Synthesis of [CNN] pincer nickel(II) NHC chlorides and their catalytic effects on the hydrosilylation of aldehydes and ketones under mild conditions†

Shaobo Cao,[a] Shangqing Xie,[a] Qingshuang Li,[a] Xiaoyan Li,[a] Hongjian Sun,*[a] Olaf Fuhr[b] and Dieter Fenske[b]

Eight [CNN] pincer nickel NHC chlorides, [$^{R}C_{carbene}N_{amido}{}^{R'2}N_{amine}$–Ni–Cl] (R/R′2 = quinolinyl/^{n}Bu (**3a**), quinolinyl/Me (**3b**), quinolinyl/$PhCH_2$ (**3c**), $(CH_2)_4$/^{n}Bu (**5a**), $(CH_2)_4$/^{i}Pr (**5b**), Me_2/^{n}Bu (**5c**), Me_2/^{i}Pr (**5d**), and Me_2/$PhCH_2$ (**5e**)), were prepared by the reactions of related asymmetric [CNN] NHC preligands with $Ni(DME)Cl_2$ *via* N–H bond activation. The molecular structures of complexes **3a**, **3b** and **5a** were investigated using single crystal XRD. The catalytic experiments showed that the nickel complexes could catalyze the hydrosilylation of unsaturated compounds like aldehydes and ketones, and complex **3b** was found to exhibit the best catalytic activity at 30 °C. Using $NaBHEt_3$ as an additive, the catalytic activity of **3b** was greatly improved. Furthermore, it was found that good to complete conversion of aldehydes could be achieved within 1.5 h at 30 °C after pre-reacting **3b** and $NaBHEt_3$ with silane for 0.5 h. The substrate ketones could be converted to alcohols in good yields by prolonging the reaction time to 2.5 h at 30 °C. It is worth mentioning that all eight [CNN] pincer nickel NHC chlorides are stable in air, and this is rare in nickel catalysts for hydrosilylation of aldehydes and ketones. Moreover, the substrate universality of the catalytic system is also very good, with good functional group tolerance. The molecular structures of complexes **3a**, **3b** and **5a** were investigated using single crystal XRD and a possible reaction mechanism was proposed.

Introduction

Alcohol compounds are closely related to our daily life, and are widely used in cosmetics, agricultural chemistry, the pharmaceutical industry, fine chemicals, *etc.*[1,2] Reduction of aldehydes and ketones to alcohols is a good way to produce alcohols.[3] Hydrosilylation of carbonyl compounds is a method to convert carbonyl compounds to alcohols using organic silane as a hydrogen source and transition metal complexes as catalysts.[4–6] In recent years, hydrosilylation of carbonyl compounds has gradually attracted people's attention because it does not require high-pressure hydrogen as a hydrogen source and is safer. Additionally, the reaction conditions are milder. This method was first discovered by Ojima's group in 1972.[7] They used a Rh complex as a catalyst, cyclohexanone and triethoxysilane as template substrates, and found that hydrosilylation could occur at room temperature. When the reactant was an aromatic ketone, it was necessary to increase the temperature to carry out the reaction. In the same year, Kumada explored the catalytic effect of Pt complexes.[8] Since then, this field has been developing rapidly, but the catalysts are still dominated by noble metals such as Rh and Pt.[3,8,9] In recent years, scientists have found that base transition metals can also well promote the hydrosilylation of carbonyl compounds.[10,11] Among the metal complexes, iron is the dominant metal in this direction[12] and there is less research on nickel. As a platinum homologous element, nickel has good catalytic activity for many reactions. The high abundance and low price of nickel are also important reasons it is worth studying.[13] In 2012, Sortais's group used $NaBHEt_3$ to reduce nickel chloride complexes *in situ* to achieve hydrosilylation of carbonyl compounds. At room temperature, aldehydes completely reacted, but the reaction time of ketones was 17 h (Fig. 1).[14] In 2018, Trovitch reported the hydrosilylation of aldehydes at rt with a nickel complex catalyst. Although it took 24 hours, the loading

[a] *School of Chemistry and Chemical Engineering, Key Laboratory of Special Functional Aggregated Materials, Ministry of Education, Shandong University, Shanda Nanlu 27, 250100 Jinan, People's Republic of China. E-mail: hjsun@sdu.edu.cn*

[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*

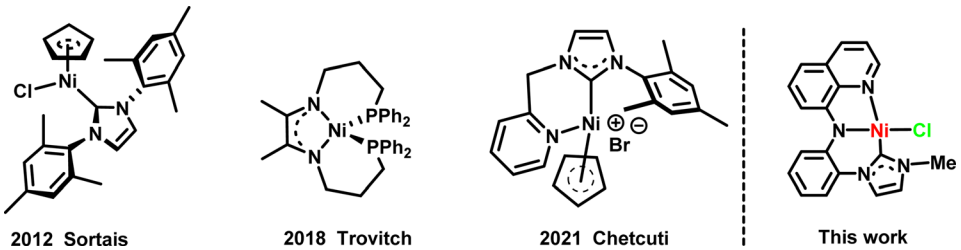
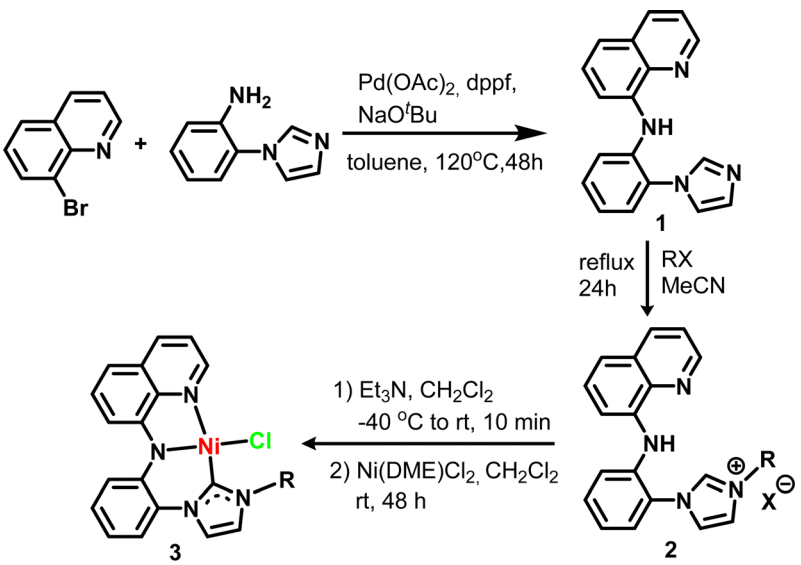


Fig. 1 Nickel catalysts for hydrosilylation of aldehydes and ketones.

of the catalyst was reduced to 0.1%. However, for hydrosilylation of ketones, the temperature still needed to be increased to 60 °C.[15] In 2021, Chetcuti's group studied hydrosilylation of aldehydes with nickel complexes as catalysts at different temperatures (40–60 °C). When the substrate was ketone, the required temperature was higher.[16] From these reports, we can know that ketone hydrosilylation needs a higher temperature or longer time in comparison with aldehydes and these nickel catalysts are unstable in air.

In addition to the central metal, ligands are also important for the catalytic activity of metal complexes.[17] Pincer ligands have attracted extensive attention due to their unique structures and regulatability.[18] Pincer ligands can not only stabilize metal complexes, but also improve their catalytic activity.[19] The introduction of N-heterocyclic carbene (NHC) into the pincer ligand can further modify the reaction properties of metal complexes. Both NHC-based pincer symmetric ligands[20] and amine-based pincer symmetric ligands[21] have been well studied. However, few studies have been carried out on the pincer asymmetric ligand [CNN] that combines NHC with an amine. We have reported several [CNN] pincer NHC preligands, and have proved that their metal complexes can catalyze transfer hydrogenation of ketones and the Kumada reactions.[22] On this basis, in this work, three new [CNN] pincer NHC preligands are synthesized and eight kinds of [CNN] pincer nickel NHC complexes are prepared through the reactions of these eight [CNN] pincer NHC preligands using $Ni(DME)Cl_2$. The experimental results show that these eight [CNN] pincer nickel complexes can promote the hydrosilylation of carbonyl compounds. Among the eight metal complexes, **3b** exhibits the best catalytic activity. **3b** is not only stable in air, but also has mild catalytic reaction conditions and a short reaction time. Catalyst



	2a (96%)	2b (90%)	2c (90%)
	3a (42%)	3b (53%)	3c (44%)
X	Br	I	Cl
R	^{n}Bu	Me	Bn

Scheme 1 Synthesis of [CNN] pincer nickel NHC complexes **3a–3c**.

stability has made a new breakthrough in the field of catalysis, but also a great step forward.

Results and discussion

Synthesis of [CNN] pincer nickel NHC complexes 3a–3c

According to the method we published, three new [CNN] pincer preligands **2** were synthesized (Scheme 1).[22] On the basis of the known preligands, only the molecular skeleton has changed. Precursor **1** could be prepared by the coupling between *o*-aminophenyl imidazole and 8-bromoquinoline under the catalysis of $Pd(OAc)_2$. **1** and haloalkane were refluxed in acetonitrile to obtain preligands **2a–2c**. Finally, [CNN] pincer NHC ligands were formed *in situ* by the reaction of Et_3N with **2a–2c**. [CNN] pincer NHC ligands reacted with $Ni(DME)Cl_2$ at room temperature. [CNN] pincer Ni(II) NHC complexes **3a–3c** as purple-red crystals could be obtained by volatilization with a mixed solvent of petroleum ether and CH_2Cl_2 in the yields of 41–52%.

In the IR spectra of preligands of **2a–2c** the N–H vibrations were recorded at 3164 (**2a**), 3195 (**2b**) and 3199 (**2c**) cm ^{1}. In the ^{1}H NMR spectra of preligands **2a–2c** the NC*H*N protons are registered at 10.41(**2a**), 9.99 (**2b**) and 11.04 (**2c**) ppm while the N*H* protons are located at 6.90 (**2a**), 7.20 (**2b**) and 7.20 (**2c**) ppm. After coordination with the nickel atom, the proton signals of the NC*H*N and N*H* groups disappeared in the ^{1}H NMR spectra of complexes **3a–3c**. Additionally, the chemical shifts of the protons of the R group (*n*-butyl (**3a**), methyl (**3b**) and benzyl (**3c**)) moved downfield after coordination with the nickel atom. In the IR spectra of complexes **3a–3c** the stretching vibrations of C C and C N bonds appear between 1562 and 1597 cm ^{1}.

The molecular structures of complexes **3a** and **3b** are presented in Fig. 2 and Fig. 3. **3a** and **3b** have distorted planar square structures centered on Ni. The central nickel atom coordinates with a C_{NHC}, an $N_{quinoline}$, an amino N and a Cl atom. Both complexes contain a penta-membered chelating ring and a hexa-membered chelating ring. And the two chelating rings share a Ni–H_{amide} bond. Because of the strong *trans*-influence of the C_{NHC} atom, Ni1–N1 = 1.947(2) Å (**3a**) and Ni1–N1 = 1.953(3) Å (**3b**) are significantly longer than Ni1–N2 = 1.869(2) Å (**3a**) and Ni1–N2 = 1.867(3) Å (**3b**). These are structural

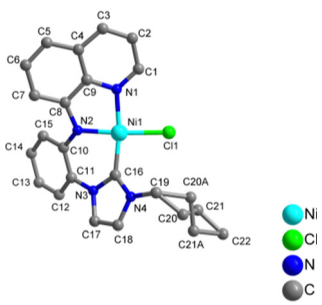


Fig. 2 Molecular structure of **3a** with selected bond lengths (Å) and angles (deg): Ni1–Cl1 2.1959(7), Ni1–N1 1.947(2), Ni1–N2 1.869(2), Ni1–C16 1.879(3); N1–Ni1–Cl1 93.17(6), N2–Ni1–Cl1 168.27(7), N2–Ni1–N1 84.49(8), N2–Ni1–C16 88.82(9), C16–Ni1–Cl1 95.78(7), C16–Ni1–N1 166.01(9).

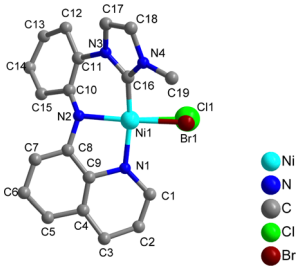


Fig. 3 Molecular structure of **3b** with selected bond lengths (Å) and angles (deg): Ni1–Cl1 2.2499(8), Ni1–Br1 2.2499(8), Ni1–N1 1.953(3), Ni1–N2 1.871(2), Ni1–C16 1.866(3); N1–Ni1–Cl1 95.74(8), N1–Ni1–Cl1 95.74(8), N2–Ni1–Cl1 167.91(8), N2–Ni1–N1 84.26(11), N2–Ni1–C16 87.97(11), C16–Ni1–Cl1 94.45(9), C16–Ni1–N1 165.32(12).

characteristics of related nickel complexes.[22] In [NNN] pincer nickel complexes, the Ni–H_{amine} is longer than Ni–H_{amide} because of the lack of the strong *trans*-influence of C_{NHC}.[23] The Ni–C_{NHC} bonds (Ni1–C16 = 1.879(3) Å (**3a**) and 1.868(4) Å (**3b**)) in **3a** and **3b** are shorter than the related Ni–C_{NHC} bonds in the double NHC nickel complexes because the two Ni–C_{NHC} bonds in the double NHC nickel complexes are in *trans*-positions, and the interaction of strong *trans*-influence of two C_{NHC} atoms between them makes the Ni–C_{NHC} bonds longer.[24,25]

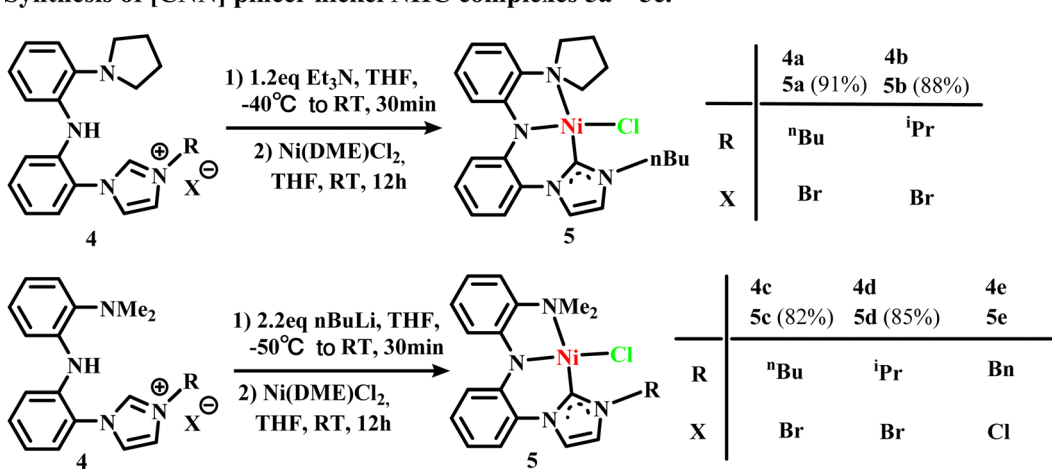
Synthesis of [CNN] pincer nickel NHC complexes 5a–5e

Four kinds of [CNN] pincer asymmetric preligands **4a–4d** were synthesized according to the literature method.[22] **4a–4d** interacted with ^{n}BuLi to form NHC compounds. NHC compounds *in situ* reacted with $Ni(DME)Cl_2$ *via* N–H cleavage with the escape of hydrogen chloride gas to afford **5a–5d** (Scheme 2). These are four [CNN] pincer nickel(II) NHC complexes. Complex **5e** has been reported in the literature.[22a] The eight [CNN] pincer nickel NHC chloride complexes (**3a–3c** and **5a–5e**) in both solution and solid state are stable for nine months in air. This is rare in nickel compounds that catalyze the hydrosilylation of carbonyl compounds. **5a** (Fig. 4) has similar structural characteristics to **3a** and **3b**.

Catalytic activity of [CNN] pincer nickel NHC complexes 3a–3c and 5a–5e for the hydrosilylation of carbonyl compounds

Preliminary experiments show that these eight [CNN] pincer nickel(II) NHC complexes act on the hydrosilylation of PhCHO with $PhSiH_3$ (entry 1, Table 1), but the reactivity is poor. In most transition metal catalyzed hydrosilylations, metal hydride is the real catalyst. The preparation and separation of nickel hydrides are difficult, so we try to add $NaBHEt_3$ *in situ* to directly reduce nickel chlorides to nickel hydrides, and then continue to explore. We found that the reactivity of these compounds was greatly improved after the addition of $NaBHEt_3$ (entry 2, Table 1). The catalytic activity of **3b** is the strongest. Therefore, in the follow-up research, complex **3b** was used as the catalyst to investigate the conditions and expand the scope of the substrates.

The catalyst conditions, including reaction time, catalyst loading, silane type, solvent and reactant addition order, were



Scheme 2 Synthesis of [CNN] pincer nickel NHC complexes **5a–5e**.

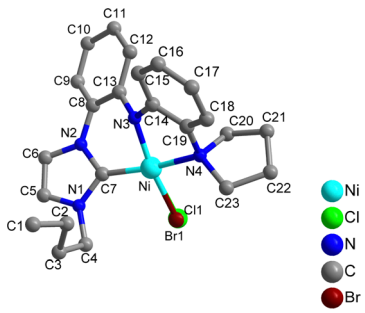
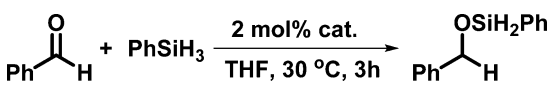


Fig. 4 Molecular structure of **5a** with selected bond lengths (Å) and angles (deg): Ni–Cl1 2.2140(12), Ni–Br1 2.2140(12), Ni–N4 2.018(4), Ni–N3 1.863(4), Ni–C7 1.872(5); N4–Ni–Cl1 94.77(11), N4–Ni–Cl1 94.77(11), N3–Ni–Cl1 168.30(13), N3–Ni–N4 84.03(15), N3–Ni–C7 87.77(2), C7–Ni–Cl1 94.53(14), C7–Ni–N4 169.65(17).

Table 1 Catalytic activity of eight nickel complexes[a]

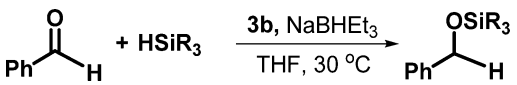


Entry	3a	3b	3c	5a	5b	5c	5d	5e
1	14	35	11	9	10	25	30	20
2[b]	61	76	60	40	50	33	40	36

[a] PhCHO (1.0 mmol), $PhSiH_3$ (1.2 mmol). Conversions were determined by GC with *n*-dodecane as an internal standard. [b] With 2 mol% $NaBHEt_3$.

screened with complex **3b** as a catalyst and benzaldehyde as a template substrate (Table 2). The amount of $NaBHEt_3$ added as an additive is the same as that of the catalyst added. It was found that if the time was 4 h, the conversion of benzaldehyde could reach 100% (entries 1 and 2, Table 2). If the amount of catalyst decreased, the conversion dropped sharply (entries 2–4, Table 2). Compared with other silanes, $PhSiH_3$ is the most suitable in this case (entries 5–10, Table 2). Compared with

Table 2 Optimization of the catalytic reaction conditions[a]

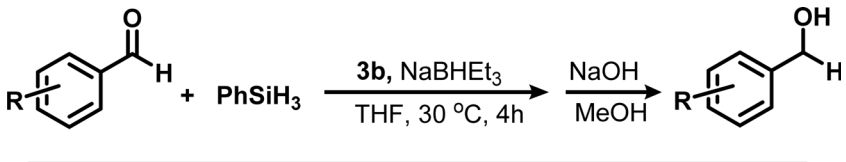


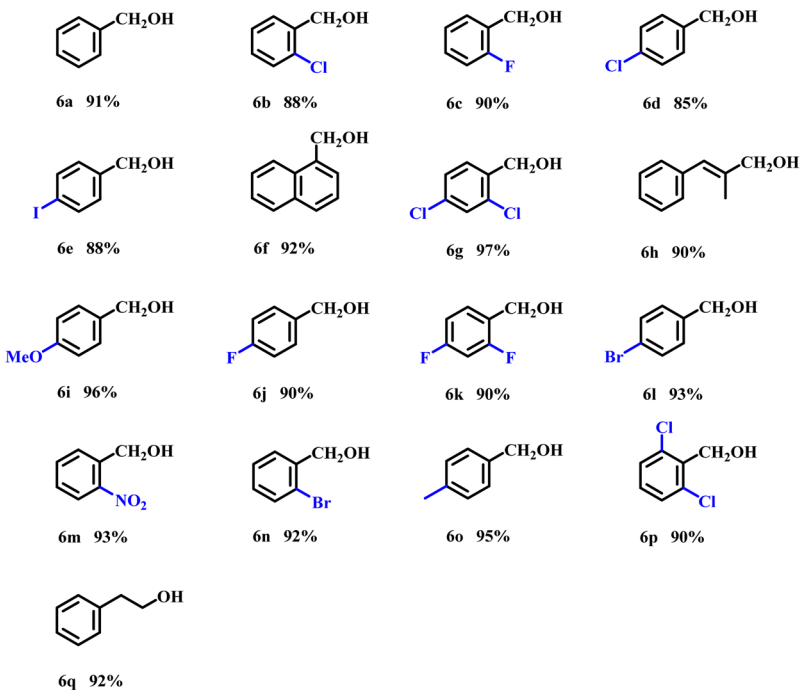
Entry	Loading (mol%)	Solvent	Silane	Temp. (°C)	Time (h)	Conversion[b] (%)
1	2	THF	$PhSiH_3$	30	3	88
2	2	THF	$PhSiH_3$	30	4	100
3	1	THF	$PhSiH_3$	30	4	53
4	0.5	THF	$PhSiH_3$	30	4	27
5	2	THF	$(EtO)_3SiH$	30	4	31
6	2	THF	Ph_2SiH_2	30	4	38
7	2	THF	Ph_3SiH	30	4	37
8	2	THF	Me_2PhSiH	30	4	12
9	2	THF	$Me(EtO)_2SiH$	30	4	47
10	2	THF	Et_3SiH	30	4	30
11	2	DMF	$PhSiH_3$	30	4	15
12	2	PhMe	$PhSiH_3$	30	4	42
13	2	*n*-Pentane	$PhSiH_3$	30	4	20
14	2	Et_2O	$PhSiH_3$	30	4	30
15	2	Dioxane	$PhSiH_3$	30	4	39
16	2	Neat	$PhSiH_3$	30	4	50
17	2	Neat	$PhSiH_3$	40	4	95
18	2	Neat	$PhSiH_3$	50	4	100
19[c]	2	THF	$PhSiH_3$	30	0.5	48
20[d]	2	THF	$PhSiH_3$	30	0.5	32
21	2	THF	$PhSiH_3$	30	0.5	26
22[c]	2	THF	$PhSiH_3$	30	1.5	100
23[d]	2	THF	$PhSiH_3$	30	1.5	78
24	2	THF	$PhSiH_3$	30	1.5	62
25[e]	2	THF	$PhSiH_3$	30	2	90
26[e]	2	THF	$PhSiH_3$	30	2.5	100

[a] PhCHO (1.0 mmol), silane (1.2 mmol). [b] Conversions were determined by GC with *n*-dodecane as an internal standard. [c] Pre-reaction of the catalyst with silane for 30 min. [d] Pre-reaction of the catalyst with benzaldehyde for 30 min. [e] The substrate is acetophenone; pre-reaction of the catalyst with silane for 30 min.

other solvents (DMF, PhMe, *n*-pentane, Et_2O and dioxane), THF is the best reaction medium (entries 11–15, Table 2). In the absence of a solvent, the aldehyde could be completely transformed by increasing the reaction temperature. However, after comprehensive consideration we chose THF as the solvent to

Table 3 Products of hydrosilylation of aldehydes[ab]





[a] Aldehyde (1.0 mmol), $PhSiH_3$ (1.2 mmol), **3b** (2.0 mol%), $NaBHEt_3$ (2 mol%), THF (2 mL), 30 °C, pre-reaction of the catalyst with silane for 30 min, 1.5 h. [b] Isolated yields.

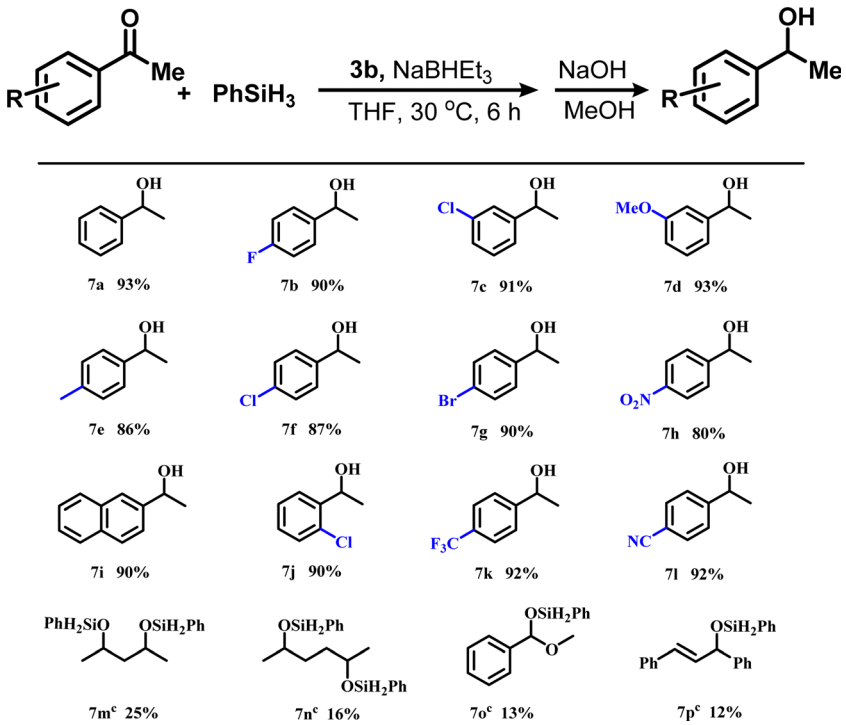
continue the screening conditions (entries 16–18, Table 2). Because the reactions were carried out at 30 °C, the temperature was not optimized. The addition sequence of the starting materials was also explored (entries 20–24, Table 2). The results indicated that the pre-reaction of **3b** and $NaBHEt_3$ with $PhSiH_3$ or benzaldehyde had a notable effect on the conversion. Upon pre-reaction of **3b** and $NaBHEt_3$ with $PhSiH_3$ (or benzaldehyde) for 30 min, a conversion with 100% or 78% could be achieved, respectively. Therefore, the optimal catalytic conditions are 2 mol% complex **3b**, 2 mol% $NaBHEt_3$, 1.2 equiv. of $PhSiH_3$, pre-reaction of the catalyst with silane for 30 min, 30 °C, THF, and 1.5 h (entry 22, Table 2). For hydrosilylation, the reactivity of ketones is weaker than that of aldehydes, so ketones are more challenging substrates. Under the optimal conditions for benzaldehyde, when the reaction time was 2.5 h, complete conversion of acetophenone was achieved (entries 25 and 26, Table 2). Therefore, the optimal catalytic conditions for ketone are: 2 mol% **3b**, 2 mol% $NaBHEt_3$, 1.2 equiv. of $PhSiH_3$, pre-reaction of the catalyst with silane for 30 min, 30 °C, THF and 2.5 h (entry 26, Table 2).

The scope of the substrates for hydrosilylation

Under the optimal conditions for aldehydes, we explored the hydrosilylation of the benzaldehydes with different substituents (Table 3). The experiments show that the catalytic system has a wide substrate scope. The isolated yields of the alcohol products are between 85% and 97%, regardless of the presence of EDGs (such as methyl or methoxy group) or EWGs (such as halogen or nitro group). When the substrate is aromatic, the position of the substituent has no effect on the yield. For the substrates with two substituent groups (**6g**, **6k** and **6p**), the reduction products with high yields could also be obtained. These results show that the functional group tolerance is good. It is worth noting that the catalyst could also selectively reduce the carbonyl group without reducing the alkenyl group with a yield of 90% (**6h**). This shows that the catalytic system also has good chemical selectivity.

Under the catalytic conditions for aldehydes, the ketones can be completely transformed by prolonging the reaction time to 2.5 h. The experiments show that **3b** also exhibits good catalytic activity for ketones (Table 4). Good isolated yields (80–93%) could be obtained for alcohols of the acetophenone substrates with different substituents. In addition, the position, *meta*-, *para*- and *ortho*-position, of the substituent on the aromatic ring (**7c**, **7f** or **7j**) has no effect on the yield (87–91%). The reduction yield of β-acetonaphthone (**7i**) could also reach 90%. We tested the catalytic efficiency with pentane-2,4-dione, hexane-2,5-dione, methylbenzoate and chalcone, but the

Table 4 Products of hydrosilylation of ketones[ab]



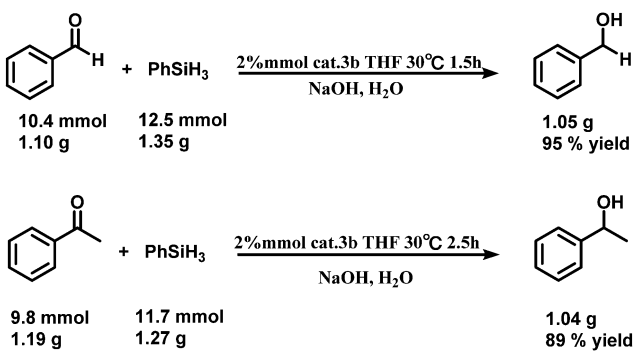
[a] Ketone (1.0 mmol), $PhSiH_3$ (1.2 mmol), **3b** (2.0 mol%), $NaBHEt_3$ (2 mol%), THF (2 mL), 30 °C, pre-reaction of the catalyst with silane for 30 min, 2.5 h. [b] Isolated yields. [c] Conversions were determined by GC with *n*-dodecane as an internal standard.

effects are poor (**7m**, **7n**, **7o** and **7p**). Although the final isolated yields are not very different from those of other catalytic systems, this catalytic system has a mild temperature (30 °C) and a stable catalyst and it is also superior to other catalytic systems for ketone hydrosilylation.[14 16]

The gram-scale reactions using 2 mol% catalyst **3b** could be smoothly performed to afford **6a** in 95% yield and **7a** in 89% yield (Scheme 3).

Mechanistic study

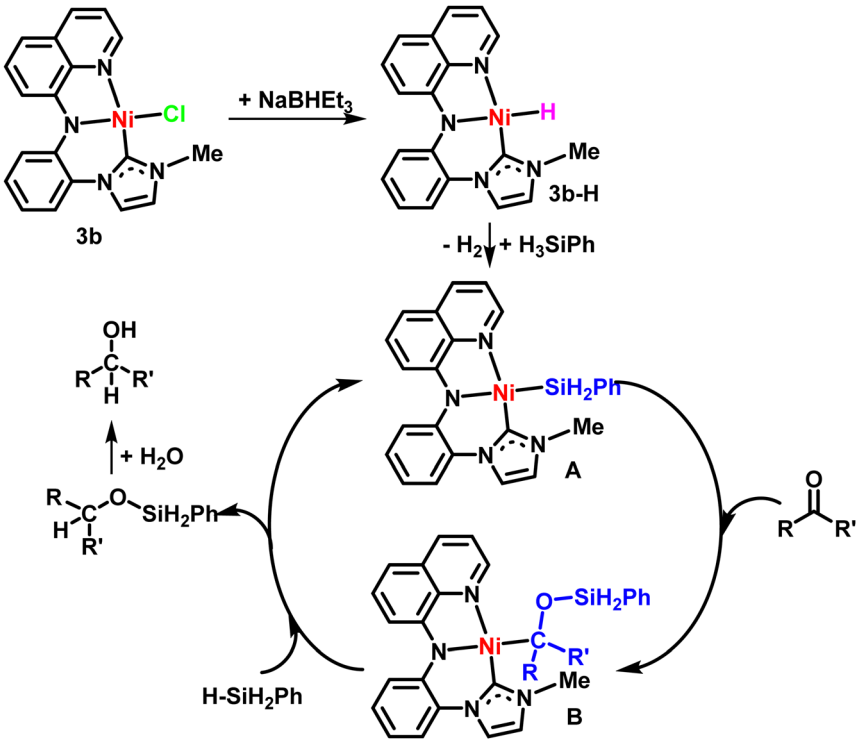
Our previous study proved that [CNN] pincer nickel(II) halide could be reduced to nickel hydride by $NaBH_4$.[26] In the presence of $NaBHEt_3$ **3b** as a precatalyst transferred to the hydrido nickel(II) complex **3b-H** (Scheme 3). **3b-H** reacted with $PhSiH_3$ to afford intermediate **A**, a silyl nickel complex, with the production of H_2, which was confirmed by GC (see the ESI†). **A** interacted with a carbonyl compound to deliver intermediate **B**. The last step is the reaction between **B** and $PhSiH_3$, delivering $RR'CHOSiH_2Ph$ with the recovery of real catalyst **A**. $RR'CHOSiH_2Ph$ was hydrolyzed to alcohol RR′CHOH (Scheme 4).



Scheme 3 Gram scale reaction.

Conclusion

In this paper, three new [CNN] pincer preligands **2a–2c** and eight [CNN] pincer nickel NHC complexes **3a–3c** and **5a–5e** were designed and synthesized. The experimental results show that these [CNN] pincer nickel NHC complexes have good catalytic activity. Among the eight complexes, **3b** is the best catalyst. Using $NaBHEt_3$ as an additive, the catalytic activity of **3b** was greatly improved. Furthermore, it was found that good to complete conversion of aldehydes could be achieved within 1.5 h at 30 °C after pre-reacting **3b** and $NaBHEt_3$ with silane for 0.5 h. The substrate ketones could be converted to alcohols in good yields by prolonging the reaction time to 2.5 h at 30 °C. The substrate expansion proved that the catalytic system has good functional group tolerance. The catalysts are stable in air whether in solution or in the solid state, and this is also the feature of this catalytic system. The molecular structures of **3a**, **3b** and **5a** were investigated using single crystal XRD and a catalytic mechanism was proposed.



Scheme 4 Proposed mechanism.

Experimental section

General procedures and materials

All reactions and operations were conducted under N_2 protection using standard Schlenk technology. All the solvents used in the experiments were dehydrated and degassed. Complexes **3a–3c**[22a] and **5a–5e**[22b] and Ni(DME)Cl_2[27] were prepared according to relevant literature reports. Other chemicals have been purchased and used to meet standards of purity. During the GC test, high-purity nitrogen was used as the carrier gas, *n*-dodecane was used as the internal standard, and a Shimadzu GC 2014 gas chromatograph was used as the test instrument. Under the protection of paraffin oil, the infrared spectra were recorded with a Bruker ALPHA FT-IR instrument with KBr as the carrier. ^{1}H and ^{13}C spectra were tested using a Bruker Avance 300 M NMR analyzer. High resolution mass spectra (HRMS) were recorded using an electrospray ionization time-of-flight (ESI-TOF) mass spectrometer.

Synthesis of 1. Under a nitrogen atmosphere, *o*-aminophenyl imidazole (1.58 g, 10 mmol), 8-bromoquinoline (2.08 g, 10 mmol), $Pd(OAc)_2$ (0.1122 g, 0.50 mmol), dppf (0.5544 g, 1.0 mmol), NaOtBu (1.248 g, 13.0 mmol) and toluene (50 mL) were successively added into a 100 mL Schlenk flask for mixing. Subsequently, the reaction mixture was heated at 120 °C for 48 h. At room temperature the reaction solution was filtered. Compound **1** was obtained by column chromatography (CH_2Cl_2/CH_3OH = 200/1) as light-yellow crystals (1.03 g, 3.50 mmol) with a yield of 35%. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K, ppm): δ 7.05 (td, J = 7.7, 1.3 Hz, 1H, Ar-H), 7.13 (d, J = 3.6 Hz, 2H, Ar-H), 7.16–7.19 (m, 1H, Ar-H), 7.25 (dd, J = 7.9, 1.5 Hz, 1H, Ar-H), 7.37–7.28 (m, 4H, Ar-H), 7.66–7.70 (m, 2H, Ar-H), 7.90 (s, 1H, N–H), 8.01 (dd, J = 8.3, 1.6 Hz, 1H, Ar-H), 8.60 (dd, J = 4.2, 1.7 Hz, 1H, Ar-H). ^{13}C NMR (75 MHz, $CDCl_3$, 298 K, ppm): δ 108.7, 117.9, 120.2, 120.8, 121.8, 122.7, 126.9, 127.2, 128.8, 129.2, 129.3, 130.0, 136.1, 137.0, 137.6, 138.8, 139.3, 147.9. HRMS (ESI-TOF): 288.1376 $[M + H]^+$; calcd for $C_{18}H_{19}N_4$: 288.1375.

Synthesis of 2a. *n*-C_4H_9Br (1.37g, 10 mmol) was added to a solution of **1** (1.43 g, 5 mmol) in 50 mL of acetonitrile. The reaction mixture was refluxed for 24 h. At room temperature the reaction solution was filtered to obtain a brown solid. The brown solid was washed three times with *n*-pentane. Compound **2a** was obtained as a brown solid (2.03 g, 96%). IR (Nujol, cm ^{1}): 3164 ν(N–H). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K, ppm): δ 0.77 (t, J = 6.4 Hz, 3H, CH_3), 1.18 (s, 2H, CH_2), 1.72 (s, 2H, CH_2), 4.44 (s, 2H, CH_2), 6.90 (d, J = 6.5 Hz, 1H, Ar-*H*), 7.21–7.51 (m, 8H, Ar-*H*), 7.71 (d, J = 6.2 Hz, 1H, Ar-*H*), 7.83 (s, 1H, Ar-*H*), 8.08 (d, J = 7.8 Hz, 1H, Ar-*H*), 8.67 (s, 1H, Ar-*H*), 10.41 (s, 1H, Ar-*H*). ^{13}C NMR (75MHz, $CDCl_3$, 298 K, ppm): δ 147.0 (N*C*N), 138.0, 137.1, 136.5, 135.6, 135.1, 130.9, 127.7, 127.2, 126.3, 126.2, 124.4, 123.6, 121.8, 121.7, 121.0, 117.6, 108.2, 49.3, 31.2, 18.3, 12.5. HRMS (ESI-TOF): 345.2078 $[M + H]^+$; calcd for $C_{22}H_{25}N_4$: 345.2079.

Synthesis of 2b. MeI (1.41 g, 10 mmol) was added to a solution of **1** (1.43 g, 5 mmol) in 50 mL of acetonitrile. The reaction mixture was refluxed for 24 h. At room temperature the reaction solution was filtered to obtain a brown solid. The brown solid was washed three times with *n*-pentane. Compound **2b** was obtained as a brown solid (1.93 g, 90%). IR (Nujol, cm ^{1}): 3195 ν(N–H). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K, ppm): δ 4.14 (s, 3H, CH_3), 6.98 (dd, J = 7.5, 1.2 Hz, 1H, Ar-*H*), 7.20 (s, 1H, Ar-*H*), 7.27–7.24 (m, 1H, Ar-*H*), 7.32 (d, J = 7.7 Hz, 1H, Ar-*H*), 7.40–7.39

(m, 3H, Ar-*H*), 7.49 (td, *J* = 7.9, 1.3 Hz, 1H, Ar-*H*), 7.58 (dd, *J* = 8.1, 1.0 Hz, 1H, Ar-*H*), 7.76 (s, 1H, Ar-*H*), 7.83 (dd, *J* = 8.0, 1.3 Hz, 1H, Ar-*H*), 8.06 (dd, *J* = 8.3, 1.6 Hz, 1H, Ar-*H*), 8.67 (dd, *J* = 4.2, 1.6 Hz, 1H, Ar-*H*), 9.99 (s, 1H, Ar-*H*). ^{13}C NMR (75 MHz, CDCl3, 298 K, ppm): δ 147.2 (N*C*N), 138.2, 137.5, 136.5, 135.4, 135.4, 131.0, 127.8, 126.9, 126.4, 126.1, 124.3, 123.3, 122.8, 121.8, 121.1, 117.8, 108.5, 36.8 (CH_3). HRMS (ESI-TOF): 303.1610 $[M + H]^+$; calcd for $C_{19}H_{19}N4$: 303.1610.

Synthesis of 2c. $PhCH_2Cl$ (1.27 g, 10 mmol) was added to a solution of **1** (1.43 g, 5 mmol) in 50 mL of acetonitrile. The reaction mixture was refluxed for 24 h. At room temperature the reaction solution was filtered to obtain a brown solid. The brown solid was washed three times with *n*-pentane. Compound **2c** was obtained as a brown solid (1.86 g, 90%). IR (Nujol, cm ^{1}): 3200 ν(N–H). ^{1}H NMR (300 MHz, CDCl3, 298 K, ppm): δ 5.80 (s, 2H, CH_2), 7.03 (d, *J* = 5.6 Hz, 1H, Ar-*H*), 7.20 (s, 1H, Ar-*H*), 7.39–7.31 (m, 8H, Ar-*H*), 7.48–7.44 (m, 2H, Ar-*H*), 7.56–7.54 (m, 2H, Ar-*H*), 7.79 (d, *J* = 9.1 Hz, 1H, Ar-*H*), 7.99 (s, 1H, Ar-*H*), 8.16 (d, *J* = 8.4 Hz, 1H, Ar-*H*), 8.75 (s, 1H, Ar-*H*), 11.05 (s, 1H, Ar-*H*). ^{13}C NMR (75 MHz, CDCl3, 298 K, ppm): δ 146.8 (NCN), 138.0, 137.3, 137.0, 135.9, 135.4, 132.1, 130.8, 128.3, 128.2, 127.8, 127.1, 126.3, 124.3, 123.3, 121.8, 120.9, 117.8, 109.1, 107.4, 106.7, 52.7. HRMS (ESI-TOF): 379.1928 $[M + H]^+$; calcd for $C_{25}H_{23}N_4$: 379.1923.

Synthesis of 3a. Et_3N (0.1 mL, 0.72 mmol) was added to a solution of **2a** (0.31 g, 0.72 mmol) in 50 mL of CH_2Cl_2 at −40 °C. The reaction solution was stirred for 10 min at room temperature. Then, a solution of Ni(DME)Cl_2 (0.2 g, 0.91 mmol) in 15 mL of CH_2Cl_2 was added to the above reaction solution at −78 °C. The reaction mixture was stirred for 48 h at room temperature to obtain a purple-red solution. The volatiles of the reaction mixture were removed by vacuum and the residue was washed with *n*-pentane (50 mL) and diethyl ether (50 mL), respectively. The residue was extracted with CH_2Cl_2. Complex **3a** (131 mg, 0.30 mmol) was obtained as purple-red crystals by volatilization with a yield of 42%. IR (Nujol, cm ^{1}): 1562.7 ν(C = C). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K, ppm): δ 0.91 (t, *J* = 7.4 Hz, 3H, CH_3), 1.52–1.42 (m, 2H, CH_2), 2.08–1.98 (m, 2H, CH_2), 4.51 (s, 2H, CH_2), 6.75–6.70 (m, 1H, Ar-*H*), 7.00–6.92 (m, 3H, Ar-*H*), 7.35–7.23 (m, 5H, Ar-*H*), 7.78 (dd, *J* = 8.4, 0.9 Hz, 1H, Ar-*H*), 8.16 (dd, *J* = 8.3, 1.2 Hz, 1H, Ar-*H*), 8.73 (dd, *J* = 5.0, 1.3 Hz, 1H, Ar-*H*). ^{13}C NMR (75 MHz, $CDCl_3$, 298 K, ppm): δ 151.1 (NCN), 149.4 ($C_{aromatic}$), 147.7 ($C_{aromatic}$), 145.9 ($C_{aromatic}$), 141.5 ($C_{aromatic}$), 138.0 ($C_{aromatic}$), 130.03 ($C_{aromatic}$), 129.7 ($C_{aromatic}$), 128.2 ($C_{aromatic}$), 126.7 ($C_{aromatic}$), 124.0 ($C_{aromatic}$), 121.3 ($C_{aromatic}$), 120.0 ($C_{aromatic}$), 117.6 ($C_{aromatic}$), 117.4 ($C_{aromatic}$), 117.3 ($C_{aromatic}$), 116.7 ($C_{aromatic}$), 114.6 ($C_{aromatic}$), 50.7 ($C_{aliphatic}$), 33.7 ($C_{aliphatic}$), 20.0 ($C_{aliphatic}$), 13.8 ($C_{aliphatic}$). HRMS (ESI-TOF): 399.1119 $[M^+ - Cl]$; calcd for $C_{22}H_{21}N_4Ni$: 399.1120.

Synthesis of 3b. Et_3N (0.1 mL, 0.72 mmol) was added to a solution of **2b** (0.31 g, 0.72 mmol) in 50 mL of CH_2Cl_2 at room temperature. The reaction solution was stirred for 10 min. Then, a solution of Ni(DME)Cl_2 (0.2 g, 0.91 mmol) in 15 mL of CH_2Cl_2 was added to the above reaction solution at −78 °C. The reaction mixture was stirred for 48 h at room temperature to obtain a purple-red solution. The volatiles of the reaction mixture were removed by vacuum and the residue was washed with *n*-pentane (50 mL) and diethyl ether (50 mL), respectively. The residue was extracted with CH_2Cl_2. Complex **3b** (148 mg, 0.38 mmol) was obtained as purple-red crystals by volatilization with a yield of 53%. IR (Nujol, cm ^{1}): 1567.6 ν(C C). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K, ppm): δ 4.10 (s, 3H, CH_3), 6.76–6.72 (m, 1H, Ar-*H*), 7.02–6.94 (m, 3H, Ar-*H*), 7.29–7.24 (m, 2H, Ar-*H*), 7.37–7.33 (m, 3H, Ar-*H*), 7.78 (dd, *J* = 8.4, 0.9 Hz, 1H, Ar-*H*), 8.16 (dd, *J* = 8.3, 1.2 Hz, 1H, Ar-*H*), 8.73 (dd, *J* = 5.0, 1.2 Hz, 1H, Ar-*H*). ^{13}C NMR (75 MHz, $CDCl_3$, 298 K, ppm): δ 151.0 (NCN), 150.0 ($C_{aromatic}$), 147.7 ($C_{aromatic}$), 145.9 ($C_{aromatic}$), 141.5 ($C_{aromatic}$), 138.1 ($C_{aromatic}$), 129.8 ($C_{aromatic}$), 129.7 ($C_{aromatic}$), 128.2 ($C_{aromatic}$), 126.8 ($C_{aromatic}$), 125.6 ($C_{aromatic}$), 124.8 ($C_{aromatic}$), 121.3 ($C_{aromatic}$), 119.9 ($C_{aromatic}$), 117.4 ($C_{aromatic}$), 117.3 ($C_{aromatic}$), 116.8 ($C_{aromatic}$), 114.8 ($C_{aromatic}$), 39.2 ($C_{aliphatic}$). HRMS (ESI-TOF): 357.0653 $[M^+ - Cl]$; calcd for $C_{19}H_{15}N_4Ni$: 357.0650.

Synthesis of 3c. Et_3N (0.1 mL, 0.72 mmol) was added to a solution of **2c** (0.31 g, 0.72 mmol) in 50 mL of CH_2Cl_2 at room temperature. The reaction solution was stirred for 10 min. Then, a solution of Ni(DME)Cl_2 (0.2 g, 0.91 mmol) in 15 mL of CH_2Cl_2 was added to the above reaction solution at −78 °C. The reaction mixture was stirred for 48 h at room temperature to obtain a purple-red solution. The volatiles of the reaction mixture were removed by vacuum and the residue was washed with *n*-pentane (50 mL) and diethyl ether (50 mL), respectively. The residue was extracted with CH_2Cl_2. Complex **3c** (151 mg, 0.32 mmol) was obtained as purple-red crystals by volatilization with a yield of 44%. IR (Nujol, cm ^{1}): 1563.8 ν(C C). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K, ppm): δ 5.80 (s, 2H, CH_2), 6.77–6.71 (m, 1H, Ar-*H*), 6.80 (d, *J* = 2.0 Hz, 1H, Ar-*H*), 7.02–6.94 (m, 2H, Ar-*H*), 7.27–7.19 (m, 3H, Ar-*H*), 7.36–7.34 (m, 5H, Ar-*H*), 7.44 (d, *J* = 6.5 Hz, 2H, Ar-*H*), 7.80 (dd, *J* = 8.4, 0.9 Hz, 1H, Ar-*H*), 8.16 (dd, *J* = 8.2, 1.2 Hz, 1H, Ar-*H*), 8.71 (dd, *J* = 5.0, 1.2 Hz, 1H, Ar-*H*). ^{13}C NMR (75 MHz, $CDCl_3$, 298 K, ppm):δ 151.0 (NCN), 150.5 ($C_{aromatic}$), 147.7 ($C_{aromatic}$), 145.9 ($C_{aromatic}$), 141.5 ($C_{aromatic}$), 138.1 ($C_{aromatic}$), 136.7 ($C_{aromatic}$), 129.9 ($C_{aromatic}$), 129.7 ($C_{aromatic}$), 128.8 ($C_{aromatic}$), 128.6 ($C_{aromatic}$), 128.2 ($C_{aromatic}$), 128.1 ($C_{aromatic}$), 126.8 ($C_{aromatic}$), 124.1 ($C_{aromatic}$), 121.3 ($C_{aromatic}$), 120.0 ($C_{aromatic}$), 117.9 ($C_{aromatic}$), 117.4 ($C_{aromatic}$), 117.4 ($C_{aromatic}$), 116.8 ($C_{aromatic}$), 114.7 ($C_{aromatic}$), 54.6 ($C_{aliphatic}$). HRMS (ESI-TOF): 433.0966 $[M^+ - Cl]$; calcd for $C_{25}H_{19}N_4Ni$: 433.0963.

Synthesis of 5a. At −40 °C, Et_3N (0.5 mL, 3.6 mmol) was slowly added to a solution of **4a** (1.31 g, 3.0 mmol) in 30 mL of THF. After the reaction solution recovered to room temperature, the reaction solution was stirred for 30 min. Then a solution of Ni(DME)Cl_2 (0.66 g, 3.0 mmol) in 20 mL of THF was added to the above reaction solution at −78 °C. When the reaction mixture was stirred at room temperature for 12 h, the color of the solution changed from gray to green. After the volatiles were removed in a vacuum, the residue was extracted with *n*-pentane (60 mL) and diethyl ether (60 mL), respectively. At −10 °C **5a** (1.24 g, 2.73 mmol) was obtained from the Et_2O solution as green needle crystals with a yield of 91%. IR (Nujol, cm ^{1}): 1584.6 ν(C = C). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K, ppm): δ 1.10 (t,

J = 7.5 Hz, 3H, CH_3), 1.29–1.21 (m, 2H, CH_2), 1.65–1.57 (m, 2H, CH_2), 1.89–1.80 (m, 2H, N(CH_2)$_4$N), 2.24– 2.11 (m, 2H, N(CH_2)$_4$N), 3.08–3.01 (m, 1H, N(CH_2)$_4$N), 3.47– 3.38 (m, 1H, N(CH_2)$_4$N), 3.97–3.88 (m, 1H, N(CH_2)$_4$N), 4.21–4.11 (m, 1H, N(CH_2)$_4$N), 4.36–4.26 (ddd, J = 12.2, 10.6, 5.9 Hz, 1H, CH_2), 4.78–4.68 (ddd, J = 12.3, 10.2, 6.2 Hz, 1H, CH_2), 6.57 (t, J = 7.5 Hz, 1H, Ar-H), 6.75 (t, J = 7.4 Hz, 1H, Ar-H), 6.95–6.86 (m, 1H, Ar-H), 7.01–6.99 (m, 1H, Ar-H), 7.04 (d, J = 1.7 Hz, 2H, Ar-H), 7.08 (d, J = 5.9 Hz, 1H, Ar-H), 7.31 (d, J = 9.0 Hz, 1H, Ar-H), 7.35 (d, J = 2.2 Hz, 1H, Ar-H), 7.58 (d, $JTZX$ = 9.1 Hz, 1H, Ar-H). ^{13}C NMR (75 MHz, $CDCl_3$, 298 K, ppm): δ 149.3 (NCN), 148.9 ($C_{aromatic}$), 145.7 ($C_{aromatic}$), 141.5 ($C_{aromatic}$), 129.6 ($C_{aromatic}$), 125.5 ($C_{aromatic}$), 125.3 ($C_{aromatic}$), 122.7 ($C_{aromatic}$), 120.6 ($C_{aromatic}$), 119.2 ($C_{aromatic}$), 118.5 ($C_{aromatic}$), 117.0 ($C_{aromatic}$), 116.2 ($C_{aromatic}$), 116.0 ($C_{aromatic}$), 114.8 ($C_{aromatic}$), 60.0 ($C_{aromatic}$), 54.1 ($C_{aromatic}$), 50.0 ($C_{aromatic}$), 32.7 ($C_{aliphatic}$), 24.3 ($C_{aliphatic}$), 21.5 ($C_{aliphatic}$), 19.0 ($C_{aliphatic}$), 12.9 ($C_{aliphatic}$). HRMS (ESI-TOF): 417.1592 [M^+ − Cl]; calcd for $C_{23}H_{27}N_4Ni$: 417.1589.

Synthesis of 5b. At −40 °C, Et_3N (0.5 mL, 3.6 mmol) was slowly added to a solution of **4b** (1.28 g, 3.0 mmol) in 30 mL of THF. After the reaction solution recovered to room temperature, the reaction solution was stirred for 30 min. Then a solution of Ni(DME)Cl_2 (0.66 g, 3.0 mmol) in 20 mL of THF was added to the above reaction solution at −78 °C. When the reaction mixture was stirred at room temperature for 12 h, the color of the solution changed from gray to green. After the volatiles were removed in a vacuum, the residue was extracted with *n*-pentane (60 mL) and diethyl ether (60 mL), respectively. At −10 °C **5b** (1.16 g 2.63 mmol) was obtained from the Et_2O solution as green needle crystals with a yield of 88%. IR (Nujol, cm ^{1}): 1583.56 ν(C C). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K, ppm): δ 1.34 (d, J = 4.9 Hz, 3H, CH_3), 1.61 (d, J = 6.9 Hz, 3H, CH_3), 1.76–1.68 (m, 2H, N(CH_2)$_4$N), 1.90–1.81 (m, 1H, N(CH_2)$_4$N), 2.07–1.95 (m, 1H, N(CH_2)$_4$N), 2.99–2.89 (m, 1H, N(CH_2)$_4$N), 3.44–3.29 (m, 1H, N(CH_2)$_4$N), 3.90–3.78 (m, 1H, N(CH_2)$_4$N), 4.08–3.96 (m, 1H, N(CH_2)$_4$N), 5.67–5.58 (m, 1H, CH(CH$_3$)$_2$), 6.48 (t, J = 7.6 Hz, 1H, Ar-H), 6.65 (t, J = 7.5 Hz, 1H, Ar-H), 6.83 (dd, J = 15.8, 8.1 Hz, 2H, Ar-H), 6.90 (t, J = 7.8 Hz, 1H, Ar-H), 6.97 (d, J = 2.3 Hz, 1H, Ar-H), 6.99 (s, 1H, Ar-H), 7.21 (d, J = 10.3 Hz, 1H, Ar-H), 7.30 (d, J = 2.3 Hz, 1H, Ar-H), 7.44 (d, J = 8.3 Hz, 1H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K, ppm): δ 149.4 (NCN), 148.9 ($C_{aromatic}$), 144.9 ($C_{aromatic}$), 141.5 ($C_{aromatic}$), 129.6 ($C_{aromatic}$), 125.5 ($C_{aromatic}$), 125.3 ($C_{aromatic}$), 120.5 ($C_{aromatic}$), 119.4 ($C_{aromatic}$), 118.7 ($C_{aromatic}$), 118.5 ($C_{aromatic}$), 117.0 ($C_{aromatic}$), 116.4 ($C_{aromatic}$), 116.1 ($C_{aromatic}$), 114.8 ($C_{aromatic}$), 59.7 ($C_{aromatic}$), 53.8 ($C_{aromatic}$), 50.8 ($C_{aromatic}$), 28.7 ($C_{aliphatic}$), 24.3 ($C_{aliphatic}$), 23.5 ($C_{aliphatic}$), 22.3 ($C_{aliphatic}$). HRMS (ESI-TOF): 403.1436 [M^+ − Cl]; calcd for $C_{22}H_{25}N_4Ni$: 403.1433.

Synthesis of 5c. At −50 °C, *n*-BuLi (2.6 mL/2.5 M, 6.6 mmol) was added into a solution of **4c** (1.21 g, 3.0 mmol) in 30 mL of THF. The reaction mixture was stirred for 30 min, until the solution became transparent. Then, Ni(DME)Cl_2 (0.66 g, 3.0 mmol) in 10 mL of CH_2Cl_2 was added to the above reaction solution at −78 °C. The reaction mixture was stirred at room temperature for 12 h to obtain a green solution. The volatiles were removed under reduced pressure. The residue was washed with *n*-pentane (30 mL) and extracted with diethyl ether (60 mL). **5c** (1.05 g, 2.45 mmol) was obtained as a green powder by rotary evaporation of the solvent with a yield of 82%. IR (Nujol, cm ^{1}): 1587.1 ν(C C). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K, ppm): δ 1.00 (t, 3H, CH_2CH_3), 1.57 (m, 2H, $CH_2CH_2CH_3$), 2.19 (m, 2H, $CH_2CH_2CH_2$), 2.63 (s, 3H, N(CH_3)$_2$), 3.00–3.11 (m, 3H, N(CH_3)$_2$), 4,18 (m, 1H, NCH_2CH$_2$), 4.72 (m, 1H, NCH_2CH$_2$), 6.57 (t, 1H, J = 9.0 Hz, Ar-H), 6.67 (t, 1H, J = 9.0 Hz, Ar-H), 6.83–6.92 (m, 3H, Ar-H), 7.09 (dd, J = 12 Hz, Ar-H), 7,19 (s, 1H, Ar-H), 7.26 (s, 1H, Ar-H), 7.50 (d, J = 9.0 Hz, 1H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K, ppm): δ 148.8 (NCN), 146.7 ($C_{aromatic}$), 141.5 ($C_{aromatic}$), 129.5 ($C_{aromatic}$), 126.1 ($C_{aromatic}$), 125.7 ($C_{aromatic}$), 122.9 ($C_{aromatic}$), 119.6 ($C_{aromatic}$), 119.2 ($C_{aromatic}$), 118.6 ($C_{aromatic}$), 117.5 ($C_{aromatic}$), 116.4 ($C_{aromatic}$), 116.2 ($C_{aromatic}$), 115.9 ($C_{aromatic}$), 115.1 ($C_{aromatic}$), 50.5 ($C_{aromatic}$), 50.3 ($C_{aromatic}$), 46.6 ($C_{aromatic}$), 32.0 ($C_{aromatic}$), 19.0 ($C_{aliphatic}$), 12.9 ($C_{aliphatic}$). HRMS (ESI-TOF): 391.1436 [M^+ − Cl]; calcd for $C_{21}H_{25}N_4Ni$: 391.1433.

Synthesis of 5d. At −50 °C, *n*-BuLi (2.6 mL/2.5M, 6.6 mmol) was added into a solution of **4d** (1.22 g, 3.0 mmol) in 30 mL of THF. The reaction mixture was stirred for 30 min, until the solution became transparent. Then, Ni(DME)Cl_2 (0.66 g, 3.0 mmol) in 10 mL of CH_2Cl_2 was added to the above reaction solution at −78 °C. The reaction mixture was stirred at room temperature for 12 h to obtain a green solution. The volatiles were removed under reduced pressure. The residue was washed with *n*-pentane (30 mL) and extracted with diethyl ether (60 mL). **5d** (1.06 g, 2.56 mmol) was obtained as a green powder by rotary evaporation of the solvent with a yield of 85%. IR (Nujol, cm ^{1}): 1583.0 ν(C C). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K, ppm): δ 1.45 (d, 3H, CH(CH_3)$_2$), 1.73 (d, 3H, CH(CH_3)$_2$), 2.70 (s, 3H, N(CH_3)$_3$), 3.06–3.19 (m, 3H, N(CH_3)$_3$), 5.74–5.86 (m, 1H, CH(CH$_3$)$_2$), 6.64 (t, 1H, Ar-H), 6.73 (t, 1H, Ar-H), 6.90–7.02 (m, 2H, Ar-H), 7.06–7.13 (m, 2H, Ar-H), 7.19–7.22 (m,1H, Ar-H), 7.28–7.29 (m, 1H, Ar-H), 7.35–7.36 (m, 1H, Ar-H), 7.55 (d, 1H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K, ppm): δ 148.8 (NCN), 147.1 ($C_{aromatic}$), 145.7 ($C_{aromatic}$), 141.3 ($C_{aromatic}$), 129.5 ($C_{aromatic}$), 126.1 ($C_{aromatic}$), 125.6 ($C_{aromatic}$), 119.6 ($C_{aromatic}$), 119.2 ($C_{aromatic}$), 118.9 ($C_{aromatic}$), 118.3 ($C_{aromatic}$), 117.5 ($C_{aromatic}$), 116.9 ($C_{aromatic}$), 116.1 ($C_{aromatic}$), 115.1 ($C_{aromatic}$), 51.6 ($C_{aromatic}$), 50.4 ($C_{aromatic}$), 46.3 ($C_{aromatic}$), 23.7 ($C_{aliphatic}$), 21.7 ($C_{aliphatic}$). HRMS (ESI-TOF): 377.1276 [M^+ − Cl]; calcd for $C_{20}H_{23}N_4Ni$: 377.1276.

General procedure for nickel-catalyzed hydrosilylation. Under a N_2 atmosphere, a 20 mL Schlenk tube containing a magnetic stirrer was added with a mixture of the nickel complex (0.02 mmol), $NaBHEt_3$ (0.02 mmol), $PhSiH_3$ (1.2 mmol) and the aldehyde (1 mmol) or ketone (1 mmol) substrate in 2 mL of THF. The catalytic mixture was heated at 30 °C for 4 h or 6 h. Using *n*-dodecane as an internal standard, the conversion was determined by gas chromatography. Methanol (2 mL) and 10% NaOH (2 mL) were added to the reaction solution and the mixture was stirred at 60 °C for 24 h to quench the reaction. The product was extracted 3 times with 60 mL of Et_2O. The product was purified by column chromatography on silica gel with petroleum ether (60–90 °C) and ethyl acetate (5 : 1, v/v) as the eluent. The pure product was characterized by NMR.

Single crystal X-ray diffraction

Single crystal data for **3a** and **3b** were collected using a Stoe Stadi Vari diffractometer at 150.15 K, using Ga-Kα radiation (λ = 1.34143 Å) and single crystal data for **5a** were collected with a 'XtaLAB Synergy, Dualflex, HyPix' diffractometer at 173.15 K using Cu-Kα radiation (λ = 1.54184 Å). The crystal structures were solved using intrinsic phasing with the Olex 2 program[28] and refined by full-matrix least-squares on F^2 using SHELXL.[29] All non-hydrogen atoms were refined anisotropically. CCDC 1865447 (**3a**), 1865452 (**3b**) and 2211202 (**5a**) contain the crystallographic data for this paper.†

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported by the NSF of China (no. 21971151/21572119) and the Major Basic Research Projects of the Natural Science Foundation of Shandong Province ZR2019ZD46.

References

1 B. Matthias and B. Carsten, *Appl. Organomet. Chem.*, 2005, **19**, 1275.
2 J. Magano and J. R. Dunetz, *Org. Process Res. Dev.*, 2012, **16**, 1156.
3 S. Díez-González and S. P. Nolan, *Org. Prep. Proced. Int.*, 2007, **39**, 523.
4 P. A. Dub and T. Ikariya, *ACS Catal.*, 2012, **2**, 1718.
5 M. C. Lipke, A. L. Liberman-Martin and T. Don Tilley, *Angew. Chem., Int. Ed.*, 2017, **56**, 2260.
6 M. Oestreich, *Angew. Chem.*, 2016, **128**, 504.
7 I. Ojima, M. Nihonyanagi and Y. Nagai, *J. Chem. Soc., Chem. Commun.*, 1972, 938.
8 K. Yamamoto, T. Hayashi and M. Kumada, *J. Organomet. Chem.*, 1972, **46**, C65.
9 W. Dumont, J. C. Poulin, T. P. Dang and H. B. Kagan, *J. Am. Chem. Soc.*, 1973, **95**, 8295.
10 R. Morris Bullock, *ChemCatChem*, 2011, **3**, 780.
11 (*a*) X. Du, X. Qi, K. Li, X. Li, H. Sun, O. Fuhr and D. Fenske, *Appl. Organomet. Chem.*, 2021, **35**, e6286; (*b*) A. Sanagawa and H. Nagashima, *Organometallics*, 2018, **37**, 2859; (*c*) T. Takayama, R. Kariya, Y. Nakaya, S. Furukawa, S. Yamazoe and T. Komatsu, *Chem. Commun.*, 2021, **57**, 4239.
12 A. Raya, P. O. Burgos and I. Fernandez, *ACS Catal.*, 2019, **9**, 5400.
13 Charles E. Tucker and Johannes G. de Vries, *Top. Catal.*, 2002, **19**, 111.
14 L. P. Bheeter, M. Henrion, L. Brelot, C. Darcel, M. J. Chetcuti, J. Sortais and V. Ritleng, *Adv. Synth. Catal.*, 2012, **354**, 2619.
15 C. L. Rock, T. L. Groy and R. J. Trovitch, *Dalton Trans.*, 2018, **47**, 8807.
16 F. Ulm, S. Shahane, L. Truong, T. Romero, V. Papaefthimiou, M. Chessé, M. J. Chetcuti, C. Pham, C. Michon and V. Ritleng, *Eur. J. Inorg. Chem.*, 2021, 3074.
17 (*a*) K. A. Gudun, M. Segizbayev, A. Adamov, P. N. Plessow, K. A. Lyssenko, M. P. Balanay and A. Y. Khalimon, *Dalton Trans.*, 2019, **48**, 1732; (*b*) S. Chakraborty, P. Bhattacharya, H. Dai and H. Guan, *Acc. Chem. Res.*, 2015, **48**, 1995.
18 G. van Koten, K. Timmer, J. G. Noltes and A. L. Spek, *J. Chem. Soc., Chem. Commun.*, 1978, 250.
19 (*a*) J. Zhang, G. Leitus, Y. B. David and D. Milstein, *J. Am. Chem. Soc.*, 2005, **127**, 10840; (*b*) X. Zhang and Z. Wang, *J. Org. Chem.*, 2012, **77**, 3658; (*c*) J. Choi, A. H. Roy MacArthur, M. Brookhart and A. S. Goldman, *Chem. Rev.*, 2011, **111**, 1761.
20 R. E. Andrew, L. González-Sebastián and A. B. Chaplin, *Dalton Trans.*, 2016, **45**, 1299.
21 (*a*) Y. Nakahara, T. Toda, A. Matsunami, Y. Kayaki and S. Kuwata, *Chem. – Asian J.*, 2018, **13**, 73; (*b*) R. A. Wahyuono, B. Schulze, M. Rusu, M. Wchtler, J. Dellith, M. Seyring, M. Rettenmayr, J. Plentz, A. Ignaszak, U. S. Schubert and B. Dietzek, *ChemPlusChem*, 2016, **81**, 1281.
22 (*a*) Z. Wang, X. Li, S. Xie, T. Zheng and H. Sun, *Appl. Organomet. Chem.*, 2019, **33**, e4932; (*b*) Y. Sun, X. Li and H. Sun, *Dalton Trans.*, 2014, **43**, 9410.
23 T. D. Franco, M. Stojanovic, S. C. Keller, R. Scopelliti and X. Hu, *Helv. Chim. Acta*, 2016, **99**, 830.
24 M. Asay, M. Q. Miriel, J. R. O. Sanfelice and D. M. Otero, *J. Organomet. Chem.*, 2018, **859**, 10.
25 J. D. Cope, N. P. Liyanage, P. J. Kelley, J. A. Denny, E. J. Valente, C. E. Webster, J. H. Delcamp and T. K. Hollis, *Chem. Commun.*, 2017, **53**, 9442.
26 Z. Wang, X. Li, H. Sun, O. Fuhr and D. Fenske, *Organometallics*, 2018, **37**, 539.
27 A. Kermagoret and P. Braunstein, *Organometallics*, 2008, **27**, 88.
28 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339.
29 G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, **A64**, 112.