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Silyl–pyridine–amine pincer-ligated iridium complexes for catalytic silane deuteration *via* room temperature C–D bond activation of benzene-d_6†

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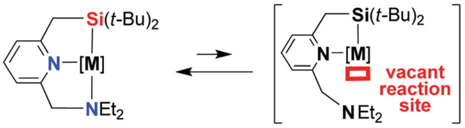
Iridium–hydrido complexes bearing a hemilabile silyl–pyridine–amine pincer ligand were synthesised. They were found to catalyse Si–H deuteration of trialkylsilanes with excess benzene-d_6 in 99–94% conversion at room temperature through C–D bond activation and H/D exchange.

The design of supporting ligands for metal catalysts toward activation and transformation of the inert C–H/C–D bonds of organic molecules is still a major challenge in coordination and synthetic chemistry.[1] As candidates for such supporting ligands, pincer ligands involving a silyl ligand moiety have recently attracted considerable attention.[2–4] Strong σ-donating and *trans*-labilising properties of the silyl ligand are expected to be effective for generating an electron-rich and coordinatively-unsaturated metal centre. These properties of the metal centre would facilitate oxidative addition of C–H/C–D bonds to it. For instance, Turculet *et al.* have reported that a PSiP-type pincer-ligated iridium complex cleaved a C–D bond of benzene-d_6 (C_6D_6) at room temperature.[3] Nevertheless, examples of silyl pincer complexes that serve as efficient catalysts for C–H/C–D bond transformation are still very limited.[2,4]

Metal catalysed bond activation of C_6D_6 is known to be applicable for Si–H deuteration of hydrosilanes *via* H/D exchange that gives deuteriosilanes.[5–8] These products are useful for mechanistic studies of reactions involving Si–H bond activation and for isotope labelling of organic compounds.[9] Catalytic silane deuteration using C_6D_6 is regarded as a safer and straightforward method compared with a conventional one using the reaction of chlorosilanes with $LiAlD_4$. Furthermore, as a deuterium source, C_6D_6 is more readily available than D_2 gas, although the latter is still more commonly used for metal-catalysed deuteration of hydrosilanes.[10] Only a few examples of catalytic silane deuteration reactions with C_6D_6 that proceed efficiently have recently been reported.[6–8] These reactions, however, require heating at 70–80 °C for > 90% conversion.

In this work, we designed a silyl–pyridine–amine (SiNN-type) pincer ligand[4] with a lutidine backbone, abbreviated as "Lut^{SiNN}" (Scheme 1).[11,12] Because coordination of the amine moiety in metal–Lut^{SiNN} complexes is weakened by the strong *trans* influence of the silyl ligand, Lut^{SiNN} is expected to serve as a hemilabile ligand that generates a vacant reaction site at the metal centre for accommodation and bond-activation of substrates under mild conditions (Scheme 1).[13] Herein, we report the synthesis of iridium–Lut^{SiNN} complexes and their high catalytic efficiency for deuteration of trialkylsilanes *via* C–D bond activation of C_6D_6 at room temperature.

Iridium–hydrido complexes bearing the silyl–pyridine–amine pincer ligand Lut^{SiNN} were synthesised by reactions of a ligand precursor, 2-(di-*tert*-butylsilyl)methyl-6-[(diethylamino)methyl]-pyridine (HLut^{SiNN}), with $[IrCl(coe)_2]_2$ (Scheme 2). Thus, treatment of HLut^{SiNN} with $[IrCl(coe)_2]_2$ (0.4 equiv.) at 60 °C for 24 h in toluene afforded a mixture of a 16-electron iridium complex, Ir(Lut^{SiNN})(H)Cl (**1**), and an unidentified iridium complex **A** containing the Lut^{SiNN} and hydrido ligands (see the ESI† for NMR data of **A**). For the purpose of converting these products into isolable compounds, the mixture was treated with 4-(dimethylamino)-pyridine (DMAP, 1.1 equiv. to Ir) at room temperature for 10 min to give a DMAP-coordinated complex Ir(Lut^{SiNN})(H)(DMAP)Cl (**2**) in 62% isolated yield (Scheme 2).[14] DMAP-free complex **1** was eventually synthesised in 75% isolated yield by heating a 0.4 : 1 mixture of $[IrCl(coe)_2]_2$ and HLut^{SiNN} in toluene at a higher temperature (70 °C) for a longer period (3 days). At this stage,



Scheme 1 Silyl–pyridine–amine pincer ligand (Lut^{SiNN}) and its expected hemilability.

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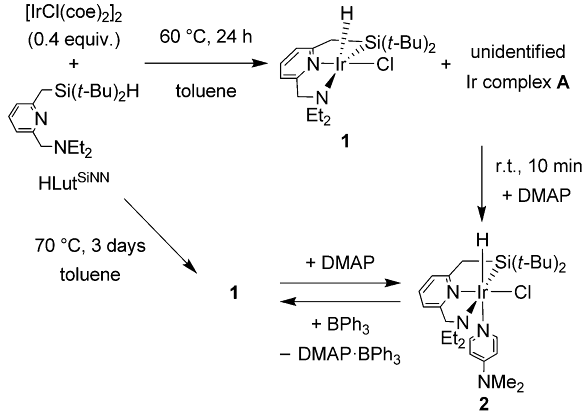
† Electronic supplementary information (ESI) available: Synthetic and experimental procedures, characterisation data, details of X-ray crystallographic analysis and NMR spectra. CCDC 1590105 (for **1**), 1590106 (for **2**) and 1879207 (for **2′**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c8cc09178a



Scheme 2 Synthesis of iridium–Lut^{SiNN} pincer complexes.

unidentified complex **A** mostly diminished. These results imply that unidentified complex **A** is an intermediate for the formation of **1**. The ^{1}H and ^{29}Si{^{1}H} NMR spectra of **1** and **2** in C_6D_6 show Ir–H signals at −25.58 (**1**) and −21.21 (**2**) ppm and Ir–Si signals at 25.2 (**1**) and 7.4 (**2**) ppm, respectively. Complexes **1** and **2** were also found to be interconvertible: **1** reacted instantaneously with DMAP (1 equiv.) in C_6D_6 at room temperature to give **2** quantitatively, while the reverse reaction proceeded by treatment of **2** with Lewis acid BPh_3 (1 equiv.) at room temperature accompanied by the formation of DMAP·BPh_3 (Scheme 2).

Single crystal X-ray analysis revealed that complex **1** (Fig. 1(a)) possesses a five-coordinate Ir centre with Lut^{SiNN}, hydrido and chlorido ligands, where the Ir–H bond is tilted toward the silyl silicon (Si–Ir–H angle = avg. *ca.* 60°).[15] The position of this hydrido hydrogen was also supported by a DFT optimised structure of **1** (Si–Ir–H = 64°, see the ESI†). On the other hand, complex **2** (Fig. 1(b)) has a six-coordinate, octahedral geometry with a tridentate Lut^{SiNN} ligand in a meridional coordination mode. The Ir–N(amine) bond distance of **2** (2.386(4) Å) is considerably elongated in comparison with that of **1** (avg. 2.24 Å)[15] by *ca.* 0.15 Å. In contrast, the Ir–Si and Ir–N(pyridine ring of Lut^{SiNN}) bond distances of **2** (2.2938(11) and 2.019(4) Å, respectively) remain almost unchanged from the corresponding bond distances of **1** (avg. 2.30 and 2.00 Å,[15] respectively). This observation indicates that the strength of the Ir–N(amine) coordinate bond varies flexibly depending on the steric environment around the metal centre and possibly its electronic properties. The Ir–N(DMAP) bond distance of **2** (2.212(4) Å) is longer than that of the Ir–N(pyridine ring of Lut^{SiNN}) bond by 0.19 Å, which is attributable to the large *trans* influence of the hydrido ligand trans to DMAP.

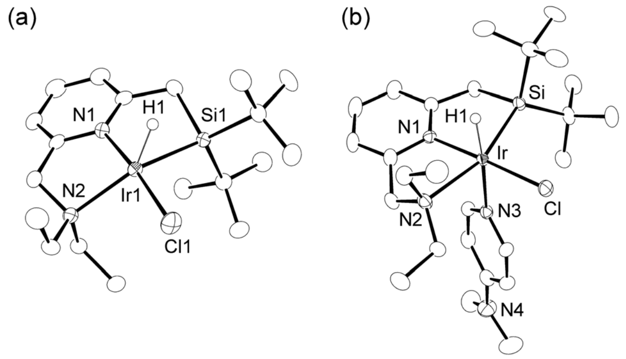
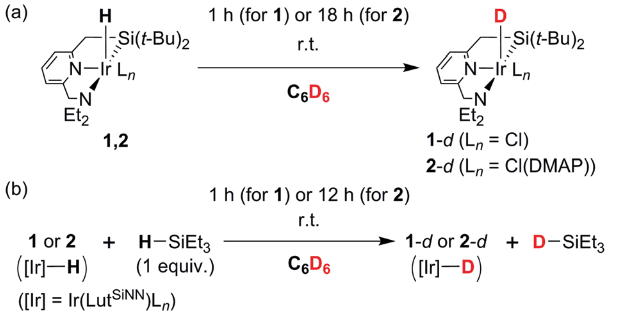


Fig. 1 Crystal structures of complexes **1** (left, (a)) and **2** (right, (b)) (50% probability ellipsoids for all non-hydrogen atoms). Hydrogen atoms except the hydrido hydrogen are omitted for clarity. For **1**, because there is no significant difference between the structures of two crystallographically independent molecules **1**-A and **1**-B, only the structure of **1**-A is depicted. For selected interatomic distances and angles, see the ESI.†

DMAP complex **2** in solution shows dynamic behaviour possibly caused by the dissociation of the amine coordinating moiety of the pincer ligand Lut^{SiNN}.[16] In the ^{1}H NMR spectrum of **2** in toluene-d_8 at 300 K, two remarkably broadened signals for the methyl groups of NEt_2 of Lut^{SiNN} appeared at 0.59 and *ca.* 1.1–1.6 ppm while two signals for the *t*-Bu groups on Si remained inequivalent (see Fig. S2 in ESI†). Upon cooling the solution to 260 K, the broad signals for the NEt_2 methyl groups changed to two triplets (0.53 and 1.41 ppm). A 2D EXSY NMR spectrum was measured at this temperature, which showed cross peaks between these triplets (Fig. S3 in ESI†). These observations indicate that the dynamic behaviour involves the exchange of the two inequivalent ethyl groups on the amine nitrogen. This behaviour is considered to occur through dissociation/coordination of the amine nitrogen accompanied by nitrogen inversion (see Scheme S1 in the ESI†). We therefore can regard that Lut^{SiNN} serves as a hemilabile ligand.

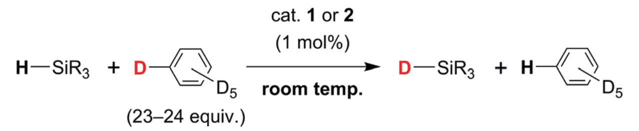
The Ir–H hydrogens of complexes **1** and **2** were readily deuterated in benzene-d_6 (solvent, 1×10^3 equiv.) at room temperature (Scheme 3(a)). ^{1}H NMR monitoring of the reaction of **1** or **2** with C_6D_6 at room temperature showed that the intensity of the Ir–H signal gradually decreased. The deuteration reaction of coordinatively-unsaturated complex **1** was much faster than that of **2**: 97% deuteration of Ir–H of **1** was achieved in 1 h while that of **2** took 18 h. The ^{2}H NMR spectrum of each of the reaction mixtures of deuteration showed an Ir–D signal at −25.2 (**1**-*d*) or −21.0 (**2**-*d*) ppm.

When the reaction of **1** or **2** with excess C_6D_6 as a solvent was performed in the presence of a stoichiometric amount of hydrosilane, not only Ir–H but also Si–H was deuterated *via* activation of the C–D and Si–H bonds (Scheme 3(b)). Thus, treatment of complex **1** or **2** with 1 equiv. of triethylsilane in benzene-d_6 at room temperature for 1 h (for **1**) or 12 h (for **2**) gave



Scheme 3 (a) Deuteration of Ir–H of complexes **1** and **2** with excess C_6D_6 and (b) Si–H deuteration reactions of $HSiEt_3$ in the presence of a stoichiometric amount of **1** or **2**.

Table 1 Deuteration of hydrosilanes with C_6D_6 catalysed by SiNN pincer-ligated iridium complex **1** or **2**[a]



Entry	Hydrosilane	Cat.	Time (h)	Deuterium incorporation[b] (%D)
1	$HSiMe_2Et$	**1**	1	97
2	$HSiMe_2$(i-Pr)	**1**	3	97
3	$HSiMe_2$(*t*-Bu)	**1**	9	94
4	$HSiEt_3$	**1**	2	98
5	HSi(*n*-Pr)$_3$	**1**	3	99
6	$HSiMe(OSiMe_3)_2$	**1**	9	12
7	$HSiMe_2Ph$	**1**	173	81 (50% NMR yield)[d]
8	H_2SiEt_2	**1**	1	~0
9	$HSiMe_2Et$	**2**	7	95
10	$HSiMe_2Et$	**2**	23[c]	85
11	$HSiMe_2$(i-Pr)	**2**	52	96
12	$HSiMe_2$(*t*-Bu)	**2**	72	95
13	$HSiEt_3$	**2**	12	97
14	HSi(*n*-Pr)$_3$	**2**	14	94
15	$HSiMe(OSiMe_3)_2$	**2**	47	20
16	H_2SiEt_2	**2**	6	~0

[a] Conditions: catalyst (3 μmol), C_6D_6 (0.6 mL, 6.8 mmol; neat solvent) and $HSiR_3$ (0.28–0.30 mmol). [b] Deuterium incorporation (%D) of deuterated silane $DSiR_3$ was determined by comparison of the intensity ratio of the ^{1}H NMR signals of Si–H and selected C–Hs of other substituents R with the corresponding intensity ratio for the original hydrosilane $HSiR_3$. [c] 1 mol% DMAP was added. [d] Scrambling products H/DSiMe$_3$, H/DSiMePh$_2$ and H/DSiPh$_3$ were also formed (see the ESI).

deuterated silane $DSiEt_3$ with 95–97% deuterium incorporation together with **1**-*d* or **2**-*d*. The ^{2}H NMR spectrum of the reaction mixture showed a signal of $DSiEt_3$ at 3.9 ppm.

On the basis of the stoichiometric reactions summarised in Scheme 3, we examined the catalytic Si–H deuteration of hydrosilanes using complex **1** or **2** as a catalyst and C_6D_6 as a deuterium source (Table 1). In the presence of 1 mol% 16-electron complex **1**, treatment of trialkylsilanes $HSiR_3$ (SiR_3 = $SiMe_2Et$, $SiMe_2$(i-Pr), $SiMe_2$(*t*-Bu), $SiEt_3$ and Si(*n*-Pr)$_3$) with excess C_6D_6 (23 equiv.) at room temperature gave the corresponding deuterated silanes $DSiR_3$ with high deuterium incorporation (99–94% D) (see entries 1–5 and the ESI†).[17] DMAP complex **2** is also catalytically active for silane deuteration (entries 9 and 11–14), but the reaction rates are slower than those of the corresponding reactions catalysed by **1** under the same conditions. When the deuteration of $HSiMe_2Et$ catalysed by **2** was carried out in the presence of 1 mol% DMAP (entry 10), the reaction was considerably slowed down. Even after a longer reaction time of 23 h, compared with 7 h in the absence of DMAP (entry 9) that led to 95% deuterium incorporation, only 85% deuterium incorporation of $DSiMe_2Et$ was attained. This implies that the catalytically-active species is 16-electron complex **1**, which can be generated from **2** (a catalyst precursor) by dissociation of DMAP. The reaction rate for the deuteration of $HSiMe_2R$ (R = Et, i-Pr or *t*-Bu) decreases as the trialkylsilane becomes bulkier in the following order Et > i-Pr > *t*-Bu (entries 1–3, 9, 11 and 12). A preparative-scale reaction was also examined by the use of 1.0 g of HSi(*n*-Pr)$_3$, C_6D_6 (25 equiv.) and 0.1 mol% **2** at 28 °C for 19 h, which gave DSi(*n*-Pr)$_3$ (98% D) in 76% isolated yield.

On the other hand, reactions of the siloxy-substituted tertiary silane ($HSiMe(OSiMe_3)_2$) and the dihydrosilane (H_2SiEt_2) in the presence of 1 mol% **1** or **2** (entries 6, 8, 15 and 16) resulted in low or undetectable deuterium incorporation. In the reaction of aryl-substituted tertiary silane $HSiMe_2Ph$ catalysed by **1** (entry 7), scrambling of the Me and Ph substituents occurred competitively, and deuterium incorporation in the resulting hydrosilanes was high (*ca.* 74–88%) in most cases (see the ESI†).

Nevertheless, the catalytic activity of **1** and **2** for the Si–H deuteration of trialkylsilanes with C_6D_6 is significantly higher than that of previously-reported catalysts.[5–8] On the basis of the observation of the dynamic behaviour of complex **2** in solution *via* dissociation of the amine nitrogen of Lut^{SiNN} (hemilability of Lut^{SiNN}), we tentatively propose a mechanism for catalytic Si–H deuteration shown in Scheme S2 (see the ESI†). In this mechanism, the labile amine nitrogen of Lut^{SiNN} in catalytic intermediates easily dissociates to generate enough space to activate the C–D/Si–H bonds on iridium. This phenomenon possibly contributes to the high catalytic activity of **1** and **2**.

In conclusion, we have demonstrated that silyl–pyridine–amine pincer-ligated iridium–hydrido complexes **1** and **2** served as powerful catalysts for Si–H deuteration of trialkylsilanes with benzene-d_6. This deuteration proceeds *via* C–D/Si–H bond activation and H/D exchange on iridium at room temperature. The activation of the inert C–D bonds is considered to be accelerated not only by the electron-rich Ir centre generated by the strong σ-donation of the silyl ligand, but also by the facile generation of a vacant site on Ir due to the hemilability of the pincer ligand Lut^{SiNN}.

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Conflicts of interest

There are no conflicts of interest to declare.

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14 Complex **2** was found to isomerise nearly quantitatively upon heating at 60 °C for 3 days in toluene to a thermodynamically more stable complex **2′** through exchange of the positions of the DMAP and chlorido ligands of **2** (see the ESI† for the synthetic procedure and characterisation of **2′**).

15 The average bond distance or angle for the two crystallographically independent molecules of **1**.

16 Five-coordinate complex **1** was also found to show dynamic behaviour in solution on the basis of variable-temperature ^{1}H NMR measurements (see the ESI†). However, in this case, exchange of the two Et groups on the amine nitrogen, the two *t*-Bu groups on silicon and each of the two methylene protons of the py-CH_2-N and py-CH_2-Si moieties occurs simultaneously. For instance, the ^{1}H NMR spectrum of a solution of **1** in toluene-d_8 at 300 K shows a sharp triplet for the Me groups of NEt_2 at 1.11 ppm and a single broad signal for the *t*-Bu groups at 1.30 ppm (see Fig. S1 in the ESI†). Upon cooling the solution to 230 K, these ^{1}H NMR signals split into two inequivalent triplets (1.09 and 1.13 ppm for Me) and singlets (1.24 and 1.55 ppm for *t*-Bu), respectively. This behaviour can be explained by migration of the hydrido ligand in the NMR timescale between the upper and lower sides of the SiNN plane.

17 Deuterated silanes were identified by ^{1}H, ^{2}H and ^{29}Si NMR spectroscopy (see the ESI†).