

Synthesis of Silyl Cobalt Hydride and its Catalytic Performance in Kumada

Coupling Reactions

Shilu Xu,^[a] Peng Zhang,^[a] Xiaoyan Li,^[a] Benjing Xue,^[a] Hongjian Sun,^{*[a]} Olaf Fuhr,^[b] Dieter Fenske^[b]

The first two authors contribute to this work equally.

Abstract:

In this paper, we reported the syntheses of four silyl [P,Si]-chelate cobalt complexes (2-5) through the chelate-assisted Si-H activation of bidentate preligand o-HSi(Me)₂(PPh₂)C₆H₄(1) with CoMe(PMe₃)₄ and CoCl(PMe₃)₃. The silvl Co(I) complex, Co(PMe₃)₃(1-Si(Me)₂-2-(PPh₂)C₆H₄) (2), was synthesized by Si-H activation of 1 with CoMe(PMe₃)₄ or the combination of complex 5 with MeLi and PMe₃. Complex 2 was treated with CH₃I or EtBr and generating the silvl Co(II) products $CoI(PMe_3)_2(1-Si(Me)_2-2-(PPh_2)C_6H_4)$ (3) and $CoBr(PMe_3)_2(1-Si(Me)_2-2-(PPh_2)C_6H_4)$ The Co(III) (4). silyl hydride, $CoHCl(PMe_3)_2(1-Si(Me)_2-2-(PPh_2)C_6H_4)$ (5), was obtained by the reaction of complex 1 with CoCl(PMe₃)₃. The catalytic performance of complex 5 was explored for the Kumada coupling reactions. With a load of 2 mol% of catalyst, complex 5 displayed good to excellent catalytic efficiency for the reactions of aryl chlorides or aryl bromides with Grignard reagents. It is noteworthy that the synthesis of 5 as a chelate complex is easier than that of our early reported [PSiP]-pincer cobalt hydride. With similar catalytic efficiency for the Kumada reactions, the catalyst loading (2%) of **5** is lower than that (5%) of [PSiP]-pincer cobalt hydride.

Supporting information of this article can be found under http://dx.doi.orxxxxxxxxxx

 ^[a] School of Chemistry and Chemical Engineering, Key Laboratory of Special Functional Aggregated Materials, Ministry of Education, Shandong University, Shanda Nanlu 27, 250199 Jinan, People's Republic of China
 ^[b] Institut für Nanotechnologie (INT) und Karlsruher Nano-Micro-Facility (KNMF), Karlsruher Institut für Technologie (KIT), Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany

Introduction:

The silvl transition metal complexes have received much attention due to the growing interest of silicon chemistry. Transition metal silyl complexes synthesized via Si-H bond activation have extensive application and they can be used either as reactants or as catalysts in organic reactions.^[1-5] Iwasawa's group used pincer-type hydrido palladium complexes to realize hydrocarboxylation of allene with CO₂.^[6] In Turculet's work, tridentate pincer-type bis(phosphino)silyl ligand [PSiP] was used to synthesize a ruthenium(II) dinitrogen complexes $[Ru(H)(N_2)(PSiP-Ph)]$ under nitrogen atmosphere.^[7] Shimada reported that the tridentate pincer-type bis(phosphino)silyl ligands (PSiP-R, R = Cy, ^{*i*}Pr, or ^{*t*}Bu) were used to prepare a rare example of thermally stable iridium(III) dinitrogen complex $[Ir(H)_2(N_2)(PSiP-R)]$.^[8] Li's group prepared several cyclometalated iridium(III) compounds [IrCl(H)(PSiP)] via Si-H bond activation and they showed good to excellent catalytic activity in the transfer hydrogenation of ketones.^[9] In 2013, we disclosed an iron hydrido complex with a tridentate bis(phosphino)silvl ligand ((σ -Ph₂PC₆H₄)2SiMeH, [PSiP]-H).^[10] In 2015, we published the synthesis and characterization of a series of Co, and Fe complexes bearing a tridentate bis(phosphino)silyl ligand (HSiMe(NCH₂PPh₂)₂C₆H₄, [PSiP]-H). The hydrido cobalt(III) complex [PSiP]Co(H)(Cl)(PMe₃) was found to be an excellent catalyst for Kumada coupling reactions under mild condition.^[11]

In comparison with the silvl tridentate transition metal complexes, although the synthesis of the silvl bidentate transition metal complexes is easier, the reports on the silvl bidentate transition metal complexes are very few.^[12-16] Because silvl bidentate ligands can form only one chelate ring, their transition metal complexes have less stability, but higher reactivity. Sabo-Etienne and co-workers used pyridine-2-amino(methyl)dimethylsilane ligands to afford a series of ruthenium complexes with multicenter Ru-H-Si interactions. In hydrogen atmosphere, these complexes display different degrees of Si-H bond activation.^[17-19] Chou's group reported several phosphine-substituted organo silanes and their Ir(III) complexes.^[20] In 2015, Maleczka and Smith III reported several cyclometalated [P,Si]-chelate iridium complexes and found that they are catalytically effective for ortho-borylation 2

reaction.^[3]

In addition, most of the research in this field is based on precious metals. Similar study on non-noble metals is rare. Therefore, we selected a bidentate [P,Si]-chelate silyl preligand to synthesize its cobalt complexes. It was also confirmed that the [P,Si]-chelate silyl hydrido cobalt complex is catalytically active for the Kumada coupling reaction. Our results indicate that the synthesis of **5** as a chelate complex is easier than that of our early reported [PSiP]-pincer cobalt hydride.^[11] With similar catalytic efficiency for the Kumada reactions, the catalytic loading (2%) of **5** is lower than that (5%) of [PSiP]-pincer cobalt hydride.

Results and discussion

Syntheses and Structures of the [P,Si]-Chelate Cobalt Complexes



When preligand **1** was combined with MeCo(PMe₃)₄ at -78°C, the color of the solution changed from orange to red. The mixture was stirred at room temperature for 12 h. The resulted deep red solution was evaporated to dryness and the residue was extracted with pentane and diethyl ether. Complex **2** as deep red crystals was obtained from pentane solution (eq. (1)). In the IR spectrum of complex **2**, no signal at 2122 cm⁻¹ (v(Si-H) for preligand **1**) was observed. This indicates that the activation of the Si-H bond occurred. In the ¹H NMR spectrum of complex **2**, two sets of signals were identified at 0.86 and 1.18 ppm for two chemically different PMe₃ ligands in the integral ratio of 1 : 2. In the ³¹P NMR of complex **2**, three sets of signals were distinguished at -2.40, 20.94 and 71.32 ppm, respectively, corresponding to the three kinds of P atoms in the integral ratio of 2 : 1 : 1.

The structure of **2** was confirmed by single crystal X-ray crystal diffraction as a trigonal bipyramid with the cobalt atom in the center (**Fig. 1**). The axial direction was determined by the angle Si1-Co1-P2 ($173.22(2)^{\circ}$), deviating from 180°. The equatorial

epted Manuscrip

plane is constructed by P1, P3, P4 and Co1 atom. The sum of the bond angles centered at Co1 in the equatorial plane (P1-Co1-P3 112.36(2); P3-Co1-P4 115.12(2) and P1-Co1-P4 130.05(2)°) is 357.53°. This implies that the planarity of the equatorial plane is not good. The distortion observed in the X-ray parameters for **2** might presumably arise from the chelating bonding of the ligand. The distance of Co1-P2 (2.2193(5) Å) located at the opposite position of the silicon atom is longer than those of the other three Co-P distances(Co1-P1 2.1679(5); Co1-P3 2.1722(5); Co1-P4 2.1912(5) Å) due to the strong *trans*-influence of silyl group.



Fig. 1 ORTEP plot of complex 2 at the 50% probability level (hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles (deg): Co1-P2 2.2193(5), Co1-Si1 2.3353(5), Co1-P4 2.1912(5), Co1-P1 2.1679(5),Co1-P3 2.1722(5); P2-Co1-Si1 173.22(2),P4-Co1-P2 92.29(2),P4-Co1-Si1 86.42(2),P1-Co1-P2 96.38(2),P1-Co1-Si1 79.46(2),P1-Co1-P4 130.05(2), P3-Co1-P2 97.28(2),P3-Co1-Si1 89.29(2),P3-Co1-P4 115.12(2)



The silyl [P,Si]-chelate cobalt(I) complex 2 could react with MeI to afford the single-electron oxidative product 3 (eq (2)). Complex 3 was obtained as red crystals from diethyl ether in a yield of 69%. The NMR results have confirmed the $\frac{4}{4}$

paramagnetic character of complex **3** due to the existence of the single electron. This reaction might undergo a radical mechanism. CH_3I split into methyl radical and iodine radical *via* homolytic cleavage. Two methyl radicals formed ethane and the iodine radical combined with the cobalt center of complex **2** to furnish complex **3** with the dissociation of PMe₃ ligand.



Fig. 2 ORTEP plot of complex 3 at the 50% probability level (hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles (deg): Co1-P1 2.1722(9), Co1-P2 2.2383(9), Co1-P3 2.2926(9), Co1-Si1 2.3368(9), Co1-I1 2.5923(5); P1-Co1-P3 107.30(4), P1-Co1-P2 100.20(3), P3-Co1-P2 97.22(4), P1-Co1-Si1 80.25(3), P3-Co1-Si190.45(4), P2-Co1-Si1 171.77(4), P1-Co1-I1 136.73(3), P3-Co1-I1 112.92(3), P2-Co1-II 90.16(3), Si1-Co1-II 84.07(3).

The structure of complex **3** was confirmed by single crystal X-ray diffraction. Complex **3** has a triangular bipyramid coordination geometry, similar with that of complex **2**. The bond angle Si1-Co1-P2 $(171.77(4)^\circ)$ formed the axial position. The equatorial plane was determined by I1, P1, P3 and Co1 atom. In the equatorial plane, the angle I1-Co1-P1 $(136.73(3)^\circ)$ is larger than the angle I1-Co1-P3 $(112.92(3)^\circ)$ because of the steric effect of the bulky diphenyl phosphino group (-PPh₂).



The reaction of complex **2** with EtBr afforded Co(II) bromide **4**. Complex **4** as a derivative of complex **3** is also paramagnetic. Complex **4** as red crystals was isolated from the diethyl ether solution in a yield of 77%.



When preligand **1** was combined with CoCl(PMe₃)₃ in THF at low temperature, the color of the solution changed from blue to yellow immediately (Eq (4)). After stirring for 18h at room temperature, the volatiles were evaporated under reduced pressure and residue was extracted with pentane and diethyl ether. Complex **5** as yellow crystals were obtained in a yield of 74%. In the IR spectrum of complex **5**, the typical Co-H vibration was found at 1931 cm⁻¹. In the ¹H NMR of complex **5**, the hydrido signal appeared at -11.68 ppm and split into ddd peak due to the coupling effect of two chemically different PMe₃ ligands and -PPh₂ group. Three sets of signals appeared at -5.04, 9.90 and 77.68 ppm, respectively in the ³¹P NMR of complex **5**.



Fig. 3 ORTEP plot of complex **5** at the 50% probability level (hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles (deg): Co1-P1 2.1844(10),

10.1002/asia.201700144

Co1-P3 2.2076(12), Co1-P2 2.2202(10), Co1-Si1 2.2735(10), Co1-Cl1 2.3746(9), Co1-H 1.30(5); P1-Co1-P3 157.19(4), P1-Co1-P2 102.41(4), P3-Co1-P2 99.36(5), P1-Co1-Si1 88.28(4), P3-Co1-Si1 95.56(4), P2-Co1-Si1 97.63(4), P1-Co1-Cl1 85.82(4), P3-Co1-Cl1 84.82(4), P2-Co1-Cl1 97.02(4), Si1-Co1-Cl1 165.07(4), P1-Co1-H 85(2), P3-Co1-H 75(2), P2-Co1-H 166(2), Si1-Co1-H 70.8(19), Cl1-Co1-H 95.0(19).

Single crystal X-ray diffraction has verified that complex **5** has a distorted octahedral coordination geometry with the cobalt atom in the center. If the angle H-Co1-P2 ($166(2)^{\circ}$) was taken as the axial direction, Si1, Cl1, P1, P3 and Co1 atom are in the equatorial plane. The five-membered chelate ring [Co1P1C4C3Si1] and the phenyl ring [C3C4C5C6C7C8] are in one plane. The angle P1-Co1-P3 ($157.19(4)^{\circ}$) orientates towards the Co1-H direction due to the small size of the hydrido ligand. Co1-H distance is 1.30 Å. This value is remarkably shorter than those of the known Co-H bonds (1.40-1.50 Å).^[10]

Complex **5** is the result of an oxidative addition of the Si-H bond of the prelignad **1** at the cobalt(I) center. Although PMe₃ is stronger Lewis base, no reductive elimination between Co-H and Co-Cl in complex **5** was observed. Nevertheless, if a strong base, like MeLi, was added to the solution of complex **5**, complex **5** could be reduced to the cobalt(I) complex **2** in the presence of PMe₃ ligand. During this process, HCl was formed via reductive elimination. HCl reacted with MeLi to afford LiCl and CH₄. The newly-added PMe₃ filled the uncoordinated sites at the cobalt center.



Catalytic Application of Silyl Hydrido Complex 5 in Kumada Coupling Reaction We reported that [PSiP]-pincer silyl hydrido cobalt chloride could catalyze the

10.1002/asia.201700144

Kumada coupling reactions.^[11] Complex **5** is a hydrido silyl [P,Si]-chelate Co(III) chloride with a Co-H and a Co-Cl bond together. This structure was assumed to be an unstable structure under certain conditions. Therefore, it is possible that complex **5** could be a potential catalyst. Encouraged by these results, a series of Kumada coupling reactions catalyzed by complex **5** were studied (Table 1).

At first, the reaction of 1-chloro-4-methoxybenzene with phenyl magnesium bromide was studied as a **test** reaction (Table 1, entries 1-12). It was found that there was little homocoupling product of the Grignard reagents could be detected by GC analysis when the reaction temperature was below 80°C. If toluene was replaced by THF or dioxane, the conversion declined sharply. It could be speculated that the catalyst decomposed under this conditions. According to the entries 7, 9 and 10, the best yield could be reached when the catalyst loading was 2 mol%. Therefore, the optimized catalytic conditions can be summarized as follows: 80°C, 48 hours, catalyst loading of 2 mol% and toluene as the solvent (Table 1, entry 7).

Under the optimized conditions, more substrates were selected to explore the scope of this catalytic system (Table 1, entries 13-18). It can be concluded that higher yield could be obtained from chlorobenzene than from the substituted chlorobenzene. The electron-donating groups (methyl or methoxy group) make the yields poor.

At the same time, from Table 1 (entries 19-30) it can be summarized that the optimized catalytic conditions for the reaction between 1-bromo-4-methylbenzene and phenyl magnesium bromide catalyzed by **5** are: 40°C, 24h, THF and 2 mol% loading of complex **5**. It is obvious that the conditions are milder (lower temperature and shorter reaction time) than those of entries 1-12 because aryl bromide is more active than aryl chloride for the Kumada coupling reaction.

Under the optimized conditions, more substrates of aryl bromides were selected to explore the scope of this catalytic system (Table 1, entries 31-39). These results showed us that the positions of the substituents (Me- or MeO-) at the phenyl ring of the bromo benzene have no significant influence upon the yields of the products.

Chemistry - An Asian Journal

10.1002/asia.201700144

pt

Table 1 Kumada Reactions of Grignard Reagents with Aromatic Halides Catalyzed by 5

5 R

Entry	ArMgX	Ar'X	Product	t/h	Temp./ºC	Cayalst/mol%	Solvent	Conversion/Yield(%)
1	MgBr	CIOMe	OMe	24	25	2	S THE	20 ^{<i>a</i>}
2	MgBr	CIOMe	OMe	48	25	2	THF	50ª
3	MgBr	CIOMe	ОМе	48	50	2		60ª
4	MgBr	CIOMe	ОМе	48	25	2	Contraction Toluene	30ª
5	MgBr	СІОМе	OMe	48	50	2	Toluene	65 °
6	MgBr	СІОМе	OMe	24	80	2	Toluene	70 <i>°</i>
7	MgBr	СІОМе	ОМе	48	80	2	Toluene	85ª
8	MgBr	СІОМе	OMe	48	100	2	Toluene	30 ^{<i>a</i>}
9	MgBr	CIOMe	OMe	48	80	5	Toluene	70 ^a

10	MgBr	CI	OMe	48	80	10	Toluene	65 °
11	MgBr	CIOMe	ОМе	48	25	2	Dioxane	2ª
12	MgBr	CIOMe	ОМе	48	50	2	Dioxane	5 ^a
13	MeMgBr	ci		48	80	2	Toluene	84 ^b
14	OMeMgBr	ci	MeO-	48	80	2	Toluene	70 ^b
15	MgBr	CI	Me	48	80	2	Toluene	80 ⁶
16	MeO-MgBr	CIMe	MeO-Me	48	80	2	Toluene	72 ^b
17	MgBr	CIOMe	ОМе	48	80	2	Toluene	65 ^b
18	MeMgBr	CIOMe		48	80	2	Toluene	67 ^b
19	MgBr	Br — Me	Me	24	25	2		88ª
20	MgBr	BrMe	Me	24	25	2	Toluene	77 ^a
21	MgBr	BrMe	Me	24	25	2		45ª
22	MgBr	Br Me	Me	24	25	2	Dioxane	57ª

23	MgBr	BrMe	Me	24	40	2	THF	92ª
24	MgBr	BrMe	Me	24	40	2	Toluene	85ª
25	MgBr	Br-Me	Me	24	40	2		65 °
26	MgBr	BrMe	Me	24	40	2	Dioxane	72ª
27	MgBr	BrMe	Me	24	40	5		85ª
28	MgBr	BrMe	Me	24	25	1	THF	65 °
29	MgBr	BrMe	Me	24	25	0.5		40 ^a
30	MgBr	BrMe	Me	24	40	0.5		55 °
31	MeMgBr	Br		24	40	2	THF	82 ^b
32	MeO-MgBr	Br	Meo	24	40	2		69 ⁶
33	MgBr	Br Me	Me	24	40	2	THF	80 ^b
34	MeOMgBr	BrMe	MeO	24	40	2	THF	72 ^b
35	MgBr	BrOMe	OMe	24	40	2	THF	74 ^b



^a Conversions.

^b Isolated Yields.

Accepted Manusc

Conclusion

The silyl [P,Si]-chelate cobalt complexes 2 - 5 were obtained via Si-H bond activation. With a catalyst loading of 2mol%, complex **5** displayed good activity in the Kumada cross-coupling reactions of aryl chlorides or aryl bromides with Grignard reagents. It is noteworthy that the synthesis of **5** as a chelate complex is easier than that of our early reported [PSiP]-pincer cobalt hydride.^[11] With similar catalytic efficiency for the Kumada reactions, the catalytic loading (2%) of **5** is lower than that (5%) of [PSiP]-pincer cobalt hydride.

Experimental section

General Procedures and Materials. Standard vacuum techniques were used in the manipulations of volatiles and air-sensitive materials. Solvents were dried by metal sodium and distilled under nitrogen before use. The ligand **1** was prepared according to the literature.^[20] The MeCo(PMe₃)₄ and CoCl(PMe₃)₄ were prepared according to literature procedures.^[21] Infrared spectra (4000-400 cm⁻¹), as obtained from Nujol mulls between KBr disks, were recorded on a Bruker ALPHA FT-IR instrument. NMR spectra were recorded using Bruker Avance 300 MHz spectrometer. Elemental analyses were carried out on an Elementar Vario ELIII instrument.

Synthesis of 2. (a) At -78°C, MeCo(PMe₃)₄ (0.47 g, 1.25 mmol) in 10 mL pentane was added to a solution of 1 (0.40 g, 1.25 mmol) in 20 mL pentane, the mixture was warmed to room temperature and the color changed to deep red. After stirring for 12 h, the solution was evaporated to dryness at reduced pressure. The residue was extracted with pentane and diethyl ether. Complex 2 was obtained as red cubic crystals from pentane in a yield of 72% (0.55 g, 0.9 mmol). (b) To a solution of 5 (0.49 g, 0.87 mmol) in 20 mL diethyl ether was added CH₃Li (0.54 mL / 1.6 M Et₂O, 0.87 mmol) and PMe₃ (0.066 g, 0.87 mmol) at -78°C, the mixture was warmed to room temperature and the color changed from yellow to red. After stirring at room temperature for 6 h, the volatiles were evaporated to dryness and the residue was extracted with pentane and diethyl ether, complex 2 was obtained as a red powder in a $\frac{13}{13}$

Accepted Manuscrip

yield of 81% (0.43 g, 0.70 mmol). Anal. Calcd. for C₂₉H₄₇CoP₄Si (606.17 g/mol): C, 57.46; H, 7.81. Found: C, 57.87; H, 7.66. IR: (Nujol, KBr): 3046 (ArH), 1576 (ArC=C), 939 (PMe₃) cm⁻¹. ¹H NMR: (300 MHz, benzene-d₆, 300 K, δ): 0.46 (s, Si*Me*, 6H), 0.86 (d, *J* = 6 Hz, P*Me*₃ 9H), 1.18 (s, P*Me*₃, 18H), 7.01 (s, *Ar*, 7H), 7.18-7.25 (m, *Ar*, 2H), 7.5 (br, *Ar*, 4H), 7.73 (d, *J* = 7 Hz, *Ar*, 1H); ³¹P NMR (121 MHz, benzene-d₆, 300 K, δ): -2.4 (m, *P*Me₃, 2P), 20.9 (m, *P*Me₃, 1P), 71.3 (m, *P*Ph₂, 1P) ppm. ¹³C NMR (75 MHz, benzene-d₆, 300 K, δ): 14.20 (PCH₃), 22.66 (PCH₃), 30.16 (SiCH₃), 34.38 (SiCH₃), 133.11 (*C*_{Ph}), 141.01 (*C*_{Ph}), 148.80 (*C*_{Ph}), 150.53 (*C*_{Ph}), 152.24 (*C*_{Ph}), 158.78 (*C*_{Ph}), 159.99 (*C*_{Ph}) ppm. ²⁹Si NMR (79.5MHz, benzene-d₆, 300K, δ): 41.65 (m) ppm.

Synthesis of 3. At 0°C, MeI (0.04 g, 0.28 mmol) was added into a solution (20 mL) of complex 2 (0.16 g, 0.26 mmol). After stirring for 24h at room temperature, the volatiles were removed at reduced pressure. The residue was extracted with diethyl ether. Complex 3 as dark red crystals was isolated from its diethyl ether solution in a yield of 73% (0.12 g, 0.19 mmol). Anal. Calcd. for $C_{26}H_{38}CoIP_3Si$ (657.43 g/mol): C, 47.50; H, 5.83. Found: C, 47.87; H, 5.65. IR: (Nujol, KBr): 3043 (ArH), 1582 (ArC=C), 935 (PMe₃) cm⁻¹. Complex 3 was paramagetic.

Synthesis of 4. At 0°C, EtBr (0.03 g, 0.27 mmol) was added into a solution (20 mL) of complex **2** (0.15 g, 0.25 mmol). After stirring for 24 h at room temperature, the volatiles were removed at reduced pressure. The residue was extracted with diethyl ether. Complex **4** as dark red crystals was isolated from its diethyl ether solution in a yield of 77% (0.12 g, 0.19mmol). IR: (Nujol, KBr): 3043 (ArH), 1582 (ArC=C), 935 (PMe₃) cm⁻¹. Anal. Calcd. for C₂₆H₃₈BrCoP₃Si (610.43 g/mol): C, 51.16; H, 6.27. Found: C, 51.37; H, 6.56. IR: (Nujol, KBr): 3047 (ArH), 1581 (ArC=C), 935 (PMe₃) cm⁻¹. Complex **4** was paramagetic.

Synthesis of 5. To a solution of 1 (0.4 g, 1.25 mmol) in 20 mL THF was added $CoCl(PMe_3)_3$ (0.4 g, 1.25 mmol) in 30 mL THF at 0°C. The mixture was allowed to warm to the ambient temperature. The color changed from blue to yellow. After 14

stirred at room temperature for 12 h, the volatiles were evaporated under reduced pressure. The resulting yellow powder was extracted with pentane and diethyl ether. Complex 5 was obtained as light yellow cubic crystals from diethyl ether in a yield of 74% (0.52 g, 0.9 mmol). Anal. Calcd. for C₂₆H₃₉ClCoP₃Si (566.95 g/mol): C, 55.08; H, 6.93. Found: C, 54.87; H, 7.16. IR: (Nujol, KBr): 3054 (ArH), 1931 (Co-H), 1575 (ArC=C), 940 (PMe₃) cm⁻¹. ¹H NMR: (300 MHz, benzene-d₆, 300 K, δ): -11.68 (ddd, J = 87, 48, 57 Hz, CoH, 1H), 0.63 (s, SiMe, 6H), 0.86 (d, J = 6 Hz, PMe₃, 9H), 1.54 (d, J = 9 Hz, PMe₃, 9H), 7.11 (m, Ar, 6H), 7.45 (m, Ar, 1H), 7.71 (m, Ar, 2H), 8.29 (m, Ar, 5H); ³¹P NMR (121 MHz, benzene-d₆, 300 K, δ): -5.04 (s, PMe₃, 1P), 9.9 (m, *P*Me₃,1P), 77.68 (m, *P*Ph₂, 1P) ppm. ¹³C NMR (75 MHz, benzene-d₆, 300 K, δ): 5.83 $(d, J = 5 Hz, SiCH_3), 12.96 (d, J = 6 Hz, SiCH_3), 18.48 (d, J = 22 Hz, PCH_3), 20.00 (d, J = 20 Hz,$ J = 28 Hz, PCH₃), 131.66 (s, C_{Ph}), 131.69 (t', J = 5 Hz, C_{Ph}), 131.82 (s, C_{Ph}), 133.81 (s, C_{Ph}), 133.88 (d, J = 10 Hz, C_{Ph}), 134.41 (d, J = 8 Hz, C_{Ph}), 137.50 (s, C_{Ph}), 137.92 (s, C_{Ph}), 138.90 (d, J = 5 Hz, C_{Ph}), 139.60 (d, J = 5Hz, C_{Ph}), 143.05 (s, C_{Ph}), 143.70 (s, C_{Ph}), 159.90 (d, J = 3 Hz, C_{Ph}), 160.63 (d, J = 4 Hz, C_{Ph}) ppm. ²⁹Si NMR (79.5MHz, benzene-d₆, 300K, δ): 38.48 (s) ppm.

General procedure for the Kumada reaction catalyzed by complex 5. In 25 mL Schlenk tube was added 1 mmol bromo toluene, 1.1 mmol Grignard reagent, 0.02 mmol 5, and 2.5 mL THF. The resulting solution was sealed and stirred at room temperature for 24 h and monitored by TLC and GC. Then the mixture was added 10 ml 10% HCl and stirred vigorously for 2 h at room temperature. The resulting mixture was extracted by 50 mL diethyl ether for three times. The organic phase was combined and dried over Na₂SO₄. The yield was determined by GC with *n*-dodecane as an internal standard.

Single crystal X-ray diffraction. Single crystal X-ray diffraction data of the complexes **2**, **3** and **5** were collected on a STOE STADIVARI Cu or Stoe IPDS2 diffractometer. Using Olex2,^[22] the structures were solved with ShelXS^[23] structure solution program using Direct Methods and refined with the ShelXL^[24] refinement ¹⁵

package using Least Squares minimization. CCDC-1534302 (2), 1534303 (3) and 1534301 (5) contain supplementary crystallographic data for this paper. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgements. We gratefully acknowledge the financial support by NSF China No. 21272138/21572119.

Keywords: Cobalt hydride \cdot Si-H activation \cdot Silyl cobalt complex \cdot Kumada Coupling

References

- [1] J. Y. Corey, Chem. Rev. 2011, 111, 863-1071.
- [2] J. Y. Corey, Chem. Rev. 2016, 116, 11291-11435.
- [3] B. Ghaffari, S. M. Pershlock, D. L. Plattner, R. J. Staples, P. E. Maligres, S. W. Krska, R. E.Jr. Maleczka, M. R.III. Smith, J. Am. Chem. Soc. 2014,136, 14345-14348.
- [4] C. C. H. Atienza, T. Diao, S. A. Weller, K. M. Nye, J. P. G. Lewis, J. L. Delis, A. K. Boyer, P. J.Roy, P. J. Chirik, J. Am. Chem. Soc. 2014,136, 12108-12116.
- [5] C. Cheng, J. F. Hartwig, J. Am. Chem. Soc. 2014,136, 12064-12072.
- [6] J. Takaya, N. Iwasawa, J. Am. Chem. Soc. 2008,130, 15254-15255.
- [7] M. MacInnis, D. F. MacLean, R. Lundgren, R. McDonald, L. Turculet, Organometallics 2007,26, 6522-6525.
- [8] H. Y. Fang, Y. K. Choe, Y. H. Li, S. Shimada, *Chem.-Asian J.* 2011, 6, 2512-2521.
- [9] Y. H. Li, Y. Zhang, X. H. Ding, *Inorg. Chem. Commun.* **2011**,*14*(8), 1306-1310.
- [10] S. Wu, X. Li, Z. Xiong, G. Xu, Y. Lu, H. Sun, Organometallics 2013,32(11), 3227-3237.
- [11] Z. Xiong, X. Li, S. Zhang, Y. Shi, H. Sun, *Organometallics* **2016**,*35*, 357-363.
- [12] X. Yu, B. O. Patrick, B. R. James, *Organometallics* 2006,25, 4870-4877.

- [13] X. Hiroto, N. Saori, Y. Yasuhito, O. Joji, K. Atsuaka, *Org.Lett.* 2006,8, 4157-4159.
- [14]S. Eiji, Y. Youko, N. Yoshiaki, O. Shinichi, T. Teruhisa, H. Tamejiro, Angew. Chem. Int. Ed. 2004,43, 3448-3451.
- [15] J. Zhang, H. Wang, M. Xian, O. Joji, K. Atsuaka, J. Am. Chem. Soc. 2009,131, 3854-3855.
- [16] H. Sun, L. She, S. Fang, X. Li, *Polyhedron* 2008,27, 854-860
- [17] K. A. Smart, M. Grellier, L. Vendier, S. A. Mason, S. C. Cappelli, A. Albinati, S. Sabo-Etienne, *Inorg. Chem.* 2013, 52, 2654-2661.
- [18] K. A. Smart, M. Grellier, Y. Coppel, L. Vendier, S. A. Mason, S. C. Cappelli, A. Albinati, V. Montiel-Palma, M. A. Munoz-Hernandez, S. Sabo-Etienne, *Inorg. Chem.* 2014, *53*, 1156-1165.
- [19] V. Montiel-Palma, M. A. Munoz-Hernandez, T. Ayed, J.-C. Barthelat, M. Grellier,
 L. Vendier, S. Sabo-Etienne, *Chem. Commun.* 2007, 3963-3965.
- [20] F. Zhang, L. Wang, S. Chang, K. Huang, Y. Chi, W. Hung, C. Chen, G. Leed, P. Chou, *Dalton Trans.* 2013,42, 7111-7119.
- [21] H.-F. Klein, H. H. Karsch, *Chem. Ber.*1975, 108, 944-955.
- [22] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, J. Appl. Cryst. 2009, 42, 339.
- [23] G. M. Sheldrick, *ActaCryst*.2008, *A64*, 112.
- [24] G. M. Sheldrick, *ActaCryst*. 2015, *C71*, 3.

TOC

Synthesis of Silyl Cobalt Hydride and its Catalytic Performance in Kumada Coupling Reactions

Shilu Xu,^[a] Peng Zhang,^[a] Xiaoyan Li,^[a] Benjing Xue,^[a] Hongjian Sun,^{*[a]} Olaf Fuhr,^[b] Dieter Fenske^[b]

