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Mononuclear Heteroscorpionate Zwitterionic Zinc Terminal Hydride: Synthesis, Reactivity, and Catalysis for Hydrosilylation of Aldehydes

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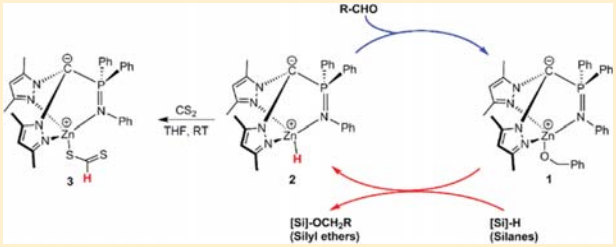
Supporting Information

ABSTRACT: Treatment of heteroscorpionate zinc benzyloxy complex LZnOBn (**1**, L = $(^{Me}Pz)_2CP(Ph)_2NPh$, ^{Me}Pz = 3,5-dimethylpyrazolyl) with phenylsilane ($PhSiH_3$) gave a zinc hydride complex LZnH (**2**) containing a rare terminal hydride fragment. X-ray diffraction analysis and the DFT calculation confirm the zwitterionic structure of complex **2**. The stoichiometric reaction of **2** with CS_2 readily afforded a dithioformate complex LZnSCH(S) (**3**) of the C═S insertion into the Zn−H product. Moreover, complex **2** was an efficient catalyst for the hydrosilylation reaction of a series of silanes and aldehydes under mild conditions, featuring excellent functional group tolerance. The preliminary mechanistic study revealed that both zinc benzyloxy complex **1** and zinc hydride complex **2** were involved in the hydrosilylation process as the reaction intermediates.



INTRODUCTION

Zinc hydride (ZnH_2) has been used as a reducing agent in organic synthesis;[1] however, its poor thermal stability and insolubility in organic solvents narrow its application range.[2] Therefore, considerable efforts have been directed to synthesize more stable and soluble organozinc hydrides supported by the anionic ancillary ligands. To date, many anionic ancillary ligands have been synthesized, such as di(2-pyridylmethyl)-amine,[3] tris(pyrazoyl)hydroborates,[4] β-diketiminates,[5] 2,6-dialkylphenyls,[6] pyridyl-substituted tris(trimethylsilyl)-methanides,[7] tris(4,4-dimethyl-2-oxazolinyl)phenylborate,[8] tris-(2-pyridylthio)methyl,[9] diamine phenolate,[10] bis(NHC)methyl,[11] and pentamethylcyclopentadienyl (Cp*).[12] However, it is still difficult to obtain well-defined mononuclear zinc terminal hydride complexes that may transfer readily to dimer, cluster, or cubic structures via the formation of hydride bridges, because the small steric hydride ligand is not bulky enough to stabilize the hydride complex in a mononuclear structure.[13] Such structures are chemically inactive as compared to the terminal ones. With respect to the reactivity, the zinc hydride complexes have exhibited promising catalysis such as in alcoholysis of silanes,[8b,11,14] hydrogenation of imines,[12] and hydrosilylation of carbon dioxide,[14] ketones,[15] nitriles,[15] and alkenes.[11] Particularly, the hydrosilylation of aldehydes involving the formation of a Si−O bond, an important process in surface derivatization and preparation of silicone-based materials such as coatings, adhesives, and cured rubbers,[16] has mainly relied on precious metal catalysts for a long period,[17] and few reports related to the cheap zinc hydrido catalysts exist.[3,14,15]

Herein, we report the synthesis and characterization of a new type of zwitterionic zinc terminal hydride complex based on a rigid and bulky heteroscorpionate ligand. The hydride complex can conduct the reaction with CS_2 and catalyze hydrosilylation of aldehydes at a low catalyst load. In addition, a possible mechanism of the above reaction is explicated by means of isolating a reaction intermediate.

RESULTS AND DISCUSSION

Synthesis and Characterization of Zinc Terminal Hydride Complex 2. Treatment of heteroscorpionate zinc benzyloxy complex LZnOBn (**1**, L = $(^{Me}Pz)_2CP(Ph)_2NPh$, ^{Me}Pz = 3,5-dimethylpyrazolyl) with phenylsilane ($PhSiH_3$) gave a zinc terminal hydride complex LZnH (**2**) as a white solid in good yield (Scheme 1, a).[18] In the ^1H NMR spectrum in benzene-d_6, the terminal hydride (Zn−*H*) resonance appears at 5.38 ppm, which is close to the corresponding zwitterionic tris(substituted-pyrazoyl) hydroborate zinc hydrides (δ 5.36 ppm for $Tp^{tBu}ZnH$,[4a] 5.26 ppm for $Tp^{p\text{-Tol, }Me}ZnH$[4b]), but shifts

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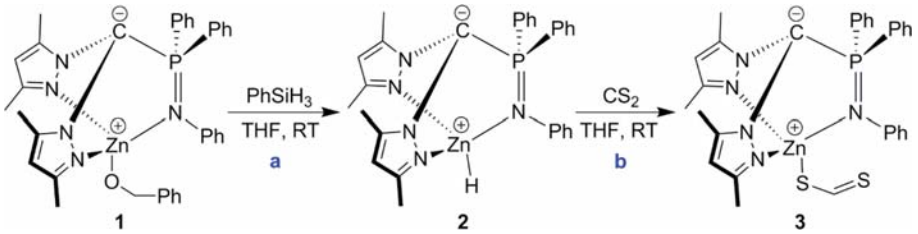
Scheme 1. Synthesis of Heteroscorpionate Zinc Hydride 2 and Dithioformate Complex 3



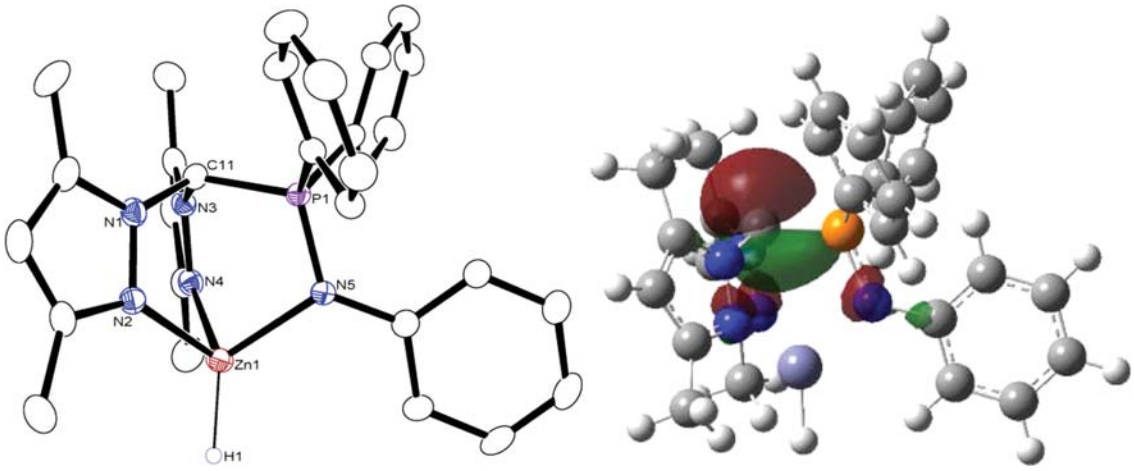


Figure 1. Crystal structure of zinc hydride **2** (left) and the isosurface for the molecular orbital HOMO−1 (right). Hydrogen atoms except Zn−H are omitted for clarity. Selected bond lengths (Å) and angles (deg): Zn(1)−H(1) 1.57(4), Zn(1)−N(2) 2.064(3), Zn(1)−N(4) 2.100(3), Zn(1)−N(5) 2.056(3); N(5)−Zn(1)−N(2) 97.96(11), N(5)−Zn(1)−N(4) 93.30(11), N(2)−Zn(1)−N(4) 89.89(11), N(1)−C(11)−N(3) 111.7(3), N(1)−C(11)−P(1) 113.1(2), N(3)−C(11)−P(1) 110.3(2).

Table 1. Hydrosilylation of Various Aldehydes Catalyzed by Complex 2[a]

run	substrate	silane (equiv)	time (h)[b]	product[c]
1	PhCHO	$PhSiH_3$ (1/3)	10	$PhSi(OCH_2Ph)_3$
2	PhCHO	$PhSiH_3$ (1)	7	$PhSi(H)_x(OCH_2Ph)_{3-x}$ (x = 0−1)
3[d]	PhCHO	$PhSiH_3$ (1/3)	13	$PhSi(OCH_2Ph)_3$
4	PhCHO	Ph_2SiH_2 (1/2)	12	$Ph_2Si(OCH_2Ph)_2$
5	PhCHO	Ph_2SiH_2 (1)	4	$Ph_2SiH(OCH_2Ph)$
6	PhCHO	EtO_3SiH (1)	96	$(EtO)_xSi(OCH_2Ph)_{4-x}$ (x = 2−4)
7	2-PyCHO	$PhSiH_3$ (1/3)	0.5	$PhSi(OCH_2Py)_3$
8	*o*-F-PhCHO	$PhSiH_3$ (1/3)	5	$PhSi(OCH_2$-*o*-F-$Ph)_3$
9	*o*-Br-PhCHO	$PhSiH_3$ (1/3)	7	$PhSi(OCH_2$-*o*-Br-$Ph)_3$
10	*o*-MeO-PhCHO	$PhSiH_3$ (1/3)	10	$PhSi(OCH_2$-*o*-MeO-$Ph)_3$
11	*o*-EtO-PhCHO	$PhSiH_3$ (1/3)	6	$PhSi(OCH_2$-*o*-EtO-$Ph)_3$
12	*t*-BuCHO	$PhSiH_3$ (1/3)	5	$PhSi(OCH_2CMe_3)_3$
13	*p*-vinyl-PhCHO	$PhSiH_3$ (1/3)	6	$PhSi(OCH_2$-*p*-vinyl-$Ph)_3$
14	*p*-vinyl-PhCHO	$PhSiH_3$ (1)	6	$PhSi(H)_x(OCH_2$-*p*-vinyl-$Ph)_{3-x}$ (x = 0−1)
15	2-(C_4H_3O)CHO	$PhSiH_3$ (1/3)	6	$PhSi(OCH_2C_4H_3O)_3$
16	2-(C_4H_3S)CHO	$PhSiH_3$ (1/3)	20	$PhSi(OCH_2C_4H_3S)_3$
17[e]	PhCHO	$PhSiH_3$ (1/3)	10	$PhSi(OCH_2Ph)_3$

[a]Reaction conditions (unless specified otherwise): substrate (1.0 mmol), LZnH catalyst (1.0 mol %), T = 25 °C, C_6D_6 (ca. 0.6 mL), under N_2. [b]Reaction times were determined via ^{1}H NMR spectroscopy after complete consumption of substrate or silane. [c]The identity of product was based on ^{1}H NMR spectra and/or GC-MS. [d]Catalyst load 0.25 mol %. [e]Benzyloxy complex **1** was used.

obviously downfield as compared with those in many other neutral mononuclear zinc hydrides reported previously (3.99−5.02 ppm).[5e,10]

The molecular structure of complex **2** was well resolved by a single-crystal X-ray diffraction study (Figure 1, left), where the heteroscorpionate ligand moiety caps the zinc ion with three nitrogen atoms in the κ^3-coordination mode, appearing as a mononuclear structure bearing a single zinc terminal hydride species. The terminal Zn(1)−H(1) bond length is 1.57(4) Å, falling in the normal range for mono zinc hydride complexes reported previously.[19] The measured distance from the metal Zn(1) to the apical carbon anion C(11) is 3.036 Å, far beyond

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Scheme 2. Proposed Catalytic Mechanism

the normal bond length range, suggesting the zwitterionic structure. The bond angles of N−C_{apical}−N and N−C_{apical}−P are 111.7(3)°, 113.1(2)°, and 110.3(2)°, respectively, close to 109.5°, meaning that the apical carbon has a nonplanar geometry indicating the formal sp^3 hybridization. Moreover, the structure of **2** is well simulated by DFT (density functional theory) calculations, which give the Zn(1)−H(1) bond length of 1.557 Å, as well as comparable N−C_{apcal}−N (111.71°) and two N−C_{apical}−P (112.58° and 111.80°) bond angles. The molecular orbital HOMO−1 is predominantly localized on the apical carbon (Figure 1, right), and the net atomic charge of the apical carbon is −0.441 (calculated from natural bond orbital analysis). Both the X-ray diffraction and the DFT calculation suggest the zinc hydride complex **2** to be a zwitterion.

Hydrosilylation Reaction of Aldehydes. To investigate the catalytic performance of the zwitterionic zinc hydride, hydrosilylations of aldehydes with silanes in the presence of **2** (1.0 mol %) were conducted in an NMR tube and monitored by ^{1}H NMR spectroscopy (benzene-d_6) at room temperature (Table 1). Benzaldehyde (PhCHO) reacted with 1/3 equiv of $PhSiH_3$ for 10 h to give silyl ether $(PhCH_2O)_3SiPh$ as the only product, where the zinc hydride efficiently catalyzed the insertion of all three Si−H bonds of $PhSiH_3$ into the C═O bond of PhCHO (Table 1, run 1). The attempt to obtain a single insertion product under the PhCHO-to-$PhSiH_3$ feed ratio of 1:1 failed (Table 1, run 2), evidenced by ^{1}H NMR and GC-MS analyses (see the Supporting Information), which afforded a mixture of double and triple insertion products ($(PhCH_2O)_2SiHPh$ and $(PhCH_2O)_3SiPh$) without the desired product $PhCH_2OSiH_2Ph$.[20] This was probably because the silyl ether formed during the aldehyde reduction enhanced the reactivity of the remaining Si−H bonds.[17e] A low catalyst load (0.25 mol %) of complex **2** also worked well, which is the lowest catalyst concentration reported to date for a zinc hydride system (Table 1, run 3). Delightedly, the hydrosilylation of PhCHO with the secondary silane Ph_2SiH_2 was rather controllable to afford the single ($PhCH_2OSiHPh_2$) or double insertion ($(PhCH_2O)_2SiPh_2$) products in the feed ratios of 1:1 and 2:1, respectively (Table 1, runs 4 and 5).[3,21] When tertiary silane $(EtO)_3SiH$ was employed, the hydrosilylation reaction with PhCHO proceeded sluggishly (4 days) to give the anticipated $(EtO)_3SiOCH_2Ph$ as the major product accompanied by some byproducts (Table 1, run 6), such as $(EtO)_4Si$, $(EtO)_3SiOSi(OEt)_3$, and $(EtO)_2Si(OCH_2Ph)_2$ according to the GC-MS.[15,22] To investigate the functional group tolerance of this catalyst system, a series of functionalized aldehydes were also used as substrates. The hydrosilylation of *p*-vinylbenzaldehyde with 1 equiv of $PhSiH_3$ gave a mixture similar to that of PhCHO mentioned above, and the residual $PhSiH_3$ did not react with the *p*-vinyl group even at elevated temperature (50 °C) for 10 h (Table 1, runs 13, 14; Figure S17), suggesting that complex **2** can selectively catalyze the hydrosilylation of the carbonyl group in the presence of a vinyl group. In addition, other aromatic aldehydes (2-pyridylaldehyde, 2-furaldehyde, thiophene-2-aldehyde) (Table 1, runs 7, 15, 16) and aliphatic aldehyde ^{t}BuCHO (Table 1, run 12) were also explored to react with $PhSiH_3$ under the same conditions. The reaction of $PhSiH_3$ with 2-pyridylaldehyde proceeded fastest (0.5 h), while that with thiophene-2-aldehyde the slowest (20 h). Noteworthy is that both electron-withdrawing groups (−Py, −F, and −Br) (Table 1, runs 7−9) and electron-donating groups (−^{t}Bu, −OMe, and −OEt) (Table 1, runs 10−12) could increase the reaction rates to some extent (for the kinetic study, see Figure S1). This observation is contrary to the previous report where the electron-withdrawing groups in the *para* position accelerated the reaction while the electron-donating groups decelerated the reaction.[2g] In our system, the electron-withdrawing groups at the *ortho* position lower the electron density of the aromatic ring and the carbonyl carbon atom, which should facilitate the anionic attack of Zn−H on the carboxyl carbon *C*═O. On the other hand, the electron-donating groups at the *ortho* position increase the electron density, which might promote the coordination of C═*O* oxygen to the cationic zinc center.

For the zinc-catalyzed hydrosilylation, two mechanisms have been established: the activation of the aldehyde[23] or silane substrate[15] on a Lewis acidic zinc center and insertion/heterolytic splitting.[3,14,24] In both procedures, the zinc hydride moiety is usually proposed to be the intermediate; however, no solid and direct evidence has been provided. To elucidate the mechanism of the hydrosilylation by this zwitterionic system, the reaction of zinc hydride complex **2** with PhCHO was monitored by ^{1}H NMR spectroscopy (Figures S31 and S32), which revealed the formation of zinc benzyloxy complex **1**, suggesting that zinc hydride and alkoxide species might be interconverted (complex **2** was synthesized from complex **1**, *vide supra*). Moreover, benzyloxy complex **1** can also catalyze the hydrosilylation of PhCHO as efficiently as zinc hydride **2** (Table 1, run 17). On the basis of the above experimental results, we postulated that the hydrosilylation undergoes an insertion mechanism as shown in Scheme 2.

Reactivity with CS_2. Furthermore, we also examined whether the terminal zinc hydride could catalyze the hydrosilylation of carbon dioxide and its derivative of carbon disulfide. The reaction of hydride and carbon dioxide was complicated and uncontrollable. However, the stoichiometric reaction of **2** with CS_2 in THF at room temperature readily afforded the dithioformate complex **3** as a yellow solid (Scheme 1, b). In the process, the hydride transferred from zinc to the carbon atom of CS_2 via the insertion of the Zn−H bond into the C═S double bond. The newly generated SC*H*(S) group gives a sharp singlet at 11.91 ppm (benzene-d_6) in the ^{1}H NMR

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spectrum. The crystal structure of **3** (Figure 2) reveals that the dithioformate moiety adopts the σ-coordination mode in agreement with the previous literature report, and the relative bond lengths and angles also fall in the normal range.[25]

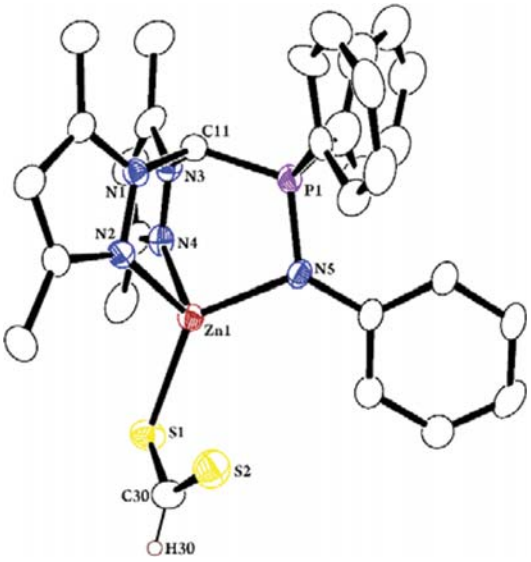

Figure 2. Crystal structure of zinc dithioformate **3**. Hydrogen atoms except the SC*H*(S) have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Zn(1)−S(1) 2.285(2), S(1)−C(30) 1.702(6), S(2)−C(30) 1.633(7); S(2)−C(30)−S(1) 127.2(3), Zn(1)−S(1)−C(30) 100.81(19), N(1)−C(11)−N(3) 110.9(6), N(1)−C(11)−P(1) 114.6(5), N(3)−C(11)−P(1) 111.9(5).

CONCLUSION

In conclusion, we have demonstrated that by using a sterically bulky heteroscorpionate ligand, the zwitterionic zinc terminal hydride complex has been readily synthesized by treatment of its benzyloxy precursor with phenylsilane. The zinc hydride reacts with CS_2 under mild conditions through the Zn−H bond insertion into the unsaturated C═S bond to give a dithioformate complex bearing the Zn-σ-S species. More importantly, the zinc hydride can efficiently catalyze the hydrosilylation of various aldehydes with silanes to prepare silyl ethers with the lowest catalyst load. In addition, we prove for the first time that both the zinc alkoxide and zinc hydride species are the intermediates in the aldehyde hydrosilylation process.

EXPERIMENTAL SECTION

General Procedures. All reactions were carried out under a dry nitrogen atmosphere using standard Schlenk techniques or in a glovebox filled with dry nitrogen. Hexane and toluene were purified using an SPS Braun system. THF was dried by distillation over sodium/benzophenone under a nitrogen atmosphere and was stored over freshly cut sodium in a glovebox. Samples for NMR spectroscopic analysis were prepared in a glovebox using NMR spectroscopy tubes and then sealed with a paraffin film. ^{1}H, ^{31}P, and ^{13}C{^{1}H} NMR spectra were recorded using a Bruker AV400 spectrometer.

X-ray Crystallographic Studies. Crystals for X-ray analysis were obtained as described in the preparations. The crystals were manipulated in a glovebox. Data collections were performed at −88.5 °C on a Bruker SMART APEX diffractometer with a CCD area detector, using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). The determination of crystal class and unit cell parameters was carried out by the SMART program package.[26] The raw frame data were processed using SAINT and SADABS to yield the reflection data file.[27] The structures were solved by using the SHELXTL program.[28] Refinement was performed on F^2 anisotropically for all non-hydrogen atoms by the full-matrix least-squares method. The hydrogen atoms were placed at calculated positions and were included in the structure calculations without further refinement of the parameters. The terminal hydrogen atom in complex **2** has been refined anisotropically. Molecular structures were generated using the ORTEP program.

Synthesis of Zinc Hydride Complex LZnH (2). To a solution of zinc benzyloxy complex **1** (0.52 g, 0.8 mmol) in THF was added $PhSiH_3$ (0.108 g, 1.0 mmol) or EtO_3SiH (0.164 g, 1.0 mmol), and the mixture was stirred for 10 h at room temperature. The volatile was removed under reduced pressure, and hexane (5 mL) was added. The white precipitate was isolated by filtration and dried under vacuum (yield, 0.33 g, 76%). Crystals suitable for single-crystal X-ray diffraction were obtained from a saturated THF/hexane solution kept at −30 °C. Anal. Calcd for $C_{29}H_{30}N_5PZn$: C, 63.92; H, 5.55; N, 12.85. Found: C, 63.88; H, 5.50; N, 12.83. ^{1}H NMR (400 MHz, C_6D_6): δ 7.74−7.69 (m, 4H; *o*-PPh_2), 7.53 (d, $^3J_{H-H}$ = 8.1 Hz, 2H; *o*-NPh), 7.03−6.89 (m, 8H; Ph-*H*), 6.66 (t, $^3J_{H-H}$ = 7.3 Hz, 1H; *p*-NPh), 5.38 (d, $^3J_{P-H}$ = 2.4 Hz, 1H; Zn-*H*), 5.29 (s, 2H; Pz-*H*), 2.22 (s, 6H; Pz-CH_3), 1.89 ppm (s, 6H; Pz-CH_3). ^{31}P NMR (162 MHz, C_6D_6): δ 34.2 ppm. ^{1}H NMR (400 MHz, THF-d_8): δ 7.64−7.59 (m, 4H; *o*-PPh_2), 7.42−7.38 (m, 2H; *p*-PPh_2), 7.32−7.28 (m, 4H; *m*-PPh_2), 6.93 (d, $^3J_{H-H}$ = 8.1 Hz, 2H; *o*-NPh), 6.78 (m, 2H; *m*-NPh), 6.46 (t, $^3J_{H-H}$ = 7.3 Hz, 1H; *p*-NPh), 5.59 (s, 2H; Pz-*H*), 4.38 (d, $^3J_{P-H}$ = 2.5 Hz, 1H; Zn-*H*), 2.24 (s, 6H; Pz-CH_3), 1.99 ppm (s, 6H; Pz-CH_3). ^{31}P NMR (162 MHz, THF-d_8): δ 20.5 ppm. ^{13}C NMR (100 MHz, THF-d_8): δ 151.5, 151.4 (C^3 or C^5), 146.0, 145.9, (C^3 or C^5), 148.5 133.8, 133.7, 132.2, 132.1, 129.9, 129.1, 128.9.128.8, 122.7, 122.6, 118.4, 104.4 (C^4), 64.5 (d, $^1J_{P-C}$ = 91.4 Hz; P-*C*), 13.4 (Pz-CH_3), 11.8 ppm (Pz-CH_3).

Synthesis of Dithioformate Complex LZnSCHS (3). A solution of carbon disulfide (0.023 g, 0.3 mmol) in THF (2 mL) was added to a solution of complex **2** (0.163 g, 0.3 mmol) of THF (8 mL) to give a yellow solution. The mixture was stirred for 2.5 h at room temperature and concentrated to about 1.0 mL; then several drops of hexane was added. Yellow crystals were obtained at −30 °C 2 days later (yield, 0.081 g, 43%). Anal. Calcd for $C_{30}H_{30}N_5PS_2Zn$: C, 58.01; H, 4.87; N, 11.28. Found: C, 57.97; H, 4.82; N, 11.25. ^{1}H NMR (400 MHz, C_6D_6): δ 11.92 (s, 1H; SC*H*S), 7.75−7.70 (m, 4H; *m*-PPh_2), 7.25 (d, $^3J_{H-H}$ = 8.4 Hz, 2H; *o*-NPh), 7.99−6.88 (m, 8H; Ph-*H*), 6.63 (t, $^3J_{H-H}$ = 7.3 Hz, 1H; *p*-NPh), 5.24 (s, 2H; Pz-*H*), 2.16 (s, 6H; Pz-CH_3), 1.83 ppm (s, 6H; Pz-CH_3). ^{31}P NMR (162 MHz, C_6D_6): δ 35.9 ppm. ^{13}C NMR (100 MHz, C_6D_6): δ 149.7, 149.6, (C^3 or C^5) 145.3, 145.2, (C^3 or C^5) 148.7, 133.1, 133.0, 131.6, 129.3, 129.0, 127.5, 122.1, 122.0, 119.3 (*Ph*), 104.5 (C^4) 63.5 (d, $^1J_{P-C}$ = 96.4 Hz; P-*C*), 13.0 (Pz-CH_3), 11.6 ppm (Pz-CH_3).

Catalytic Hydrosilylation Reaction of Aldehydes with Zinc Hydride Complex 2. In a typical experiment zinc hydride complex **2** (0.0055 g, 10 μmol, 1.0 mol %) was added to a C_6D_6 (ca. 0.6 mL) solution of silane and aldehyde substrate; then the mixture was transferred into a J. Young NMR tube and monitored by ^{1}H NMR spectroscopy until the resonance of C*H*O or Si*H* disappeared (it is difficult to weigh the substrates and silanes accurately following the feed ratio we have designed, so one of them may be residual in the *in situ* monitoring ^{1}H NMR spectra, *vide infra*).

Hydrosilylation of PhCHO with $PhSiH_3$ (3:1). Zinc hydride complex **2** (0.0055 g, 10 μmol, 1.0 mol %) was added to a solution of $PhSiH_3$ (0.036 g, 0.33 mmol) and PhCHO (0.106 g, 1.0 mmol, 3 equiv) substrate in C_6D_6 (ca. 0.6 mL); then the mixture was transferred into a J. Young NMR tube and monitored by ^{1}H NMR spectroscopy until the resonance of Si*H* disappeared. After that, volatiles were removed under reduced pressure; then hexane (2 mL) was added. The crude product was filtered through a short plug of silica, and removal of the solvent gave the product $PhSi(OCH_2Ph)_3$. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77−7.75 (m, 2H; *o*-SiPh), 7.52−7.48 (m, 1H; *p*-Ph), 7.44−7.41 (m, 2H; *m*-SiPh), 7.36−7.28 (m, 15H; OCH_2Ph-*H*), 4.92

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ppm (s, 6H; OCH_2Ph). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.2, 135.1, 130.8, 129.9, 128.4, 128.1, 127.4, 126.8 (*Ph*), 65.2 ppm (OCH_2Ph).

Hydrosilylation of PhCHO with $PhSiH_3$ (1:1). Zinc hydride complex **2** (0.0055 g, 10 μmol, 1.0 mol %) was added to a solution of $PhSiH_3$ (0.108 g, 1.0 mmol) and PhCHO (0.106 g, 1.0 mmol) substrate in C_6D_6 (ca. 0.6 mL); then the mixture was transferred into a J. Young NMR tube and monitored by ^1H NMR spectroscopy until the resonance of PhC*H*O disappeared. Then the mixture was analyzed with GC-MS. $PhSiH(OCH_2Ph)_2$: t_R = 13.92 min; m/z 320 (M^+). $PhSi(OCH_2Ph)_3$: t_R = 17.42 min; m/z 426 (M^+).

Hydrosilylation of PhCHO with Ph_2SiH_2 (2:1). Product $(PhCH_2O)_2Si(Ph)_2$: ^1H NMR (400 MHz, $CDCl_3$): δ 7.64−7.52 (m, 8H; *o*-SiPh), 7.45−7.27 (m, 12H; Ph-*H*), 4.92 ppm (s, 4H; SiO-C*H*$_2$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.5, 135.1, 132.5, 130.6, 128.4, 128.1, 127.3, 126.7 (*Ph*), 65.1 ppm (SiO-CH_2). GC-MS: t_R = 16.43 min; m/z 396 (M^+).

Hydrosilylation of PhCHO with Ph_2SiH_2 (1:1). Product $PhCH_2OSiH(Ph)_2$: ^1H NMR (400 MHz, $CDCl_3$): δ 7.76−7.33 (m, 15H; Ph-*H*), 5.60 (s, 1H; Si*H*), 4.95 ppm (s, 2H; $SiOCH_2$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.2, 134.9, 134.4, 133.8, 130.6, 128.4, 128.2, 127.5, 126.9 (*Ph*), 66.7 ppm (SiO-CH_2). GC-MS: t_R = 13.20 min; m/z 290 (M^+).

Hydrosilylation of PhCHO with EtO_3SiH. Zinc hydride complex **2** (0.0055 g, 10 μmol, 1.0 mol %) was added to a solution of $(EtO)_3SiH$ (0.164 g, 1.0 mmol) and benzaldehyde (0.106 g, 1.0 mmol) substrate in C_6D_6 (ca. 0.6 mL); then the mixture was transferred into a J. Young NMR tube and monitored by ^1H NMR spectroscopy until the resonance of Si*H* (δ 4.58 ppm) disappeared. Then the mixture was analyzed with GC-MS. $(EtO)_3SiOCH_2Ph$ (major product): t_R = 9.757 min; m/z 270 (M^+). $(EtO)_4Si$ (byproduct): t_R = 4.670 min; m/z 208 (M^+). $(EtO)_3SiOSi(OEt)_3$ (byproduct): t_R = 6.955 min; m/z 342 (M^+). $(EtO)_2Si(OCH_2Ph)_2$ (byproduct): t_R = 16.945 min; m/z 331 (M^+).

$PhSi(OCH_2$-o-F-Ph$)_3$. ^1H NMR (400 MHz, $CDCl_3$): δ 7.75−7.66 (m, 2H; *o*-SiPh), 7.50−7.46 (m, 4H; Ph-*H*), 7.43−7.39 (m, 2H; *m*-SiPh), 7.28−7.22 (m, 3H; Ph-*H*), 7.14−7.10 (m, 3H; Ph-*H*), 7.03−6.98 (m, 3H; Ph-*H*), 4.96 ppm (s, 6H; SiO-C*H*$_2$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.5. 159.0, 135.1, 131.0, 129.4, 129.1, 129.0, 128.2, 127.3, 127.1, 124.1, 115.2, 115.0 (*Ph*), 59.3 ppm (SiO-CH_2). GC-MS: t_R = 16.51 min; m/z 479 (M^+).

$PhSi(OCH_2$-o-Br-Ph$)_3$. ^1H NMR (400 MHz, $CDCl_3$): δ 7.82−7.79 (m, 2H; *o*-SiPh), 7.59 (d, $^3J_{H-H}$ = 7.5 Hz, 3H; Ph-*H*), 7.51 (m, 4H; Ph-*H*), 7.45 (dd, $^3J_{H-H}$ = 7.2, 7.2 Hz, 2H; *m*-SiPh), 7.31 (t, $^3J_{H-H}$ = 7.3 Hz, 3H; Ph-*H*), 7.15−7.11 (m, 3H; Ph-*H*), 5.02 ppm (s, 6H; SiO-C*H*$_2$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.0, 135.0, 132.4, 131.2, 128.8, 128.3, 128.2, 127.5, 121.7 (*Ph*), 65.0 ppm (SiO-CH_2).

$PhSi(OCH_2$-o-MeO-Ph$)_3$. ^1H NMR (400 MHz, C_6D_6): δ 7.96−7.92 (m, 2H; *o*-SiPh), 7.75 (d, $^3J_{H-H}$ = 7.5 Hz, 3H; Ph-*H*), 7.17−7.06 (m, 6H; Ph-*H*), 6.90 (t, $^3J_{H-H}$ = 7.4 Hz, 3H; Ph-*H*), 6.48, (d, $^3J_{H-H}$ = 8.1 Hz, 3H; Ph-*H*), 5.29 (s, 6H; SiO−C*H*$_2$), 3.23 ppm (s, 9H; Ph-OC*H*$_3$). ^1H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, $^3J_{H-H}$ = 6.7 Hz, 2H; Ph-*H*), 7.51 (d, $^3J_{H-H}$ = 7.4 Hz, 3H; Ph-*H*), 7.43 (t, $^3J_{H-H}$ = 7.3 Hz, 1H; Ph-*H*), 7.36 (t, $^3J_{H-H}$ = 7.2 Hz, 2H; Ph-*H*), 7.22 (t, $^3J_{H-H}$ = 7.7 Hz, 3H; Ph-*H*), 6.94 (t, $^3J_{H-H}$ = 7.4 Hz, 3H; Ph-*H*), 6.80 (d, $^3J_{H-H}$ = 8.1 Hz, 3H; Ph-*H*), 4.99 (s, 6H; SiO-C*H*$_2$), 3.74 ppm (s, 9H; Ph-OC*H*$_3$). GC-MS: t_R = 26.16 min; without molecular ion (M^+) (M_w = 516.7), the largest ion is $[Si(OCH_2$-*o*-MeO-Ph$)_3]^+$ (439).

$PhSi(OCH_2$-o-EtO-Ph$)_3$. ^1H NMR (400 MHz, C_6D_6): δ 7.95−7.93 (m, 2H; Ph-*H*), 7.80−7.77 (m, 3H; Ph-*H*), 7.17−7.07 (m, 6H; Ph-*H*), 6.94−6.90 (m, 3H; Ph-*H*), 6.52 (d, $^3J_{H-H}$ = 7.8 Hz, 3H; Ph-*H*), 5.31 (s, 6H; SiO-C*H*$_2$), 3.52 (q, $^3J_{H-H}$ = 7.0 Hz, 6H; Ph-OC*H*$_2$CH$_3$), 1.01 ppm (t, $^3J_{H-H}$ = 7.0 Hz, 9H; Ph-OCH$_2$C*H*$_3$).

Hydrosilylation of p-Vinylbenzaldehyde with $PhSiH_3$ (3:1). ^1H NMR (400 MHz, C_6D_6): δ 7.87 (m, 2H; Ph-*H*), 7.23 (m, 15H; Ph-*H*), 6.58 (dd, $^3J_{H-H}$ = 17.6, 10.9 Hz, 3H; vinyl-*H*), 5.60 (d, $^3J_{H-H}$ = 17.6 Hz, 3H; vinyl-*H*), 5.07 (d, $^3J_{H-H}$ = 10.9 Hz, 3H; vinyl-*H*), 4.86 ppm (s, 6H; SiO-C*H*$_2$).

$PhSi(OCH_2C_4H_3O)_3$. Zinc hydride complex **2** (0.0055 g, 10 μmol, 1.0 mol %) was added to a solution of $PhSiH_3$ (0.036 g, 0.33 mmol) and 2-furaldehyde (0.096 g, 1.0 mmol, 3 equiv) substrate in C_6D_6 (ca. 0.6 mL); then the mixture was transferred into a J. Young NMR tube and monitored by ^1H NMR spectroscopy until the resonance of Si*H* disappeared. ^1H NMR (400 MHz, C_6D_6): δ 7.78 (m, 2H; Ph-*H*), 7.17 (m, 3H; Ph-*H*), 7.07, 6.09, 6.04 (m, 3 × 3H; furan-*H*), 4.76 ppm (s, 6H; $SiOCH_2$). ^{13}C NMR (100 MHz, C_6D_6): δ 153.9 (C^2 of furan, 142.6 (C^5 of furan), 135.4, 130.9, 130.3, 128.2 (*Ph*), 110.6, 108.4 (C^3 or C^4 of furan), 57.9 ppm ($SiOCH_2$).

$PhSi(OCH_2C_4H_3S)_3$. Zinc hydride complex **2** (0.0055 g, 10 μmol, 1.0 mol %) was added to a solution of $PhSiH_3$ (0.036 g, 0.33 mmol) and thiophene-2-aldehyde (0.112 g, 1.0 mmol, 3 equiv) substrate in C_6D_6 (ca. 0.6 mL); then the mixture was transferred into a J. Young NMR tube and monitored by ^1H NMR spectroscopy until the resonance of Si*H* disappeared. ^1H NMR (400 MHz, C_6D_6): δ 7.63−7.81 (m, 2H; Ph-*H*), 7.23−7.18 (m, 3H; Ph-*H*), 6.90, 6.79, 6.71 (m, 3 × 3H; thiophene-*H*), 4.95 (s, 6H; $SiOCH_2$). ^{13}C NMR (100 MHz, C_6D_6): δ 143.8, 135.4, 131.1, 130.1, 126.8, 125.5, 60.5 ppm ($SiOCH_2$). GC-MS: t_R = 20.91 min; m/z 444 (M^+).

$PhSi(OCH_2Py)_3$. ^1H NMR (400 MHz, C_6D_6): δ 8.41 (d, $^3J_{H-H}$ = 4.7 Hz, 3H; Py-H), 7.88 (dd, $^3J_{H-H}$ = 1.7, 7.6 Hz, 2H, Ph-H), 7.46 (d, $^3J_{H-H}$ = 7.9 Hz, 3H; Py-H), 7.23−7.16 (m, 4H; Py-H × 3 and Ph-H × 1), 7.15 (dd, $^3J_{H-H}$ = 1.8, 7.7 Hz, 2H; Ph-*H*), 6.66 (dd, $^3J_{H-H}$ = 5.0, 7.3 Hz, 3H; Py-H), 5.25 ppm (s, 6H; SiO-C*H*$_2$).

$PhSi(OCH_2CMe_3)_3$. Zinc hydride complex **2** (0.0055 g, 10 μmol, 1.0 mol %) was added to a solution of $PhSiH_3$ (0.036 g, 0.33 mmol) and pivaldehyde (0.0861 g, 1.0 mmol, 3 equiv) substrate in C_6D_6 (ca. 0.6 mL); then the mixture was transferred into a J. Young NMR tube and monitored by ^1H NMR spectroscopy until the resonance of Si*H* disappeared. After complete conversion volatiles were removed under reduced pressure, then hexane (2 mL) was added. The crude product was filtered through a short silica plug, and removal of the solvent gave the product $PhSi(OCH_2CMe_3)_3$. ^1H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, $^3J_{H-H}$ = 7.7 Hz, 2H; Ph-*H*), 7.45−7.36 (m, 3H; Ph-*H*), 3.50 (s, 6H; OCH_2CMe_3), 0.95 ppm (s, 27H; OCH_2CMe_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.1, 131.8, 130.2, 127.8 (*Ph*), 73.2 (OCH_2CMe_3), 33.0 (OCH_2CMe_3), 26.5 ppm (OCH_2CMe_3). GC-MS: t_R = 7.189 min; m/z 366 (M^+).

Hydrosilylation of PhCHO with $PhSiH_3$ Catalyzed by Zinc Benzyloxy Complex ***1***. Zinc benzyloxy complex **1** (0.0065 g, 10 μmol, 1.0 mol %) was added to a solution of $PhSiH_3$ (0.036 g, 0.33 mmol) and PhCHO (0.106 g, 1.0 mmol, 3 equiv) substrate in C_6D_6 (ca. 0.6 mL); then the mixture was transferred into a J. Young NMR tube and monitored by ^1H NMR spectroscopy until the resonance of Si*H* disappeared. The result is similar to that of zinc hydride **2**.

CCDC-1014967 (**2**) and 1014968 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.5b00413.

Complete crystallographic data for complexes **2** and **3**, computational details, calculated coordinates for complex **2** (PDF)

Crystallographic data for **2** and **3** (CIF)

XYZ

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Notes

The authors declare no competing financial interest.

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