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ARTICLE



Constructing Reactive Fe and Co Complexes from Isolated Picolyl-Functionalized *N*-Heterocyclic Carbenes[†]

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We report the isolation of free picolyl-functionalized *N*-heterocyclic carbenes (NHCs), which serve as versatile precursors to access low coordinate iron and cobalt complexes. The reactivities of these new iron and cobalt complexes towards catalytic hydrosilylation of ketones have also been explored. For example, low loadings (0.05–1 mol%) of a four-coordinate iron complex bearing two deprotonated picolyl-NHC ligands can effect the fast catalytic reduction of ketones using the inexpensive industrial byproduct polymethylhydrosiloxane (PMHS) as the reductant at ambient temperature.

Introduction

The N-heterocyclic carbenes (NHCs) are widely used ancillary ligands in coordination chemistry.¹ Their strong σ -donating and weak π -accepting nature leads to electron rich and stable complexes.¹ Recently iron- and cobalt-NHC complexes have gained considerable attention, due to their potential applications as inexpensive and environmentally benign catalysts. Most of these complexes bear monodentate NHC ligands.² The incorporation of NHCs in a chelating scaffold can enhance complex stability and enable bifunctional or hemilabile ligand designs.³ The *N*-picolyl-NHC ligands can be easily synthesized with different substitution patterns on the pyridine ring and the NHC, allowing fine-tuning of the steric and electronic properties. As such, the bidentate N-picolyl-NHC ligands have been used to coordinate with many transition metals.⁴ The lability of the picolyl arm and the bifunctional behavior of the ligand have been described in several stoichiometric and catalytic processes.^{5,6}

The reported *N*-picolyl-NHC metal complexes were prepared via one of the following two methods: (1) reacting a metal precursor with the *in situ* generated carbene from the corresponding imidazolium salt and a strong base, and (2) transferring the ligand from a silver complex to a metal precursor.⁴⁻⁶ However, both methods have their limitations. The coordination chemistry using *in situ* generated NHCs can be problematic, in that, the counteranion of the imidazolium salt, the cation of the base, and even the conjugate acid of the base may cause unwanted reactions. The silver-NHC route is useful for preparing NHC complexes of 4d and 5d metals, but

metals. Moreover, silver-NHC complexes are generally lightsensitive. Occasionally, the silver induced degradation of the imidazolium precursors^{7a,b} or the oxidation of the metal precursors^{7c} may occur. The use of free carbenes in their pure form is a more desirable method and offers more flexibility in choosing metal precursors and solvents. However, the instability of the free carbene form of the *N*-picolyl-NHC ligand originated from the high acidity of the bridging CH₂ and basicity of the carbene carbon presents a serious hurdle to the free NHC route.^{40,p} Herein, we report the syntheses and isolation of the free *N*-picolyl-NHCs and their reactivities towards [M(HMDS)₂] precursors (where M = Fe, Co; HMDS = hexamethyldisilazide), along with the preliminary data on the hydrosilylation of ketones catalyzed by the new Fe and Co complexes.

the carbene transfer reaction is much less generic for 3d

Results and discussion

Synthesis of free *N*-picolyl-NHCs

The free *N*-picolyl-NHCs (HL) **2a/2b** were prepared by deprotonating the corresponding imidazolium salts (H₂LBr) **1a**⁴¹/**1b**^{4m} in diethyl ether using KO^tBu at ambient temperature (Scheme 1). The free ligands **2a/2b** were isolated in good yields as crystalline solids, where the prompt workup after 1 h is critical. Crystallizations from concentrated diethyl ether solutions allowed for structural characterization by X-ray crystallography (Fig. 1). The ¹³C NMR shifts of the carbene carbons are at ~218 ppm. In both the solid state and solution, **2a/2b** slowly decompose into complicated mixtures at ambient temperature, but are stable for weeks at ~35 °C.

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[†] Electronic Supplementary Information (ESI) available: NMR spectra and X-ray crystallographic experimental details. CCDC 1830450-1830460. See DOI: 10.1039/x0xx00000x

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2b R = Mes, 79%

Scheme 1 Syntheses of picolyl-NHCs.

1b R = Mes



Fig. 1 Molecular structures of 2a (top) and 2b (bottom). Ellipsoids are shown at 50% probability. Hydrogen atoms have been omitted for clarity.



Scheme 2 Syntheses of 3[Fe]/3[Co].



Scheme 3 Reactions of picolyl-NHCs 2a/2b with M(HMDS)₂ (M = Fe, Co)



Fig. 2 Molecular structures of **3[Co]**. The ellipsoids are shown at 30% probability. All hydrogen atoms are omitted for clarity. Only one disordered component is shown. Selected bond lengths (Å) and angles (°): Co(1)-C(10) 1.961(4), Co(1)-N(3) 1.971(3), Co(1)-C(28) 2.00(1), Co(1)-N(6) 1.970(3), N(3)-C(18) 1.362(5), C(18)-C(17) 1.353(5), C(17)-C(16) 1.408(6), C(16)-C(15) 1.341(5), C(15)-C(14) 1.440(5), C(14)-N(3) 1.394(4), C(14)-C(13) 1.365(5), C(13)-N(2) 1.416(4), N(6)-C(36) 1.353(5), C(36)-C(35) 1.364(5), C(35)-C(34) 1.400(7), C(34)-C(33) 1.327(7), C(33)-C(32) 1.449(6), C(32)-N(6) 1.399(5), C(32)-C(31) 1.42(1), C(31)-N(5) 1.40(1), C(10)-Co(1)-N(3) 9.9(1), N(3)-Co(1)-C(28) 117.6(3), C(28)-Co(1)-N(6) 94.5(4), N(6)-Co(1)-C(10) 115.2(1), N(2)-C(13)-C(14) 126.3(3), N(5)-C(31)-C(32) 123.9(9).



Scheme 4 Protonolysis of complexes 4 and 5

Coordination chemistry of N-picolyl-NHCs

We have recently reported the synthesis of **3[Fe]** from the imidazolium salt **1a**, 2 equiv. of *n*BuLi and 0.5 equiv. of FeBr₂.^{6a} Using the free ligand **2a** and $[M(HMDS)_2]$ in a 2 : 1 ratio in toluene at ambient temperature gave **3[Fe]/3[Co]** in good yields (Scheme 2). As shown in Fig. 2, the structure of **3[Co]** features a distorted tetrahedral Co(II) center with two L⁻ ligands bearing the dearomatized pyridine rings. The metric parameters of **3[Co]** are similar to those of **3[Fe]**. This synthetic route leading to **3[Fe]/3[Co]** shows a versatile complementary alternative to access low-coordinate complexes and dearomatized *N*-picolyl-NHC ligand, where low temperature handling and strong alkyllithium bases are avoided.

The reaction of 2a/2b with $[Fe(HMDS)_2]$ in a 1 : 1 ratio at ambient temperature gave the three-coordinate complexes (4[Fe]/4[Co] and 5[Fe]/5[Co]) in good yields within 10 minutes

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Dalton Transactions

Dalton Transactions

(Scheme 3). The X-ray structures (Fig. 3) show that the carbon donor coordinates to $M(HMDS)_2$ while the pyridine *N*-donor is dangling. The metric parameters are similar to those found in $[M(HMDS)_2(NHC)]$ (M = Fe, Co).⁸ The planarity around each metal center is evidenced by the sum of bond angle data of

359.86(7), 359.95(8), 360.1(2), and 360.0(1)° for **4[Fe]**, **4[Co]**, **5[Fe]**, and **5[Co]**, respectively. The Fe–C bonds are longer than the Co–C bonds, while the difference between Fe–N and Co–N bonds is less pronounced.



Fig. 3 Molecular structures of 4[Fe] (top left), 4[Co] (bottom left), 5[Fe] (top right) and 5[Co] (bottom right). The ellipsoids are shown at 30% probability. All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°), for 4[Fe]: Fe(1)–N(4) 1.949(2), Fe(1)–N(5) 1.966(2), Fe(1)–C10 2.138(2), N(4)–Fe(1)–N(5), 126.16(7), N(4)–Fe(1)–C(10), 122.32(7), N(5)–Fe(1)–C(10) 111.38(7); for 4[Co]: Co(1)–N(4) 1.930(2), Co(1)–N(5) 1.956(2), Co(1)–C(10) 2.077(2), N(4)–Co(1)–N(5) 126.06(8), N(4)–Co(1)–C(10) 122.19(8), N(5)–Co(1)–C(10) 111.66(8); for 5[Fe]: Fe(1)–N(4) 1.961(4), Fe(1)–N(5)–1.970(4), Fe(1)–C(10) 2.145(5), N(4)–Fe(1)–N(5) 127.0(2), N(4)–Fe(1)–C(10) 121.7(2), N(5)–Fe(1)–C(10) 111.4(2); for 5[Co]: Co(1)–N(4) 1.929(3), Co(1)–N(5) 1.961(2), Co(1)–C(10) 2.078(3), N(4)–Co(1)–N(5) 125.7(1), N(4)–Co(1)–C(10) 122.5(1), N(5)–Co(1)–C(10) 111.8(1).

At ambient temperature, the pale-yellow solution of 4[Fe] turns into a dark green colour in a few hours. Crystallization from pentane at -35 °C yields red crystals of the dimeric complex 6[Fe] (Scheme 4). It is conceivable that the formation of 6[Fe] may start with the coordination of pyridine N-donor followed by the deprotonation of the pyridylic CH₂ group by one of the HMDS ligands. The resulting three-coordinate [Fe(HMDS)L] intermediate 6'[Fe] dimerizes in a head-to-tail fashion with iron atoms Fe(1) and Fe(2) bound to the pyridylic carbon atoms C(37) and C(13), respectively (Fig. 4). Interestingly, the X-ray structure reveals an approximate C_2 symmetry instead of a centre of inversion (i.e., the two stereocentres C(37) and C(13) within any given molecule have the same configuration), presumably due to the π - π stacking interaction between the two pyridine rings (e.g., the centroidcentroid distance is ~3.6 Å, the shortest contact distance is \sim 3.0 Å, and the dihedral angle is \sim 21°). The Fe(1)–C(37) and Fe(2)–C(13) bond distances of 2.218(4) Å are longer than typical Fe-alkyl bonds reported.9 Similar dimeric structures have been reported for [Fe{Ph₂PC(H)py}(HMDS)]₂ and [Zn(bis- $NHC^{*}(R)]_{2}$ (where bis-NHC^{*} = methylidyne-3,3'-bis(N-tertbutylimidazol-2-ylidene) and R = Et, H, SiH₂Ph, O(CH)Ph₂, OCHO, or N(ⁱPr)CH(ⁱPr)).¹⁰ Upon cooling under an argon atmosphere, the dark green solution of 6[Fe] in toluene- d_8

turns reddish brown, accompanied by the appearance of a set of new signals in the ¹H NMR spectrum. Such changes are fully reversible. This phenomenon makes us believe that although **6[Fe]** is dimeric in the solid-state, it exists in solution (C_6D_6 , toluene- d_8) as a monomer [Fe(HMDS)L] (**6'[Fe]**) at ambient temperature. At -35 °C in toluene- d_8 , the **6[Fe]**:**6'[Fe]** ratio is ~3:1. Our attempted synthesis of the analogous cobalt complex led to a complicated mixture of products. Recrystallization of the mixture afforded green brown crystals of an unexpected di-Co structure, i.e., a [CoL₂] unit bound to a [Co(HMDS)₂] unit via the pyridylic carbon (see ESI⁺). We were unable to obtain a pure sample of this di-Co compound.

The conversions of 5[Fe]/5[Co] to 7[Fe]/7[Co] are much slower, due to the steric hindrance around the pyridine Ndonors. Heating 5[Fe]/5[Co] at 90 °C in toluene overnight leads to the full conversion to 7[Fe]/7[Co] (Scheme 4). The X-ray structures of 7[Fe]/7[Co] reveal three-coordinate pyramidalized metal centers (Fig. 5), with the metal centres sitting outside the C(10)-N(3)-N(4) planes by ~0.3 Å due to the steric. The sums of bond angles around the metal centres are 353.96(9) and 352.8(1)° for 7[Fe] and 7[Co], respectively. The bite angle of the chelate ligand in 7[Co] (94.4(1)°) is similar to the bite angles of both ligands in 3[Co] (94.5(4) and 93.9(1)°), while the bite angle of the chelate ligand in 7[Fe]

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(92.36(9)°) is similar to that of one of the two ligands in **3[Fe]** (92.23(9)°) and smaller than the other (93.3(1)°). The alternating long–short bond distances in the C₅N rings support a dearomatized pyridine structure. Complexes **7[Fe]/7[Co]** are thermally robust, i.e., no noticeable change in their ¹H NMR spectra after heating their solutions in C₆D₆ under N₂ at 90 °C for several days.

Catalytic hydrosilylation of ketones

The hydrosilylation of carbonyl groups is an important synthetic transformation that is widely employed in the



Fig. 4 Molecular structures of 6[Fe]. The ellipsoids are shown at 30% probability. All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Fe(1)–N(3) 2.147(3), Fe(1)–C(10) 2.077(4), Fe(1)–N(4) 1.980(3), Fe(1)–C(37) 2.218(4), Fe(2)–N(7) 2.140(3), Fe(2)–C(34) 2.082(4), Fe(2)–N(8) 1.983(3), Fe(2)–C(13) 2.218(4), N(3)–Fe(1)–C(10) 89.1(1), C(10)–Fe(1)–N(4) 119.3(1), N(4)–Fe(1)–N(3) 109.6(1), N(3)–Fe(1)–C(37) 96.0(1), C(37)–Fe(1)–C(10) 109.9(1), C(37)–Fe(1)–N(4) 123.8(1), N(2)–C(13)–C(14) 115.8(3), N(2)–C(13)–Fe(2) 113.5(2), C(14)–C(13)–Fe(2) 108.3(2), N(7)–Fe(2)–C(34) 88.2(1), C(37)–Fe(2)–N(7) 110.8(1), N(7)–Fe(2)–C(13) 97.3(1), C(13)–Fe(2)–C(34) 110.2(1), C(13)–Fe(2)–N(7) 110.8(1), N(7)–Fe(2)–C(13) 97.3(1), C(13)–Fe(2)–C(34) 110.2(1), C(37)–Fe(1) 107.3(2).

laboratory and in industry.¹¹ In recent years, carbonyl hydrosilylation catalysts based upon inexpensive first-row transition metals, such as ${\rm iron}^{12\cdot14}$ and ${\rm cobalt},^{15}$ have been developed.¹⁶ Despite the recent contributions made toward the development of iron-catalyzed carbonyl hydrosilylation, there is still a great demand for such transformations at room temperature employing low loadings (≤1 mol% of Fe).¹³ Having prepared the iron and cobalt complexes 3-7, we explored their catalytic activity towards the hydrosilylation of ketones. Our initial screening using PhSiH₃ (1.2 equiv.) and acetophenone, 3[Fe] proved most effective, i.e., the complete conversion was achieved within 2 h with a 0.05 mol% catalyst loading at ambient temperature (Table S4). Such a catalytic performance is comparable to that of the best performing catalyst in the literature. $^{\rm 13c,d}$ For example, Yang and Tilley reported that a >98% conversion of acetophenone was achieved within 18 h at ambient temperature in the presence of 0.03 mol% Fe(HMDS)₂ and 1.6 equiv. of Ph₂SiH₂;^{13c} Sydora, Stradiotto, Turculet and co-workers reported that the complete conversion of acetophenone was achieved within 4 h at ambient

temperature in the presence of 0.015 mol% of iron(N-phosphinoamidinate)(HMDS) and 1 equiv. of $PhSiH_3$.^{13d}

Our initial findings prompted us to test the catalytic reaction using the industrial byproduct polymethylhydrosiloxane (PMHS), an inexpensive and less reactive silane, in lieu of PhSiH₃. Several iron-catalyzed hydrosilylation reactions using PMHS have been reported.¹⁴ However, high catalyst loadings (≥1 mol% of Fe) or temperatures are required due to the lower activity of PMHS.¹⁴ At a 0.05 mol% loading of 3[Fe] in neat PMHS, the complete consumption of acetophenone was achieved within 2 h at ambient temperature. The corresponding alcohol was obtained after hydrolysis (Table 1). In comparison, a 5% conversion was observed when Fe(HMDS)₂ was used under



Fig. 5 Molecular structures of 7[Fe] (top) and 7[Co] (bottom). The ellipsoids are shown at 30% probability. All hydrogen atoms are omitted for clarity. Only one disordered component is shown. Selected bond lengths (Å) and angles (°), for 7[Fe]: Fe(1)–N(3) 2.001(2), Fe(1)–C(10) 2.053(2), Fe(1)–N(4) 1.925(2), N(2)–C(13) 1.408(3), C(13)–C(14) 1.361(3), C(14)–C(15) 1.447(4), C(15)–C(16) 1.340(4), C(16)–C(17) 1.419(4), C(17)–C(18) 1.354(4), C(18)–N(3) 1.380(3), N(3)–C(14) 1.404(3), N(3)–Fe(1)–C(10) 92.36(9), C(10)–Fe(1)–N(4) 129.13(9), N(4)–Fe(1)–N(3) 132.48(9), N(2)–C(13)–C(14) 126.9(2); for 7[Co]: Co(1)–N(3) 1.962(2), Co(1)–C(10) 1.982(3), Co(1)–N(4) 1.902(2), N(2)–C(13) 1.408(4), C(13)–C(14) 1.365(4), C(14)–C(15) 1.439(4), C(15)–C(16) 1.341(4), C(16)–C(17) 1.414(4), C(17)–C(18) 1.355(4), C(18)–N(3) 1.380(4), N(3)–C(14) 1.394(4), N(3)–Co(1)–C(10) 94.4(1), C(10)–Co(1)–N(4) 130.2(1), N(4)–Co(1)–N(3) 128.2(1), N(2)–C(13)–C(14) 126.3(3).

Table 1. Hydrosilylation of ketones catalyzed by 3[Fe].^a

Dalton Transactions



 o General reaction conditions: ketone (3.34 mmol) in PMHS (0.5 mL) for liquid ketones or in a mixture of PMHS (0.2 mL) + THF or toluene co-solvent (0.3 mL) for solid ketones, ambient temperature. Under each substrate, the isolated yield in percentage, the catalyst loading in mol%, and the reaction time are given sequentially. b 50 °C.

the otherwise same conditions (Table S4). Sydora, Stradiotto, Turculet, and coworkers reported negligible reactivity using their iron complex of *N*-phosphinoamidinate as the precatalyst and PMHS as the reducing reagent.^{13d}

We then surveyed the substrate scope with other ketones (Table 1). Acetophenone derivatives bearing various functional groups, the pyridyl and furyl variants, and benzophenone were reduced efficiently. Sterically hindered 2,4,6-trimethylacetophenone was successfully converted to the desired alcohols, using a higher catalyst loading at 50 °C. The cyclic and dialkyl ketones were suitable substrates as well. The alkene functionality remote from the carbonyl group remains intact during the reduction.

Conclusions

In summary, we have isolated and structurally characterized two picolyl-functionalized NHC ligands in the free-carbene form for the first time. These free picolyl-NHCs are thermally unstable at ambient temperatures but stable at low temperatures in the solid state. The isolation of the free carbene form of these ligands enables the easy entry to the corresponding rich coordination chemistry, avoiding all the issues with the indirect and in situ synthetic routes towards metal complexes. We have also further demonstrated the catalytic activity of the resulting base-metal complexes towards the hydrosilylation of ketones, featuring low catalyst loadings, mild conditions, and a broad substrate scope. It is worth noting that even the sterically demanding substrates can be converted into the corresponding alcohols in excellent yields using PMHS under relatively mild conditions. Further synthetic applications of these free carbenes and the reactivity chemistry of the resulting complexes are being investigated in our laboratory.

Experimental Section

General remarks

All reactions were carried out in a dinitrogen-filled glovebox or using the standard Schlenk techniques under dinitrogen. Glassware was dried in a 180 °C oven overnight. Diethyl ether, hexanes, pentane, and toluene solvents were dried by a Grubbs-type solvent purification system manufactured by Innovative Technology and degassed prior to use. THF solvent was dried by refluxing and distilling over sodium benzophenone ketyl under dinitrogen. C6D6 was degassed through three consecutive freeze-pump-thaw cycles. All solvents were stored over 3 Å molecular sieves prior to use. Unless otherwise noted, all NMR spectra were recorded on an Agilent DD2 600 MHz spectrometer at 25 °C. Chemical shifts are referenced to the solvent signals. NMR assignments were made based on ¹H-COSY, ¹H-¹³C-HSQC, and ¹H-¹³C-HMBC NMR spectroscopy. Solution magnetic moments were measured at 25 °C by the method originally described by Evans with stock and experimental solutions containing a known amount of a cyclohexane standard.¹⁷ Elemental analyses were carried out by ANALEST at the University of Toronto. KO^tBu was purchased from Sigma-Aldrich. $Fe(HMDS)_2$,¹⁸ $Co(HMDS)_2$,¹⁹ $1a^{41}$ and $1b^{4m}$ were prepared according to literature procedures.

Synthesis of 2a (1-mesityl-3-(picolyl)imidazol-2-ylidene). To the mixture of **1a** (716.6 mg, 2.00 mmol) and KO^tBu (224.4 mg, 2.00 mmol) was added 10 mL of diethyl ether. The mixture was stirred at room temperature for 1 h before filtered through Celite. The filtrate was concentrated to ~2 mL and cooled to -35 °C to afford beige Xray quality crystals of 2a. The supernatant was decanted off and the crystals were washed with cold pentane (3 × 1 mL), dried under vacuum (380.6 mg, 69%). ¹H NMR (600 MHz, C_6D_6) δ 8.43 (ddd, J = 4.8, 1.9, 0.9 Hz, 1H, py-H), 7.13 (dt, J = 7.8, 1.1 Hz, 1H, py-H), 7.02 (td, J = 7.6, 1.8 Hz, 1H, py-H), 6.77 (s, 2H, Mes-H), 6.76 (d, J = 1.5 Hz, 1H, im-H), 6.58 (ddd, J = 7.5, 4.8, 1.1 Hz, 1H, py-H), 6.37 (d, J = 1.5 Hz, 1H, im-H), 5.50 (s, 2H, CH₂), 2.13 (s, 3H, CH₃), 2.10 (s, 6H, CH₃). ¹³C NMR (151 MHz, C₆D₆) δ 218.29 (im-C²), 159.46 (py-C), 149.44 (py-C), 139.26 (Mes-C), 137.18 (Mes-C), 136.38 (py-C), 135.41 (Mes-C), 129.11 (Mes-C), 122.23 (py-C), 121.84 (py-C), 121.28 (im-C), 119.43 (im-C), 57.24 (CH₂), 21.02 (CH₃), 18.17 (CH₃). Anal. Calcd for C₁₈H₁₉N₃: C, 77.95; H, 6.90; N, 15.15. Found: C, 77.30; H, 7.10; N, 15.35.

Synthesis of 2b (1-mesityl-3-(6-mesityl-picolyl)imidazol-2-ylidene). To the mixture of **1b** (476.5 mg, 1.00 mmol) and KO^tBu (112.2 mg, 1.00 mmol) was added 5 mL of diethyl ether. The mixture was stirred at room temperature for 1 h before filtered through Celite. The filtrate was slowly concentrated to dryness under vacuum to afford 2b as a white crystalline solid, which was washed with pentane (3 × 1 mL) and dried under high vacuum (311.4 mg, 79%). Crystals suitable for X-ray crystallography were obtained by cooling a concentrated diethyl ether solution at -35 °C. ¹H NMR (600 MHz, C_6D_6) δ 7.15 – 7.10 (overlapping, 2H, py-H), 6.87 (overlapping, 2H, Mes-H), 6.81 (d, J = 1.6 Hz, 1H, im-H), 6.78 (overlapping, 2H, Mes-H), 6.76 (dd, J = 7.3, 1.3 Hz, 1H, py-H), 6.39 (d, J = 1.5 Hz, 1H, im-H), 5.52 (s, 2H, CH₂), 2.20 (s, 3H, CH₃), 2.14 (s, 3H, CH₃), 2.11 (s, 6H, CH₃), 2.08 (s, 6H, CH₃). 13 C NMR (151 MHz, C₆D₆) δ 218.35 (im-C²), 160.06 (py-C), 159.18 (py-C), 139.31 (Mes-C), 138.63 (Mes-C), 137.27 (Mes-C), 137.17 (Mes-C), 136.81 (Mes-C), 135.88 (py-C), 135.44 (Mes-C), 129.12 (Mes-C), 128.73 (Mes-C), 123.43 (py-C),

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Dalton Transactions

ARTICLE

121.17 (im-C), 119.73 (im-C), 119.54 (py-C), 57.34 (CH₂), 21.19 (CH₃), 21.02 (CH₃), 20.51 (CH₃), 18.17 (CH₃). Anal. Calcd for $C_{27}H_{29}N_3$: C, 81.99; H, 7.39; N, 10.62. Found: C, 81.65; H, 7.23; N, 10.25.

Synthesis of 3[Fe]/3[Co]. To a stirring solution of 1a (138.7 mg, 0.50 mmol) in 2 mL of toluene was slowly added M(HMDS)₂ (0.25 mmol) in 2 mL of toluene. The reaction mixture was stirred overnight, and then concentrated to dryness under vacuum. The residue was extracted into diethyl ether, filtered and slowly concentrated to dryness to afford a solid of 3[Fe]/3[Co], which was washed with cold ether (1 mL) and pentane $(3 \times 1 \text{ mL})$ and dried under high vacuum.

3[Fe]. The product was a brown solid (89.8 mg, 59%). NMR data are consistent with previously reported.^{6a}

3[Co]. The product was a dark green microcrystalline solid (102.7 mg, 67%). Crystals suitable for X-ray crystallography were obtained by cooling a concentrated diethyl ether solution at -35 °C. ¹H NMR (600 MHz, C_6D_6) δ 79.02, 54.03, 20.49, 1.72, 0.22, -0.84, -6.21, -7.32, -10.88, -64.67, -120.85. μ_{eff} (Evans): 4.0 μ_B. Anal. Calcd for C₃₆H₃₆N₆Co: C, 70.69; H, 5.93; N, 13.74. Found: C, 70.42; H, 5.86; N, 13.43.

Synthesis of 4[Fe]/4[Co]. To the mixture of M(HMDS)₂ (0.25 mmol) and 2a (69.3 mg, 0.25 mmol) was added 5 mL of pentane. The reaction mixture was stirred for 10 minutes at room temperature, filtered. The filtrate was concentrated to ~1 mL and cooled to -35 °C to yield X-ray quality crystals of 4[Fe]/4[Co], which were washed with cold pentane (1 mL) and dried under high vacuum.

4[Fe]. The product was a beige crystal (104.3 mg, 64%). ¹H NMR (600 MHz, C₆D₆) δ 41.91, 37.70, 10.78, 4.84, 4.58, 3.64, 1.50, 1.33, 0.12, -0.70, -7.51. μ_{eff} (Evans): 4.9 μ_{B} . Anal. Calcd for C₃₀H₅₅N₅Si₄Fe: C, 55.10; H, 8.48; N, 10.71. Found: C, 54.86; H, 8.52; N, 10.73.

4[Co]. The product was a pine green crystal (91.5 mg, 56%). ¹H NMR (600 MHz, C₆D₆) δ 116.69, 105.52, 15.74, 12.97, 3.56, 0.09, -0.40, -3.65, -6.28, -8.02, -8.94, -17.43. μ_{eff} (Evans): 4.6 μ_{B} . Anal. Calcd for C₃₀H₅₅N₅Si₄Co: C, 54.84; H, 8.44; N, 10.66. Found: C, 54.70; H, 8.31; N, 10.50.

Synthesis of 5[Fe]/5[Co]. To the mixture of M(HMDS)₂ (0.25 mmol) and 2b (98.9 mg, 0.25 mmol) was added 5 mL of diethyl ether. The reaction mixture was stirred for 10 minutes at room temperature, filtered. The filtrate was slowly concentrated to ~1 mL and cooled to -35 °C to yield a crystalline solid of 5[Fe]/5[Co], which was washed with cold ether (1 mL) and pentane (1 mL) and dried under high vacuum. Crystals suitable for X-ray crystallography were obtained by cooling a concentrated diethyl ether solution at -35 °C. 5[Fe]. The product was a beige microcrystalline solid (134.2 mg, 70%). ¹H NMR (600 MHz, C₆D₆) δ 45.63, 11.07, 7.16, 5.29, 4.73, 4.04, 4.04, 3.60, 1.26, 0.74, 0.60, 0.12, -0.70, -3.49, -11.27. μ_{eff} (Evans): 5.0 μ_B. Anal. Calcd for C₃₉H₆₅N₅Si₂Fe: C, 60.66; H, 8.48; N, 9.07. Found: C, 60.41; H, 8.45; N, 8.87.

5[Co]. The product was a cyan microcrystalline solid. (145.8 mg, 75%). ¹H NMR (600 MHz, C₆D₆) δ 117.13, 106.97, 14.21, 5.90, 1.66, 0.34, 0.10, -0.39, -3.97, -3.98, -6.21, -7.25, -8.71, -9.64, -17.41. μ_{eff} (Evans): 4.5 μ_{B} . Anal. Calcd for C₃₉H₆₅N₅Si₂Co: C, 60.42; H, 8.45; N, 9.03. Found: C, 61.15; H, 8.13; N, 8.49.

Synthesis of 6[Fe]. To the cold (-35 °C) mixture of Fe(HMDS), (150.6 mg, 0.4 mmol) and 2a (110.9 mg, 0.4 mmol) was added 5 mL of cold (-35 °C) pentane. The reaction mixture was stirred overnight at room temperature, filtered. The filtrate was concentrated to ~1 mL and cooled to -35 °C to yield red X-ray quality crystals of 6[Fe], which was washed with cold pentane (1 mL) and dried under high vacuum (120.4 mg, 61%). Anal. Calcd for C₄₈H₇₂N₈Si₂Fe₂: C, 58.52; H, 7.37; N, 11.37. Found: C, 58.24; H, 7.11; N, 11.16. Compound 6[Fe] is dimeric in solid state and monomeric in solution at room temperature. $\mu_{\rm eff}$ (Evans) for monomer: 5.0 $\mu_{\rm B}$.

Reaction of 2a with Co(HMDS)2. Reaction of 2a and Co(HMDS)2. To the cold (-35 °C) mixture of Co(HMDS)₂ (75.9 mg, 0.2 mmol) and 2a (55.5 mg, 0.2 mmol) was added 5 mL of cold (-35 °C) pentane. The reaction mixture was stirred overnight at room temperature, filtered. The filtrate was concentrated to ~1 mL and cooled to -35 °C to yield green brown X-ray quality crystals of [Co₂(HMDS)₂L₂], which were characterized by X-ray crystallography. Attempted isolation of pure sample for elemental analysis was unsuccessful.

Synthesis of 7[Fe]/7[Co]. To a stirring solution of M(HMDS)₂ (0.5 mmol) in 5 mL of toluene was added 2b (197.8 mg, 0.5 mmol) in 5 mL of toluene. The resulting mixture was stirred at 90 °C overnight, then concentrated to dryness under vacuum. The solid residue was extracted into diethyl ether and filtered. The filtrate was slowly concentrated to ~ 1 mL, cooled to -35 °C to afford a microcrystalline solid of 7[Fe]/7[Co]. The supernatant was decanted off and the solid was washed with cold ether (1 mL) and cold pentane (3 × 1 mL) and dried under vacuum. Crystals suitable for Xray crystallography were obtained by cooling a concentrated diethyl ether solution at -35 °C.

7[Fe]. The product was a brown microcrystalline solid (212.6 mg, 69%). ¹H NMR (600 MHz, C₆D₆) δ 63.60, 57.80, 34.84, 30.19, 7.16, 3.54, 2.42, -1.02, -3.50, -6.12, -13.54, -14.16, -26.99, -33.67, -117.22. μ_{eff} (Evans): 5.3 μ_B. Anal. Calcd for C₃₃H₄₆N₄Si₂Fe: C, 64.90; H, 7.59; N, 9.17. Found: C, 64.11; H, 7.52; N, 8.88.

7[Co]. The product was a dark green microcrystalline solid (220.4 mg, 72%). ¹H NMR (600 MHz, C_6D_6) δ 90.43, 66.55, 16.67, 15.38, 10.53, 7.16, -5.10, -5.43, -7.02, -11.69, -18.34, -40.40, -51.44. μ_{eff} (Evans): 4.4 μ_B . Anal. Calcd for C₃₃H₄₆N₄Si₂Co: C, 64.57; H, 7.55; N, 9.13. Found: C, 63.78; H, 7.56; N, 9.06.

General Procedure for the Hydrosilylation Catalysis with 3[Fe] and PMHS. In a nitrogen glovebox, catalyst (0.05-1 mol%), ketones (3.34 mmol), PMHS (0.5 mL, 8.25 mmol) and a stirbar were charged in a 2-dram borosilicate glass vial. The vial was fitted with a PTFElined rubber septum screw cap. The reaction was left stirring at ambient temperature for indicated time. The vial was then removed from the glovebox and the contents were hydrolyzed with 2M NaOH (5 mL) and stirred for 90 minutes. The mixture was extracted with diethyl ether (3 \times 10 mL). The combined organic layer was washed with brine (2 × 10 mL), dried over MgSO₄, and concentrated under reduced pressure to afford the desired alcohol.

Conflicts of interest

There are no conflicts to declare.

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The Fe(II) and Co(II) complexes prepared from isolated free carbene form of the picolyl-NHC ligands display excellent catalytic activity towards the hydrosilylation of ketones.