'Me), 1.78 (br s, 3H, Cp'Me), 1.97 (s, 3H, Cp'Me), 2.19 (s, 3H, Cp'Me), 2.2

(1H + 2H, CH₂),²⁷ 2.25 (s, 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, ${}^{3}J_{HH} = {}^{3}J_{HP} =$ 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 (br m, 12H, *m*+*p*-Ph), 7.43 (br, 2H, *o*-Ph), 7.56 (t, 2H, ${}^{3}J_{HH} = {}^{3}J_{HP} =$ 8.92 Hz, *o*-Ph), 7.66 (t, 2H, ${}^{3}J_{HH} = {}^{3}J_{HP} =$ 8.70 Hz, *o*-Ph), 7.69 (t, 2H, ${}^{3}J_{HH} = {}^{3}J_{HP} =$ 9.12 Hz, *o*-Ph). Two μ -CH₂ protons were not observed. Two isomers were observed in the ratio of 54% to 46%. Carbon signals for three *m*-Ph and one *p*-Ph were obscured by toluene-*d*₈ signals. Carbon signals for *ipso*-Ph were not observed. COSY (toluene-*d*₈, -20 °C): -1.02 to -0.55, -0.92 to -0.45, -0.87 to 0.52, 2.2–2.63, 2.45–2.86, 3.50–3.80, 3.71–4.04. ³¹P NMR (160.10 MHz, C₆D₆, RT): δ 10.76 (s, ${}^{1}J_{PPt} =$ 2078.4 MHz), 10.31 (s, ${}^{1}J_{PPt} =$ 1931.9 Hz). The integral intensity ratio of δ 10.76 to δ 10.31 is 42% to 58%. Anal. Calcd for C₃₇H₆₂OPPtSi₂Y: C 49.71, H 6.99. Found: C 49.78, H 6.68.

Preparation of ($C_5Me_4C_2H_4PPh_2$)**Lu**(**CH**₂**SiMe**₃)₂(**OC**₄**H**₈)-**PtMe**₂ (**4b**). Complex **2b** was prepared by the reaction of Lu(CH₂SiMe₃)₃(OC₄H₈) (160 mg, 0.275 mmol) with ($C_5Me_4-C_2H_4PPh_2$)H (93 mg, 0.278 mmol) in the same manner as written above. To the toluene solution of **2b** was added PtMe₂(COD) (92 mg, 0.276 mmol) dissolved in toluene (1 mL) at room temperature, and the mixture was stirred for 2 h. After removal of all the volatiles *in vacuo*, the ³¹P NMR spectrum was measured to reveal the formation of **4b** in a yield of 22.5% accompanied by the formation of unidentified byproducts, which exhibit many singlet signals, for example, at δ 14.17, 15.56, 15.63, 15.69, 17.5, etc. The resulting mixture was extracted with hexane and cooled at -35 °C to afford colorless crystalline **4b** (57 mg, 0.0582, 21.1%).

¹H NMR (399.65 MHz, C₆D₆, 60 °C): δ -0.96 (br, 1H, η ¹-CH₂), -0.88 (br, 1H, η^1 -CH₂), -0.23 (br, 1H, μ -CH₂), -0.04 (s, 9H, SiMe₃), 0.32 (s, 9H, SiMe₃), 0.57 (br m, 3H, PtMe), 0.84 (μ -CH₂),²⁷ 1.00 (d, 3H, ³J_{HP} = 5.95 Hz, ²J_{HPt} = 52.66 Hz, PtMe), 1.43 (br s, 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, CH₂), 3.91 (br s, 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, ³J_{HH} = ³J_{HP} = 8.70 Hz, o-Ph). COSY (toluene- d_8 , 50 °C): -0.96 to -0.88, -0.23 to 112, 0-1 II). COS 1 (Iblache- a_8 , 50 °C). 0.50 IO 0.08, 0.23 IO 0.84. ¹H NMR (600.17 MHz, toluene- d_8 , -20 °C): δ -1.17 (d, 1H, $^2J_{HH} = 10.98$ Hz, η^1 -CH₂), -1.03 (d, 1H, $^2J_{HH} = 11.04$ Hz, η^1 -CH₂), -0.69 (d, 1H, $^2J_{HH} = 10.98$ Hz, η^1 -CH₂), -0.61 (d, 1H, $^2J_{HH} = 10.32$ Hz, η^1 -CH₂), -0.50 (t, 1H, $^2J_{HH} = ^3J_{HP} = 6.80$ Hz, μ -CH₂), 0.06 (s, 9H, SiMe₃), 0.07 (s, 9H, SiMe₃), 0.07 (1H, μ -CH₂), -0.40 (s) SiMe₃), 0.07 (1H, μ - CH_2),²⁷ 0.44 (s, 9H, SiMe₃), 0.46 (d, 3H, ³ J_{HP} = 4.80 Hz, PtMe), 0.52 (s, 9H, SiMe₃), 0.56 (m, 1H, μ -CH₂), 0.97 (d, 3H, ³J_{HP} = 5.52 Hz, PtMe), 1.00 (d, 3H, ${}^{3}J_{HP} = 6.18$ Hz, PtMe), 1.05 (1H, μ -CH₂),²⁷ 1.23 (br m, 4H, β -THF), 1.34 (br m, 4H, β -THF), 1.15 (d, 3H, ³ $J_{\text{HP}} = 4.86$ 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, CH₂), 2.22 (m, 2H, CH₂), 2.22 (s, 6H, Cp'Me), 2.29 (s, 3H, Cp'Me), 2.33 (s, 3H, Cp'Me), 2.44 (m, 1H, CH₂), 2.64 (m, 1H, CH₂), 2.76 (d, 2H, ${}^{3}J_{\text{HP}} = 17.89$ Hz, CH₂), 2.85 (t, 1H, ${}^{2}J_{\text{HH}} = {}^{3}J_{\text{HP}} = 11.70$ Hz, CH₂), 3.50 (m, 2H, α -THF), 3.71 (m, 2H, α-THF), 3.87 (br m, 2H, α-THF), 4.12 (br m, 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, ${}^{3}J_{HH} = {}^{3}J_{HP} = 8.35$ Hz, *o*-Ph), 7.66 (t, 2H, ${}^{3}J_{HH} = {}^{3}J_{HP} = 8.25$ Hz, *o*-Ph), 7.69 (m, 2H, *o*-Ph). Two isomers were observed in the ratio of 55% to 45% in the ¹H NMR spectrum at -20 °C. COSY (toluene- d_8 , -20 °C): -1.17 to -0.69, -1.03 to -0.61, -0.50 to 0.56. ³¹P NMR (160.10 MHz, C₆D₆, RT): δ 8.22 (br, ¹*J*_{PPt} = 2037.4 Hz), 11.85 (br, ¹*J*_{PPt} = 2148.9 Hz). The integral intensity ratio of δ 8.22 to δ 11.85 is 56% to 44%. Anal. Calcd for C₃₇H₆₂OPPtSi₂Lu(Et₂O): C 46.71, H 6.88. Found: C 46.77, H 6.59. (For the use of elemental analysis, microcrystals of 4b precipitated from Et₂O solution were used.)

Formation of $(C_5Me_4SiMe_2CH_2PPh_2)Lu(\mu-\eta^1:\eta^2-CH_2SiCH_2)-(OC_4H_8)PtMe_2$ (6). Complex 3b (17 mg, 0.017 mmol) was

dissolved in C_6D_6 (0.4 mL) and heated at 90 °C for 1.5 h. Quantitative formation of **6** and SiMe₄ was confirmed by means of NMR spectroscopy. A single crystal suitable for X-ray analysis was obtained from a cold Et₂O solution of **6** (-35 °C).

¹H NMR (500.16 MHz, C₆D₆, RT): δ –0.45 (d, 1H, ²J_{HH} = 12.8 Hz, η^1 -CH₂), –0.14 (dd, 1H, ²J_{HH} = 14.66 Hz, J_{HP} = 8.70 Hz, μ -CH₂), –0.10 (s, 3H, SiMe₂CH₂P), 0.24 (d, 1H, ²J_{HH} = 12.80 Hz, η^1 -CH₂), 0.27 (s, 3H, SiMe₂CH₂P), 0.54 (s, 3H, Si-Me₂), 0.58 (s, 3H, SiMe₂), 0.75 (d, 3H, ³J_{HP} = 5.50 Hz, ²J_{HPt} = 57.30 Hz, PtMe), 1.03 (m, μ -CH₂), 1.04 (d, 3H, ³J_{HP} = 5.95 Hz, ²J_{HPt} = 54.50 Hz, PtMe), 1.21 (br m, 4H, β -THF), 1.66 (s, 3H, CH) Cp'Me), 1.71 (m, 1H, SiMe₂CH₂P), 2.23 (s, 3H, Cp'Me), 2.28 (s, 3H, Cp'Me), 2.45 (m, 1H, SiMe₂CH₂P), 2.48 (s, 3H, Cp'Me), 3.55 (br s, 2H, α-THF), 3.73 (br s, 2H, α-THF), 6.99 (t, 1H, 5.55 (b) \$, 2H, 0-1HP), 5.75 (b) \$, 2H, 0-1HP), 0.99 (t, 1H, *p*-Ph), 7.07 (m, 3H, *p*+*m*-Ph), 7.13 (d, 2H, ${}^{3}J_{HH} = 7.80$ Hz, *m*-Ph), 7.64 (t, 2H, ${}^{3}J_{HH} = {}^{3}J_{HP} = 8.48$ Hz, *o*-Ph), 7.69 (t, 2H, ${}^{3}J_{HH} = {}^{3}J_{HP} = 8.48$ Hz, *o*-Ph). ${}^{13}C$ NMR (100.40 MHz, C₆D₆, RT): δ 1.2 (d, ${}^{2}J_{CP-cis} = 4.92$ Hz, PtMe), 2.5 (d, ${}^{3}J_{CP} = 1.60$ Hz, SiMe₂CH₂P), 4.0 (d, ${}^{1}J_{CP} = 6.72$ Hz, SiMe₂CH₂P), 6.2 (d, ${}^{3}J_{CP} = 1.60$ Hz, SiMe₂CH₂P), 4.0 (d, ${}^{2}J_{CP-cis} = 4.92$ Hz, SiMe₂CH₂P), 6.2 (d, ${}^{3}J_{CP} = 1.60$ Hz, SiMe₂CH₂P), 6.2 (d, ${}^{3}J_{CP} = 1.60$ Hz, SiMe₂CH₂P), 6.2 (d, ${}^{3}J_{CP} = 1.60$ Hz, SiMe₂CH₂P), 6.2 (d, ${}^{3}J_{CP} = 0.22$ Hz, SiMe₂CH₂P), 6.2 (d, {}^{3}J_{CP} = 0.22 Hz, SiMe₂CH ${}^{3}J_{CP} = 3.3$ Hz, μ -CH₂), 6.8 (s, SiMe), 7.6 (s, SiMe), 7.9 (d, ${}^{2}J_{CP} = 99.89 \text{ Hz}, \text{ pt Me}$, 11.4 (s, Cp'Me), 12.9 (s, Cp'Me), 14.9 (d, ${}^{2}J_{CP} = 16.60 \text{ Hz}, \text{CH}_{2}$), 15.3 (s, Cp'Me), 17.2 (s, Cp'Me), 25.3 (d, ${}^{2}J_{CP} = 16.60 \text{ Hz}, \text{CH}_{2}$), 15.3 (s, Cp'Me), 17.2 (s, Cp'Me), 25.3 (s, Cp' (s, β-THF), 33.3 (s, LuCH₂), 70.3 (α-THF), 108.6 (s, Cp'-ring), 123.6 (s, Cp'-ring), 124.4 (s, Cp'-ring), 126.2 (s, Cp'-ring), 129.4 (br s, *p*-Ph), 129.8 (br s, *p*-Ph), 132.2 (d, ${}^{2}J_{CP} = 10.74$ Hz, *o*-Ph), 134.6 (d, ${}^{2}J_{CP} = 10.84$ Hz, *o*-Ph), 137.2 (d, ${}^{2}J_{CP} = 38.25$ Hz, *ipso*-Ph). *m*-Ph carbons were obscured by the solvent (C_6D_6) signals. COSY (C₆D₆, RT): -0.45 to 0.24, -0.14 to 1.03, 1.71-2.45. HMQC (C₆D₆, RT): $\delta_{\rm H} - \delta_{\rm C} - 0.45$, 0.24–33.3, -0.14, 1.03– 6.2, -0.10-2.5, 0.27-4.0, 0.54-6.8, 0.58-7.61, 0.75-1.2, 1.04-7.91, 1.21-25.3, 1.66-11.4, 1.71, 2.45-14.9, 2.48-17.2, 3.55, 3.73–70.3, 6.99–129.4, 7.07–129.8, 7.64–132.2, 7.69–134.6. ³¹P NMR (160.10 MHz, C₆D₆, RT): δ 11.19 (s, ${}^{1}J_{PPt} = 1955.3 \text{ Hz}$). Anal. Calcd for $C_{34}H_{54}OPPtSi_{2}Lu: C 43.63$, H 5.82. Found: C 44.07, H 5.92.

Reaction of 3a with [Ph₃C][B(C₆F₅₎₄]. To the Et₂O solution containing **3a** (20 mg, 0.021 mmol) was added [Ph₃C][B(C₆F₅₎₄] (19 mg, 0.021 mmol) at -30 °C. The reaction mixture was stirred at RT for 1 h, and all the volatiles were removed *in vacuo*. The resulting slurry was washed with hexane twice to afford a mixture of unidentified products. The ³¹P NMR spectrum exhibited two singlet signals at δ 8.99 and δ 10.60 with integrations of 66% and 34%, respectively. The former is similar to that of **5**.

Reaction of 4a with [Ph_3C][B(C_6F_5)_4]. To a C_6H_5Cl solution (0.5 mL) of 4a (8 mg, 0.0089 mmol) was added a C₆H₅Cl solution of $[Ph_3C][B(C_6F_5)_4]$ (8 mg, 0.0087 mmol) at -30 °C. After the mixture was stirred at RT for 2 h, hexane was added. Cooling the reaction mixture at -35 °C afforded a slurry at the bottom of the reaction vessel. All the supernatant solution was removed, and the resulting slurry was washed with hexane twice. After drying in vacuo, an oily residue was obtained. ¹H NMR (395.75 MHz, THF-d₈, RT): δ 0.05 (br, 3H, PtMe), 0.25 (t, ${}^{3}J_{\rm HP} = 11.48$ Hz, ${}^{2}J_{\rm HPt} = 49.07$ Hz, PtMe), 1.54 (br s, β -THF), 1.91 (s, 3H, Cp'Me), 1.93 (s, 3H, Cp'Me), 1.97 (s, 3H, Cp'Me), 2.25 (s, 3H, Cp'Me), 3.32 (br s, α -THF). Signals of the CH₂SiMe₃ groups were obscured and not assigned. ¹³C NMR (99.45 MHz, THF-d₈, RT): δ 2.3 (s, SiMe₃), 10.4 (s, Cp'Me), 10.4 (s, Cp'Me), 11.3 (s, Cp'Me), 12.4 (s, Cp'Me). ³¹P NMR (160.10 MHz, THF- d_8 , RT): δ 11.61 (${}^1J_{PPt} = 1967.15$ Hz).

A Typical Procedure for Isoprene Polymerization Using 4a (run 2 in Table 2). In a glovebox, to a 100 mL flask that contained a magnetic stirrer were added successively $Al^{B}Bu_{3}$ (55 μ L, 1 M, 0.055 mmol), 5 mL of a C₆H₅Cl solution of 4a (10.0 mg, 0.011 mmol), and isoprene (380.0 mg, 5.6 mmol). A C₆H₅Cl (5 mL) solution of [Ph₃C][B(C₆F₅)₄] (10.0 mg, 0.011 mmol) was added under rapid stirring. After 10 h, the flask was moved out from the glovebox and the reaction was terminated by adding methanol containing a small amount of hydrochloric acid. The precipitated polymer was isolated by decantation and washed with methanol twice. Then, the obtained polymer was dried

 Table 2. Polymerization Condition and Results

			polyisoprene				
				structure ^e			
ruı	n cat	time (h)	yield (%)	1,4- (%)	3,4- (%)	$\begin{array}{c}M_{n}^{f}\\(\times10^{5})\end{array}$	${M_{ m w}}/{M_{ m n}^{f}}$
1 <i>^a</i>	$3a/[Ph_3C][B(C_6F_5)_4]/$ Al ⁱ Bu ₃	10	4.4	33	67	2.7/3.8	3.2/1.1
2 ^{<i>b</i>}	$4a/[Ph_3C][B(C_6F_5)_4]/Al^iBu_3$	10	27.5	6	94	4.9	2.1
3^c 4^d	$\begin{array}{l} \textbf{4a}/[Ph_3C][B(C_6F_5)_4]\\ \textbf{4a}/Al^iBu_3 \end{array}$	3 3	$\begin{array}{c} 0 \\ 0 \end{array}$				

^{*a*} Complex **3a** (10.3 mg, 0.011); [IP]₀/[**3a**] = 500; [**3a**]/[Ph₃C][B(C₆F₅)₄] = 1; [AlⁱBu₃]/[**3a**] = 5. ^{*b*} Complex **4a** (10.0 mg, 0.011); [IP]₀/[**4a**] = 500; [**4a**]/ [Ph₃C][B(C₆F₅)₄] = 1; [AlⁱBu₃]/[**4a**] = 5. ^{*c*} Complex **4a** (10.0 mg, 0.011); [IP]₀/ [**4a**] = 500; [**4a**]/[Ph₃C][B(C₆F₅)₄] = 1. ^{*d*} Complex **4a** (10.0 mg, 0.011); [IP]₀/ [**4a**] = 500; [AlⁱBu₃]/[**4a**] = 5. ^{*e*} Determined by ¹H and ¹³C NMR spectroscopy. ^{*J*} Determined by gel permeation chromatography (GPC) with respect to a polystyrene standard.

in vacuo at 60 °C to a constant weight of polyisoprene (104.4 mg, 27.5% yield). *Cis/trans* content was calculated on the basis of the integral intensity of CH₂C*H*=C(Me)CH₂- signals. The regioselectivity was calculated on the basis of the integral intensity of CH₂CH=C(Me)CH₂- signals. ^{5c,21c}

The isoprene polymerizations using $3a/[Ph_3C][B(C_6F_5)_4]$, $3a/[Ph_3C][B(C_6F_5)_4]/Al^{i}Bu_3$, $4a/[Ph_3C][B(C_6F_5)_4]$, and $4a/Ali-Bu_3$ systems were performed in a similar manner. Reaction conditions and results are shown in Table 2.

Hydrogenolysis of 3a. A J-young sample tube was charged with a C_6D_6 solution containing **3a** (20 mg, 0.021 mmol). After the NMR tube was evacuated at $-196 \,^{\circ}$ C, H₂ gas was admitted. The sample was then warmed to room temperature and the reaction was monitored by ¹H and ³¹P NMR spectroscopy. After 3 days, complex **3a** was fully consumed to produce unidentified complexes, which exhibit broad signals around δ 0.3 and 2.0. In the ³¹P NMR spectrum, only one singlet, which is assigned for **5**, was observed. After removal of the all the volatiles, the residue was extracted with Et₂O and cooled at $-35 \,^{\circ}$ C to afford single crystals of **5**.

Hydrogenolysis of 4a. A J-young sample tube was charged with a C_6D_6 solution containing **4a** (10 mg, 0.011 mmol). After the NMR tube was evacuated at $-196 \,^{\circ}$ C, H₂ gas was admitted. The sample was then warmed to room temperature, and the reaction was monitored by ¹H NMR spectroscopy. After 5 h, complex **4a** was fully consumed to produce unidentified complexes, which exhibit broad signals around δ 0.3 and 2.2.

Single-Crystal X-ray Analysis for 3a, 3b, 4a, 5, and 6. Crystals for X-ray analysis were obtained as described in the preparations. The crystals were manipulated in the glovebox and were scaled in thin-wall glass capillaries. Data collections of 3a, 3b, 4a, and 6 were performed at -110 °C on a Bruker SMART APEX diffractometer with CCD area detector, using graphitemonochromated Mo K α radiation (=0.71069 Å). The determination of crystal class and unit cell parameters was carried out with the SMART program package.²⁸ The raw frame data were processed using SAINT²⁹ and SADABS³⁰ to yield the reduction data file. Data collection of **5** was performed on a Rigaku AFC-8 with a Saturn 70 CCD detector, and data processing was performed using CrystalClear.³¹ Absorption correction was performed using Numabs.³² The structures were solved by using the SHELXTL program using the Patterson method for **3a**, **3b**,

⁽²⁸⁾ SMART Software User Guide, version 4.21; Bruker AXS, Inc.: Madison, WI, 1997.

⁽²⁹⁾ SAINT PLUS, version 6.02; Bruker AXS, Inc.: Madison, WI, 1999

 ⁽³⁰⁾ Sheldrick, G. M. SADABS; Bruker AXS, Inc.: Madison, WI, 1998.
 (31) CrystalClear SM ver. 1.3.6., Rigaku/MSC Inc.: Texas, 2005.

⁽³²⁾ Higashi, T. *Numabs: Numerical Absorption Correction*; Rigaku Corporation: Tokyo, Japan, 1999.

Table 3. Experimental Data for the Crystal Structure Determinations of the Complexes 3a, 3b, 4a, 5, and 6

	3a	3b	4a	5	6
empirical formula	C38H66OPPtSi3Y	C38H60LuOPPtSi3	C37H62OPPtSi2Y	C30H36P2PtSi	C34H54LuOPPtSi2
fw	938.15	1018.16	894.02	681.71	935.98
cryst syst	monoclinic	orthorhombic	monoclinic	orthorhombic	monoclinic
space group	$P2_1/c$	$P2_{1}2_{1}2_{1}$	$P2_1/n$	Pbcn	C2/c
a (Å)	17.8199(18)	10.1882(16)	9.5886(13)	11.3220(14)	28.619(13)
$b(\mathbf{A})$	10.9688(11)	19.297(3)	20.717(3)	17.025(2)	15.3701(16)
c (Å)	21.897(2)	21.401(3)	20.136(3)	14.8474(19)	18.636(2)
α (deg)					
β (deg)	96.0210(2)		90.600(3)		109.8670(10)
γ (deg)					
$V(Å^3)$	4256.4(7)	4207.5(12)	3999.6(9)	2862.0(6)	7709.6(14)
Z	4	4	4	4	8
$D_{\rm calc} ({\rm g}{\rm cm}^{-3})$	1.464	1.607	1.485	1.582	1.613
T(K)	163	163	163	298	163
μ (Mo K α) (mm ⁻¹)	4.788	5.804	5.063	5.073	6.297
<i>F</i> (000)	1904	2008	1808	1352	3664
cryst size (mm)	$0.20 \times 0.10 \times 0.10$	0.10 imes 0.05 imes 0.02	0.10 imes 0.02 imes 0.02	0.08 imes 0.07 imes 0.06	$0.30 \times 0.20 \times 0.10$
θ range (deg)	1.87-27.56	1.42-27.51	1.41-27.54	2.16-30.03	1.51-27.55
no. of reflns collected	25885	26614	24 626	69 263	23 582
no. of reflns obsd $[I > 2\sigma(I)]$	6830	5287	3430	3452	6576
no. of indep reflns (R_{int})	9623 (0.0475)	9534 (0.1036)	9038 (0.1348)	4180 (0.0508)	8698 (0.0381)
data/restraints/params	9623/0/426	9534/0/414	9038/36/407	4180/0/157	8696/0/370
absorption corr	empirical	empirical	empirical	multiscan	empirical
goodness-of-fit on F^2	0.850	0.641	0.690	1.196	1.039
$R_1, wR_2 \left[I > 2\sigma(I) \right]$	0.0313, 0.0581	0.0478, 0.0630	0.0526, 0.0713	0.0565, 0.1227	0.0356, 0.1180
R_1 , wR_2 (all data)	0.0538, 0.0619	0.0989, 0.0732	0.1624, 0.0862	0.0681, 0.1295	0.0509, 0.1227
largest diff peak and hole (e $Å^{-3}$)	1.454 and -0.905	1.938 and -1.025	1.657 and -1.031	3.585 and -1.844	3.390 and -0.695

and **6** and the direct method for **4a** and **5**.³³ Refinement was performed on F^2 anisotropically for all the non-hydrogen atoms except disordered carbon atoms by the full-matrix least-squares methods. In the structure of **4a**, three carbons of one SiMe₃ group and four carbons of a THF molecule were disordered with occupancy of 69.5%/30.5% and 63.1%/36.9%, respectively. The hydrogen atoms on C5 in **3a** and **3b** and methylene proton on C1 and C4 were located by difference Fourier synthesis and their coordinates. Other hydrogen atoms were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters. Crystal data and processing parameters for **3a**, **3b**, **4a**, **5**, and **6** are summarized in Table 3.

(33) Sheldrick, G. M. SHELXTL, version 5.1; Bruker AXS, Inc.: Madison, WI, 1998.

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Supporting Information Available: CIF files of all crystal data and refinement parameters, atomic parameters including hydrogen atoms, and bond lengths and angles for 3a, 3b, 4a, 4b, 5, and 6. Full spectral data for 3a, 3b, 4a, and 4b at variable temperature. This material is available free of charge via the Internet at http://pubs.acs.org.