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Formation of Zn–Zn and Zn–Pd Bonded Complexes by Reactions of Terminal Zinc Hydrides with Pd(II) Species

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S Supporting Information

ABSTRACT: Divalent palladium-induced homocoupling of terminal zinc hydrides to zinc-zinc bonded complexes was achieved herein. Reactions of zinc hydrides [LZnH] (L = $CH_3C(2,6^{-i}Pr_2C_6H_3N)CHC(CH_3)(N(CH_2)_nCH_2PPh_2);$ 1a: n = 1; 1b: n = 2) with 0.5 equiv of allyl(cyclopentadienyl)palladium(II) afforded heterotrinuclear [Zn₂Pd] complexes 3 containing direct Zn-Zn and Zn-Pd bonds, with concomitant elimination of propylene and cyclopentadiene. Complexes 3 were also accessed by the reactions of zinc hydrides 1 with allylpalladium(II) chloride with release of propylene and hydrogen chloride. Treatment of zinc hydrides 1 with 1 equiv of allyl(cyclopentadienyl)palladium(II) gave Zn-Pd bonded complex 5 by elimination of propylene, which can be



transformed into heterotrinuclear complex 3 by further reaction with one additional molar equivalent of zinc hydrides. Heterobimetallic Zn-Pd complex 5b was found to be an effective catalyst in the hydrosilylation of benzaldehyde and its derivatives. Reaction of **5b** with silane reagent Ph₂SiH₂ produced [Pd₂Si₂H₂] complex **8** with cleavage of the Pd–Zn bond, which served as an initiating species in the catalytic reaction. Complexes 4b, 5, and 8 in this study were characterized by X-ray diffraction.

INTRODUCTION

Homonuclear metal-metal bonded complexes are of fundamental interest in numerous areas of chemical science.¹ The study of such complexes has flourished during the past two decades and shed light on new insights into the nature of the chemical bonds.² One of the landmark advances in this area was the discovery of the first covalent Zn(I)-Zn(I) bonded complex $[(\eta^5-Cp^*)_2Zn_2]$ (Cp* = C₅Me₅) by Carmona and coworkers in 2004.³ They obtained this unusual low-valent dizinc complex through the reductive coupling of $[Cp_{2}Zn]$ with ZnEt₂, albeit with a low isolated yield. Subsequently, the reaction was improved by adding 2 equiv of potassium hydride as the reductant, which gave the identical dizinc compound in a higher yield.⁴ Inspired by this seminal work, a variety of Zn(I)-Zn(I) bonded complexes supported by versatile ancillary ligands were prepared and characterized.⁵ The most common synthetic approach to such complexes is by the reductive coupling reaction of Zn(II) halides with alkali metals⁶ or by a recently developed method using low-valent metallic reductants, that is, $Mg(I)^{\gamma}$ and $Re(I)^{.8}$ Ligand substitution reactions of the Carmona's dizinc complex provide an alternative pathway to the desired Zn(I)-Zn(I) bonded complex.9

Furthermore, the reactivity of Zn(I)-Zn(I) bonded complexes has also been investigated. Fischer, Frenking, and co-workers reported that reactions of $[(\eta^5-Cp^*)_2Zn_2]$ with transition metal (TM) complexes resulted in the diverse formation of metal-rich complexes or clusters, in which either the [ZnCp*] or [ZnZnCp*] fragment functioned as a type of one-electron donor ligand at the TM centers.¹⁰ Additionally, their research provided examples of various organozinc ligand coordination modes, where the dizinc bond coordinated to the TM in a η^2 -fashion to form a heterotrinuclear triangular $[Zn_2M]$ (M = Cu or Ni) core structure.¹¹ Because the lowvalent Zn-Zn bond is isolobal to a dihydrogen molecule, such η^2 -Zn₂-M complexes can be viewed as zinc congeners of nonclassical dihydrogen complexes of transition metals.^{12,13}

In our previous work, a novel pathway for the formation of Zn(I)-Zn(I) bonded complexes was developed. Electron-rich TM palladium(0) species was used in the dehydrocoupling of terminal Zn(II) hydrides, resulting in the formation of a η^2 dizinc bonded complex of palladium (Scheme 1).¹⁴ Density functional theory computation studies revealed that an oxidative addition at the Pd(0) center possibly occurred to afford Pd(II) dihydride 2, followed by reductive elimination to finally afford a Zn-Zn bonded complex 3. Herein, the reactions between Zn(II) hydrides with a 0.5 equimolar equiv of Pd(II) species were further investigated, which produced identical heterotrinuclear [Zn₂Pd] complexes via

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Scheme 2. Reactions of Zinc Hydrides 1 with Palladium(II) Complexes



facile alkene eliminations. Well-defined heterobimetallic intermediate complexes featuring direct Zn–Pd bonds were observed to be effective catalysts for the hydrosilylation of aldehyde substrates.

RESULTS AND DISCUSSION

Reactions of Zinc Hydrides with Palladium(II) **Complexes.** The reaction between Zn(II) hydride 1a with a 0.5 mol equiv of a commercially available Pd(II) reagent, namely, allyl(cyclopentadienyl)palladium, in a C₆D₆ solution, was initially performed in an NMR tube. Its ¹H and ³¹P NMR spectroscopic monitoring clearly indicated the formation of the previously reported heterotrinuclear complex 3a. During the reaction, propylene [¹H: δ = 5.72 (m, 1H, CH), 5.01 (dm, 1H, CH₂), 4.95 (dm, 1H, CH₂), 1.55 (dt, 3H, CH₃) ppm] and free cyclopentadiene [¹H: δ = 6.49 (m, 2H, CH), 6.29 (m, 2H, CH), 2.69 (m, 2H, CH_2) ppm] were detected as the elimination products instead of H₂ evolution, as in our previous case.¹⁴ Accordingly, the reactions of 1 with $(\eta^3$ - C_3H_5)Pd(η^5 -Cp) were scaled up in toluene to eventually afford [Zn₂Pd] complexes 3 in high isolated yields (3a: 77%; 3b: 64%) (Scheme 2).

Subsequently, another widely used Pd(II) species, allylpalladium chloride, was also investigated for this homocoupling reaction. Reaction of zinc hydride 1a with 0.25 mol equiv of $[\eta^3-(C_3H_5)PdCl]_2$ in toluene successfully provided $[Zn_2Pd]$ complex 3a in 75% isolated yield (Scheme 2). During the reaction, generation of propylene was clearly observed from the in situ ¹H NMR spectrum. Under analogous conditions, the reaction of 1b with $[\eta^3-(C_3H_5)PdCl]_2$ led to the isolations of heterotrinuclear complex 3b and zinc chloride 4b. Complex 4b was fully characterized by multinuclear NMR spectroscopy and X-ray diffraction (Figure S4 in the Supporting Information), which possibly indicated the elimination of hydrogen chloride (HCl) during the course of the reaction. Subsequently, HCl elimination was confirmed by the treatment of complex **1b** with dry HCl gas, which resulted in the formation of complex **4b** in 63% isolated yield (for details see Experimental Section). Apparently, palladium(II) species are also applicable for the homocoupling of zinc hydrides to afford heterotrinuclear η^2 -Zn₂-Pd complexes as that of using palladium(0) species. The only difference lies in the elimination products.

It has been well-documented that the reactions of ZnR_2 (R = alkyl or Cp) with TM hydrides served as a facile synthetic strategy to form Zn-TM bonded complexes through the elimination of RH.^{15,16} However, the use of zinc hydride via oxidative cleavage to construct a Zn-TM bond is limited.¹⁷ To gain more insights into the reactions, we next investigated the reactions of zinc hydrides with Pd(II) reagent in a 1:1 molar ratio. Monitoring the reaction of complex 1b with an equimolar equivalent of $(\eta^3 - C_3H_5)Pd(\eta^5 - Cp)$ gave a new sharp resonance at δ 33.8 ppm in the ³¹P NMR spectrum and signals attributed to propylene in the ¹H NMR spectrum. Scaling up the reaction in toluene eventually produced complex 5b as a yellow solid in 62% yield (Scheme 3), which was comprehensively characterized by NMR spectroscopy, elemental analysis, and single-crystal X-ray diffraction. The molecular structure of 5b (Figure 1) exhibits a heterobimetallic core featuring a Pd-Zn bond length of 2.373(8) Å, which is significantly shorter than those in heterotrinuclear complex 3 (ca. 2.50 Å) and comparable to the shortest Pd-Zn bond reported in the literature.^{18,10a,c} The coordination sphere of the palladium atom was completed by the η^5 -cyclopentadienyl [¹H: $\delta = 5.70$ (s, 5H, C₅H₅) ppm] ligand and by the PPh₂ group on the pendant arm (Pd1-



Scheme 3. Reactions of Zinc Hydrides 1 with an Equimolar Equivalent of Allyl(cyclopentadienyl)palladium(II)

Figure 1. Molecular structure of complex **5b**. Hydrogen atoms are omitted for clarity; displacement ellipsoids are drawn at the 30% probability level. Selected bond lengths (Å) and angles (deg): Pd1–Zn1 2.373(1), Pd1–P1 2.186(2), Pd1–Cp_{centr}2.039(3), Zn1–N1 1.962(5), Zn1–N2 1.961(5), N1–C2 1.306(7), C2–C3 1.414(8), C3–C4 1.381(8), N2–C4 1.328(8), P1–Pd1–Zn1 86.8(1), N1–Zn1–N2 97.0(2), N1–Zn1–Pd1 125.3(1), N2–Zn1–Pd1 137.7(2).

Cp_{centr} 2.039(3) Å, Pd1–P1 2.186(2) Å). Notably, the coordination geometry at the zinc center is observed to be planar tricoordinated ($\Sigma Zn1^{PdNN} = 360.0(5)^{\circ}$). The Zn…P distance was found to be 3.135(2) Å, indicating a negligible interaction. The analogous reaction of zinc hydride 1a with an equimolar equivalent of (η^3 -C₃H₅)Pd(η^5 -Cp) also afforded the bimetallic [ZnPd] complex 5a (Scheme 3), albeit with a low isolated yield (36%) because of the simultaneous formation of the [Zn₂Pd] product 3a. Multinuclear NMR spectroscopic data of 5a are provided in the Experimental Section (³¹P: δ = 23.6 ppm). The structure of complex 5a was also confirmed by single-crystal X-ray diffraction and is depicted in the Supporting Information (Figure S8, Pd1–Zn1 2.388(1) Å).

To examine whether bimetallic complex 5 could be transformed into the final Zn-Zn bonded complex 3, the reaction of complex 5b with 1 equiv of zinc hydride 1b was

performed, which rapidly afforded the homocoupling product **3b** with concomitant elimination of free cyclopentadiene (Scheme 4; for details, see the Experimental Section). Thus, Pd(II)-induced dizinc bond formation occurred *via* a two-step alkene elimination process.

Catalytic Application of the Heterobimetallic Zn-Pd Complex in Hydrosilylation of Aldehydes. Bimetallic catalysis has recently attracted considerable attention because of the potential cooperativity and synergy between the two different metal centers, which may offer an advantage over existing monometallic systems in selectivity and activity.¹⁹ Although a variety of well-defined TM complexes based on organozinc metalloligands have been described,²⁰ their use in homogeneous catalysis is scarce. Very recently, Tauchert and co-workers reported a palladium(0) complex supported by a Ztype Zn(II)-based ligand, which displayed high activity in the hydrosilylation of carbon dioxide.²¹ In addition, metalcatalyzed hydrosilylation of carbonyl substrates using silanes offers an efficient protocol for the reduction of aldehydes.²² With the bimetallic Zn-Pd complex 5b in hand, this compound was subsequently tested for the hydrosilylation of aromatic aldehydes by using Ph₂SiH₂ and PhSiH₃ as reducing reagents. Excitingly, 5b was observed to be efficient for the hydrosilylation of benzaldehyde and its derivatives under mild conditions with only a 1 mol % catalyst loading, with the results summarized in Table 1. In all cases, hydrosilylation reactions were first conducted in C₆D₆ and monitored by ¹H NMR spectroscopy. After consumption of the starting aldehydes, the reaction was guenched and treated with 10% aqueous NaOH to afford the final alcohol products to determine the respective yields. When using Ph₂SiH₂ as the reductant, benzaldehyde (6a) was converted to benzyl alcohol (7a) in a 70% isolated yield after 6 h (entry 1). The reaction was significantly improved by changing the silane reagent to PhSiH₃, which resulted in a 86% yield of 7a after only 20 min, under similar conditions (entry 2). Benzaldehyde derivatives featuring polar functional groups such as methoxyl (entry 3), nitro (entry 4), and chloride (entry 5) were tolerated in the reactions. The results show that compound with electrondonating group is more reactive than compounds containing electron-withdrawing substituents (entry 3 vs entries 4 and 5) in the catalytic system herein. Reducing the amount of used silane to 0.33 equiv of PhSiH₃ required a prolonged reaction time (12 h) to achieve a satisfactory yield (entry 6).

To gain more insights into the bimetallic Zn–Pd catalysis herein, the stoichiometric reactions between complex **5b** with two types of silanes in toluene, at room temperature, were performed. The reaction of **5b** with PhSiH₃ rapidly took place to generate several unidentified complexes, which cannot be successfully separated. However, treatment of **5b** with an

Scheme 4. Reaction of Complex 5b with an Equimolar Equivalent of Zinc Hydride 1b



Table 1. Catalytic Hydrosilylation of Aldehydes by using Bimetallic Zn-Pd Complex 5b^a

	$ \begin{array}{c} 0 \\ H \\ \hline \\ C_6 D_6, \\ \hline \\ 2) 10 \end{array} $	lane, 1 mol% 5b , room temperature	OH R	
	6		7	
Entry	Substrate	Silane	Time (min)	Yield ^b
1	CHO 6a	Ph_2SiH_2	360	70%
2	CHO 6a	PhSiH ₃	20	86%
3	МеОСНО 6b	PhSiH ₃	20	90%
4	O ₂ N-CHO 6c	PhSiH ₃	40	86%
5	CI-CHO 6d	PhSiH ₃	60	87%
6 ^c	СНО 6а	PhSiH ₃	720	72%
7 ^d	СНО 6а	Ph_2SiH_2	360	74%
8 ^e	СНО 6а	PhSiH ₃	60	30%
9 ^f	СНО 6а	PhSiH ₃	60	<5%

^{*a*}Reaction conditions: 0.80 mmol of aldehyde, 0.80 mmol of silane, C_6D_6 as the solvent, room temperature. ^{*b*}Isolated yield. ^{*c*}0.27 mmol of PhSiH₃ was used. ^{*d*}0.5 mol % **8** was used as a catalyst. ^{*e*}(η^3 -C₃H₅)Pd(η^5 -Cp) (1 mol %, 8 μ mol) was used as a catalyst, and conversion was determined by ¹H NMR spectroscopy. ^{*f*}(η^3 -C₃H₅)Pd(η^5 -Cp) (1 mol %, 8 μ mol) with an equimolar amount of PPh₃ (1 mol %, 8 μ mol) was used as catalyst, and conversion was determined by ¹H NMR spectroscopy.

Scheme 5. Reaction of Bimetallic Zn-Pd Complex 5b with an Equimolar Equivalent of Ph₂SiH₂



equimolar equivalent of Ph₂SiH₂ led to isolation of the [Pd₂Si₂] complex 8 in high yield (84%) as a yellow crystalline solid (Scheme 5). H₂ evolution during the reaction process was observed. Single crystals of complex 8, suitable for the X-ray crystal structure analysis, were grown from a mixture of toluene and hexane solution at -30 °C. The molecular structure of the C₂-symmetric complex 8 (Figure 2) contained a planar



Figure 2. Molecular structure of complex **8**. Hydrogen atoms (except Pd-H) are omitted for clarity; displacement ellipsoids are drawn at the 30% probability level. Selected bond lengths (Å) and angles (deg): Si1-H1 1.66(3), Pd1-H1 1.69(3), Pd1-Pd1' 2.710(1), Pd1-Si1 2.326(1), Pd1-Si1' 2.410 (1), Pd1-P1 2.304(1), Zn1-N1 1.954(2), Zn1-N2 1.929(2), Zn1-C37 2.052(4), Zn1-C33 2.433(5), N1-C2 1.343(4), C2-C3 1.392(4), C3-C4 1.406(4), N2-C4 1.320(4), Pd1-Si1-H1 44.6(11), Pd1-H1-Si1 91.8(16).

[Pd₂Si₂] unit with two hydrides bridging the Pd-Si edges (Pd1-Si1 2.326(1) Å, Pd1-Si1' 2.410(1) Å, Pd1-H1 1.69(3) Å, Si1-H1 1.66(3) Å, Pd1-Pd1' 2.710(1) Å), which is quite similar to the previously reported dinuclear palladium complexes possessing the [Pd₂Si₂] motif by Osakada and coworkers, where such complexes were obtained by the reactions of Ph_2SiH_2 with either simple Pd(0) or Pd(II) species.^{23,24} During the course of the reaction herein, cleavage of the Zn-Pd bond occurred, and the cyclopentadienyl ligand was transferred to the zinc center exhibiting an η^2 -coordinated fashion (Zn1-C37 2.052(4) Å, Zn1-C33 2.433(5) Å) in the solid state. The phosphine pendant arm remains bound to the palladium center (Pd1-P1 2.304(1) Å). The ¹H/¹³C NMR signals of cyclopentadienyl are at δ 6.22/107.7 ppm. Additionally, a broad signal in the ¹H NMR spectrum at δ 2.57 ppm attributed to the SiH moiety was also observed.

Subsequently, complex 8 was directly applied in the catalytic hydrosilylation of benzaldehyde under the same conditions and demonstrated a similar result to that of the parent complex **5b** (Table 1, entry 7 vs entry 1), supporting the $[Pd_2Si_2H_2]$ complex as an initiating species in the hydrosilylation reaction. A control experiment, by using the starting materiel (η^3 - C_3H_5)Pd(η^5 -Cp) as a catalyst under our typical conditions, was performed, and the catalytic activity dropped significantly in comparison with that of the bimetallic complex **5b** system (Table 1, entry 8 vs entry 2). However, such a difference is still insufficient to draw a solid conclusion toward the influence of the bimetallic effect in the reaction at current stage.

CONCLUSION

In summary, divalent palladium regents, such as allyl-(cyclopentadienyl)palladium(II) and allylpalladium(II) chloride, were able to mediate stoichiometric dehydrocoupling of zinc hydrides to form heterotrinuclear η^2 -Zn₂-Pd complexes through eliminations of propylene, cyclopentadiene, or HCl. During the course of the reaction, direct Zn-Zn and Zn-Pd bonds were formed. Heterobimetallic Zn-Pd bonded complexes were also accessed by the reactions of zinc hydrides with 1 equiv of allyl(cyclopentadienyl)palladium(II) and were confirmed as intermediates for the formation of heterotrinuclear [Zn₂Pd] complexes. Such metal-metal bond-forming reactions most likely profit from the phosphine-containing β diketiminato ligands²⁵ because of the strong phosphorus affinity of the palladium metal ion. Our study herein not only provides a facile synthetic strategy to Zn-Zn or Zn-Pd bonded complexes but also gives an example by using welldefined TM-Zn bimetallic complex in homogeneous catalysis. Although the existence of the bimetallic effect currently remains ambiguous, the complex herein exhibits higher activity than that of its parent monometallic palladium complex. Further reactivity of these Zn-Zn and Zn-Pd bonded complexes, especially in multimetallic catalysis, is currently underway in our laboratory.

EXPERIMENTAL SECTION

General Procedures. All experiments were performed under a dry argon atmosphere using standard Schlenk techniques or in a glovebox. Solvents (including deuterated solvents used for NMR) were dried and distilled 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 one-dimensional (1D) and two-dimensional (2D) NMR experiments. Elemental analysis data were recorded on a Carlo-Erba EA-1110 instrument. High-resolution mass spectrometry was measured with a Bruker micrOTF-Q III. Allylpalladium(II) chloride dimer, PhSiH₃, Ph₂SiH₂, PhCHO, *p*-Cl-PhCHO, *p*-OMe-PhCHO, and *p*-NO₂-PhCHO were purchased from Strem or Adamas. η^3 -(C₃H₅)PdCp²⁶ and zinc hydrides 1¹⁴ were synthesized following the literature procedures.

Reaction of Zinc Hydride 1a with Allyl(cyclopentadienyl)palladium(II). (η^3 -C₃H₅)Pd(η^5 -Cp) (32 mg, 0.15 mmol) was added to a solution of **1a** (161 mg, 0.30 mmol) in 3 mL of toluene. After it was stirred at 60 °C for 4 h, the volatiles were removed under vacuum, and then the residue was washed with hexane (3 × 1 mL) to finally give **3a** as a yellow crystalline solid (139 mg, 77% yield).

Reaction of Zinc Hydride 1b with Allyl(cyclopentadienyl)palladium(II). Following the procedure described for 3a, reaction of 1b (165 mg, 0.30 mmol) with $(\eta^3$ -C₃H_s)Pd(η^5 -Cp) (32 mg, 0.15 mmol) gave 3b as a yellow crystalline solid (116 mg, 64% yield).

Reaction of Zinc Hydride 1a with Allylpalladium(II) Chloride. $[(\eta^3-C_3H_5)PdCl]_2$ (37 mg, 0.10 mmol) was added to a solution of 1a (214 mg, 0.40 mmol) in 3 mL of toluene. The reaction mixture was stirred at room temperature for 1 h. The volatiles were removed under vacuum, and the residue was washed with hexane (3 × 1 mL) to finally give 3a as a yellow solid (176 mg, 75% yield).

Reaction of Zinc Hydride 1b with Allylpalladium(II) Chloride. $[(\eta^3-C_3H_3)PdCl]_2$ (18 mg, 0.05 mmol) was added to a solution of 1b (110 mg, 0.20 mmol) in 3 mL of toluene. After it stood at room temperature for 1 h, the reaction solution was concentrated to ~1 mL, and then hexane (3 mL) was layered to give a mixture of complex 3b and 4b as crystalline solids. The mixture was separated manually with the aid of an optical microscope in a glovebox to finally gave 3b (36 mg, 30% yield) as yellow crystals and 4b (13 mg, 11% yield) as colorless crystals.

Reaction of Zinc Hydride 1b with HCl Gas to Give 4b. Freshly prepared hydrogen chloride gas was bubbled into a solution of 1b (275 mg, 0.5 mmol) in 5 mL of toluene. The volatiles were removed under vacuum, and the residue was washed with hexane $(3 \times 1 \text{ mL})$

to finally give **4b** as a white solid (184 mg, 63% yield). ¹H NMR (400 MHz, $C_6 D_6$, 298 K): δ = 7.60 (m, 4H, o-Ph₂P), 7.10 (m, 2H, m-NAr), 7.09 (m, 1H, p-NAr), 7.05 (m, 4H, m-Ph₂P), 7.03 (m, 2H, p-Ph₂P), 4.66 (s, 1H, MeC(N)CH), 3.51 (m, 2H, NCH₂), 3.50 (m, 2H, ArCHMe₂), 2.24 (m, 2H, PCH₂), 1.72 (s, 3H, MeC), 1.48 (s, 3H, MeC), 1.26 (overlapped with NArCHMe2, NCH2CH2), 1.21 (m, 6H, NArCHMe₂), 1.15 (d, ${}^{3}J_{HH}$ = 6.9 Hz, 6H, ArCHMe₂). ${}^{13}C{}^{1}H$ NMR (101 MHz, C_6D_6 , 298 K): $\delta = 167.2$ (MeC), 167.1 (MeC), 144.8 (*i*-NAr), 143.1 (o-NAr), 134.0 (i-Ph₂P), 134.0 (d, ${}^{2}J_{PC}$ = 12.9 Hz, o- Ph_2P), 130.6 (p- Ph_2P), 128.9 (d, ${}^{3}J_{PC} = 9.1$ Hz, m- Ph_2P), 125.9 (p-NAr), 123.9 (m-NAr), 94.6 (MeC(N)CH), 50.8 (NCH₂), 29.0 (d, ${}^{1}J_{PC} = 9.1$ Hz, PCH₂), 28.5 (ArCHMe₂), 26.4 (NCH₂CH₂), 25.0 (ArCHMe₂), 24.2 (ArCHMe₂), 24.0 (MeC), 20.7 (MeC). ³¹P{¹H} NMR (162 MHz, $C_6 D_{61}$ 298 K): $\delta = -17.3$. Anal. Calcd for C32H40ClN2PZn: C, 65.76; H, 6.90; N, 4.79. Found: C, 65.97; H, 7.23; N, 4.54%.

Preparation of 5a. $(\eta^3$ -C₃H₅)Pd $(\eta^5$ -Cp) (96 mg, 0.45 mmol) was added to a solution of 1a (241 mg, 0.45 mmol) in 5 mL of toluene. After it stirred at room temperature for 2 h, the volatiles were removed by vacuum. The residue was recrystallized in toluene (1 mL) at -30 °C to finally give 5a as a yellow crystalline solid (114 mg, 36%) yield). Crystals suitable for the X-ray crystal structure analysis were grown from a layered toluene/hexane (v/v: 1:2) solution at -30 °C. Note: During the reaction, heterotrinuclear complex 3a was simultaneously generated, which led to a low yield of 5a. ¹H NMR (400 MHz, C_6D_{62} 298 K): δ = 7.64 (m, 4H, o-Ph₂P), 7.24 (m, 3H, m, p-NAr), 7.08 (m, 4H, m-Ph₂P), 7.03 (m, 2H, p-Ph₂P), 5.58 (s, 5H, Cp), 4.77 (s, 1H, MeC(N)CH), 3.26 (m, 2H, NCH₂), 3.24 (m, 2H, ArCHMe₂), 2.24 (m, 2H, PCH₂), 1.73 (s, 3H, MeC), 1.52 (d, ${}^{3}J_{HH} =$ 6.9 Hz, 6H, ArCHMe₂), 1.49 (s, 3H, MeC), 1.19 (d, ${}^{3}J_{HH} = 6.9$ Hz, 6H, ArCHMe₂). ¹³C{¹H} NMR (101 MHz, C₆D₆, 298 K): δ = 167.3 (MeC), 166.1 (MeC), 145.7 (*i*-NAr), 142.2 (*o*-NAr), 140.7 (d, ${}^{1}J_{PC}$ = 39.4 Hz, *i*-Ph₂P), 133.2 (d, ${}^{2}J_{PC}$ = 13.9 Hz, *o*-Ph₂P), 129.5 (d, ${}^{4}J_{PC}$ = 2.2 Hz, p-Ph₂P), 128.2 (overlapped with solvent, m-Ph₂P), 126.4 (p-NAr), 124.2 (*m*-NAr), 96.2 (MeC(N)CH), 93.6 (*Cp*), 47.3 (d, ${}^{2}J_{PC}$ = 3.1 Hz, NCH₂), 35.4 (d, ${}^{1}J_{PC}$ = 34.9 Hz, PCH₂), 28.7 (ArCHMe₂), 24.6 (ArCHMe₂), 24.0 (MeC), 23.9 (ArCHMe₂), 22.2 (MeC). ³¹P{¹H} NMR (162 MHz, C₆D₆, 298 K): δ = 23.6. Anal. Calcd for C36H43N2PPdZn: C, 61.20; H, 6.13; N, 3.97. Found: C, 61.39; H, 6.04; N, 3.64%.

Preparation of 5b. $(\eta^{3}-C_{3}H_{5})Pd(\eta^{5}-Cp)$ (106 mg, 0.50 mmol) was added to a solution of 1b (275 mg, 0.50 mmol) in 5 mL of toluene. After it stirred at room temperature for 0.5 h, the volatiles were removed under vacuum. The residue was washed with hexane (3×1) mL) to finally give 5b as a yellow crystalline solid (223 mg, 62% yield). Crystals suitable for the X-ray crystal structure analysis were grown from a layered toluene/hexane (v/v: 1:2) solution at -30 °C. ¹H NMR (400 MHz, C₆D₆, 298 K): δ = 7.66 (m, 4H, o-Ph₂P), 7.19 (m, 3H, m, p-NAr), 7.08 (m, 4H, m-Ph₂P), 7.03 (m, 2H, p-Ph₂P), 5.70 (s, 5H, Cp), 4.77 (s, 1H, MeC(N)CH), 3.38 (m, 2H, NCH₂), 3.25 (m, 2H, ArCHMe₂), 2.09 (m, 2H, PCH₂), 1.73 (s, 3H, MeC), 1.65 (s, 3H, MeC), 1.62 (m, 2H, NCH₂CH₂), 1.32 (d, ${}^{3}J_{HH} = 6.9$ Hz, 6H, ArCHMe₂), 1.18 (d, ${}^{3}J_{HH} = 6.9$ Hz, 6H, ArCHMe₂). ${}^{13}C{}^{1}H{}$ NMR (101 MHz, C_6D_6 , 298 K): $\delta = 167.8$ (MeC), 166.0 (MeC), 145.4 (*i*-NAr), 142.2 (*o*-NAr), 140.1 (d, ${}^{1}J_{PC} = 37.5$ Hz, *i*-Ph₂P), 133.0 (d, ${}^{2}J_{PC} = 14.1$ Hz, *o*-Ph₂P), 129.2 (d, ${}^{4}J_{PC} = 2.2$ Hz, *p*-Ph₂P), 128.0 (overlapped with solvent, m-Ph2P), 126.2 (p-NAr), 124.1 (m-NAr), 96.3 (MeC(N)CH), 93.2 (Cp), 48.0 (d, ${}^{3}J_{PC} = 3.9$ Hz, NCH₂), 31.1 (d, ${}^{1}J_{PC}$ = 30.9 Hz, PCH₂), 28.7 (ArCHMe₂), 26.6 (NCH₂CH₂), 24.4 (ArCHMe₂), 24.0 (ArCHMe₂), 23.9 (MeC), 21.3 (MeC). ³¹P{¹H} NMR (162 MHz, C₆D₆, 298 K): δ = 33.8. Anal. Calcd for C37H45N2PPdZn: C, 61.68; H, 6.30; N, 3.89. Found: C, 61.73; H, 6.25; N, 3.58%.

Reaction of Complex 5b with 1 Equiv of Zinc Hydride 1b. Complex 1b (55 mg, 0.10 mmol) was added to a solution of 5b (72 mg, 0.10 mmol) in 3 mL of toluene. The reaction mixture was stirred at 60 °C for 4 h. The volatiles were removed under vacuum, and the residue was washed with hexane $(3 \times 1 \text{ mL})$ to finally give 3b as a yellow crystalline solid (72 mg, 59% yield).

Preparation of Complex 8. Ph₂SiH₂ (46 mg, 0.25 mmol) was added to a solution of 5b (180 mg, 0.25 mmol) in 3 mL of toluene. After it stirred at room temperature for 4 h, the volatiles were removed under vacuum. The residue was washed with hexane (3×1) mL) to finally give 8 as yellow crystalline solid (190 mg, 84% yield). Crystals suitable for the X-ray crystal structure analysis were grown from a layered toluene/hexane (v/v: 1:2) solution at -30 °C. ¹H NMR (400 MHz, C_6D_6 , 298 K): δ = 7.66 (m, 8H, o-Ph₂Si), 7.45 (m, 8H, o-Ph₂P), 7.17 (m, 12H, m, p-Ph₂Si), 7.12 (m, 6H, m, p-NAr), 6.96 (m, 12H, m, p-Ph₂P), 6.22 (s, 10H, Cp), 4.54 (s, 2H, MeC(N)CH), 3.04 (m, 4H, ArCHMe₂), 2.64 (m, 4H, NCH₂), 2.57 (br, 2H, SiH), 1.93 (m, 4H, PCH₂), 1.57 (s, 6H, MeC), 1.48 (s, 6H, MeC), 1.38 (m, 4H, NCH₂CH₂), 1.22 (d, ${}^{3}J_{\text{HH}} = 6.8$ Hz, 12H, ArCHMe₂), 1.09 (d, ${}^{3}J_{\text{HH}} = 6.8$ Hz, 12H, ArCHMe₂). ${}^{13}C{}^{1}\text{H}$ NMR (101 MHz, C₆D₆, 298 K): δ = 169.8 (MeC), 167.1 (MeC), 144.0 (*i*-NAr), 143.6 (*i*-Ph₂Si), 142.3 (o-NAr), not observed (n.o.) (i-Ph₂P), 136.3 (o-Ph₂Si), 133.5 (o-Ph2P), 129.6 (o-Ph2P), 128.5 (overlapped with solvent, m-Ph₂P), 128.2 (overlapped with solvent, m-Ph₂Si), 127.9 (overlapped with solvent, p-Ph₂P), 126.3 (p-NAr), 124.0 (m-NAr), 107.7 (Cp), 95.3 (MeC(N)CH), 51.9 (NCH₂)¹, 28.4 (ArCHMe₂), 28.3 (PCH₂)¹, 27.6 (NCH₂CH₂), 24.2 (ArCHMe₂), 24.1 (ArCHMe₂), 23.5 (MeC), 21.6 (MeC) [¹ from the ¹H, ¹³C GHSQC experiment]. ³¹P{¹H} NMR(162 MHz, C₆D₆, 298 K): $\delta = 19.9$. Anal. Calcd for C₉₈H₁₁₂N₄P₂Pd₂Si₂Zn₂: C, 65.11; H, 6.25; N, 3.10. Found: C, 65.78; H, 6.32; N, 2.94%.

General Procedure for Hydrosilylation Reactions. In the glovebox, a benzene- d_6 solution of silane (0.80 mmol) and aldehyde (0.80 mmol) was added to a vial containing 5.8 mg (0.008 mmol) of **5b**. The resulting solution was transferred into a J. Young tube, where it remained at ambient temperature. The progress of the reaction was monitored by ¹H NMR spectroscopy. When the reaction was completed, the mixture was treated with a 10% aqueous solution of NaOH (1 mL) with vigorous stirring at room temperature overnight. The organic product was extracted with Et₂O (3 × 15 mL), dried over anhydrous MgSO₄, and concentrated under vacuum. The alcohol product was further purified by silica column chromatography (with petroleum/ethyl acetate 10/1 as eluent).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.9b02062.

Characterization data and NMR spectra of new complexes (PDF)

Accession Codes

CCDC 1939594–1939597 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: + 44 1223 336033.

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The authors declare no competing financial interest.

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