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Catalytic deuteration of silanes mediated by *N*-heterocyclic carbene-Ir(III) complexes[†]

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The catalytic activity of a series of coordinatively unsaturated NHC-M(III) (M = Rh, Ir; NHC = N-heterocyclic carbene) complexes was tested in the deuteration of secondary and tertiary silanes. Among these, $[IrCl(I^tBu')_2]$ provides the highest conversions to the deuterated species. Mechanistic studies high-light the reversible nature of the *ortho*-metalation reaction.

Isotopically labeled compounds play an ever increasingly important role in chemistry. Be it as a mechanistic probe¹ or in medicinal uses,² compounds containing an unnatural abundance of rare isotopes are highly desirable. Few reports in the literature have been published which deal with the catalytic formation of deuterosilanes; despite the fact that silanes play such an important role in organic synthesis.³ Initial reports utilized Au and Cu heterogeneous catalysts for isotopic exchange of the Si–H/D bond.⁴ More generally, deuterosilanes have been prepared by reacting either KSiR₃ with D₂O or reacting the protio-silane with LiAlD₄, however both methods involve the use of potentially dangerous inorganic hydrides in stoichiometric amounts.⁵ Alternative methodologies, especially one involving a catalytic transformation would be highly desirable for this transformation.⁶

In 2004, our group reported the synthesis of a series of coordinatively unsaturated complexes, which were subsequently shown to have the ability to reversibly add H_2 .⁷ The complexes are prepared (Scheme 1) by simple substitution reaction of [MCl(coe)₂]₂ (M = Ir or Rh; coe = cyclooctene) with 4 equivalents of I^tBu (I^tBu = 1,3-bis[(*tert*-butyl)]-2*H*-imidazol-2-ylidene). Complex 1 ([MHCl(I^tBu')(I^tBu)] M = Ir and Rh) is formed within 20 h and exhibits an *ortho*-metalation of one I^tBu ligand. *Ortho*-metalation of the second I^tBu is much slower and occurs over a period of 5 days and is aided by repeated removal of liberated hydrogen using vacuum. The cationic complex is formed quickly when reacted with AgPF₆. Complexes 2 and 3 are unusual in being stable 16e⁻ and 14e⁻ structures, as previously shown. Also, the intramolecular C-H

activation of I^tBu ligand is reversible. Under $H_2,\,\mathbf{2}$ can be converted back to $\mathbf{1}.$

Additionally, complex **3** has been reported to evolve into $[Ir(I^tBu)_2(H)_2][PF_6]$ when placed under one atmosphere of hydrogen.⁸ The reversible nature of the C–H bond activation of the I^tBu ligand in tandem with the electronically unsaturated nature of the metal center in these complexes prompted us to examine **2** and **3** as potential catalysts in σ -bond metathesis reactions.^{9,10}



Scheme 1 $[MHCl(I^tBu')(I^tBu)]$ (1), $[MCl(I^tBu')_2]$ (2) and $[M(I^tBu')_2][PF_6]$ (3) (M = Rh(a), Ir (b); coe = cyclooctene) complexes.

Isotopic exchange of silanes was identified as a promising reaction for just such an undertaking. Herein, we report results of an investigation of the catalytic H/D exchange of protio-silanes utilizing ambient temperature and as little as 0.5 atm of deuterium gas using several of these NHC-M(III) (M = Rh, Ir) complexes.

Reactions were carried out in a Schlenk tube in CD_2Cl_2 as shown in eqn (1).

$$H-Si\frac{\stackrel{R^{3}}{'}}{\stackrel{R^{2}}{R^{1}}} \qquad \frac{Ir(I^{t}Bu')_{2}CI (1 \text{ mol}\%)}{D_{2} (0.5 \text{ atm}), CD_{2}CI_{2}, \text{ rt}} \qquad D-Si\frac{\stackrel{R^{3}}{'}}{\stackrel{R^{2}}{R^{2}}} (1)$$

Triphenylsilane was selected as the model substrate in initial screening studies. Conversion of this silane was expected to occur slowly in view of the crowded environment about the Si–H moiety. We hoped this reaction to be slow enough to permit unambiguous catalyst optimization studies. Reactions were monitored by ¹H and ²⁹Si NMR spectroscopies as well as by FTIR spectrometry (by monitoring the $\nu_{Si-H/D}$). The catalytic performances of both Rh and Ir systems were examined. Results of the catalyst screening are shown in Table 1. Reactions in the absence of a catalyst showed no sign of H/D exchange. Both Rh catalysts proved wanting in comparison to their Ir congeners. [IrCl(I^tBu')₂] (**2b**) exhibited the highest activity amongst catalysts tested, with a conversion of 93% to DSiPh₃ after 3 h.

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 Table 1
 Catalyst screening for isotopic exchange of silanes^a

Catalyst	Conversion $(\%)^{b}$
	0
$[RhCl(I^{t}Bu')_{2}]$ (2a)	87
$[Rh(I^{t}Bu')_{2}][PF_{6}]$ (3a)	64
$[IrHCl(I^{t}Bu)(I^{t}Bu')]$ (1b)	91
$[IrCl(I^tBu')_2]$ (2b)	93
$[Ir(I^{t}Bu')_{2}][PF_{6}] (3b)$	87

^a Reaction conditions: 0.22 mmol of HSiPh₃, 1 mol% catalyst, 0.5 atm D₂, 0.8 mL CD₂Cl₂, 25 °C. 3 h. ^b Conversion determined by ¹H NMR.

Surprisingly, the formally $14 e^{-1}$ cationic complexes **3** were less active than the neutral **2**. This may be the result of either a more stable $[M(I^tBu)_2(H)_2]$ containing species for the cationic species⁸ or possibly the result of a more stable $[M(I^tBu)_2(H)(\eta^2-H-SiR_3)]$ entity *vide infra*. Regardless, the neutral complexes were found to be more efficient catalysts in this exchange reaction.

Ten silanes were examined for H/D exchange and catalytic results are presented in Table 2. Alkyl, aryl and alkoxy silanes were readily amenable to isotopic exchange. Sterically unencumbered silanes proved relatively easy to deuterate (Table 2; entries 1 and 4). Catalyst loadings for the H/D exchange involving HSiEt₃ could be as low as 0.01% with complete conversion within 3 h. (See SI, Fig. S1).

The more sterically demanding substrate, $HSi(SiMe_3)_3$ (Table 2, entry 10) required elevated temperature and longer reaction time to reach appreciable levels of deuteration. The need for longer reaction times and more elevated temperatures for the more sterically encumbered substrates suggest the transition state of the reaction is the subject of steric constraints.

Turning our attention to mechanistic aspects of the reaction, we examined first the behavior of the Ir complexes in the presence of H_2 only. Placing red solutions of **2b** under 1 atm of H_2 converts the complex to an orange solution of **1b** within minutes (See SI, Fig. S2.) Increasing the pressure to as much as 20 atm of H_2 reverses the *ortho*-metalation of the I^tBu' arm and generates [Ir(H)₂(I^tBu)₂Cl] (**4**). Releasing the pressure of H_2 from the highpressure reactor cell rapidly converts **4** back into **1b**. Unfortunately all attempts to isolate **4** proved unsuccessful.¹¹ This reactivity is in sharp contrast to that displayed by **3b** which reacts with H_2 and leads to an isolable and stable dihydride complex.⁸

Table 2 H/D isotopic exchange of silanes using $[IrCl(I^tBu')_2](2)^a$

Entry	Product	Time (h)	Loading (mol%)	Conversion (%)
1	DSiEt ₃	0.5	1.0	99
2	DSiEt ₃	3	0.01	94
3	$DSi(^{i}Pr)_{3}^{b}$	3	1.0	90
4	DSiMe ₂ ^{<i>i</i>} Bu	3	1.0	99
5	D ₂ SiPh ₂	3	1.0	95
6	DSiMe ₂ Ph	0.5	1.0	96
7	DSiMePh ₂	1	1.0	98
8	DSiPh ₃	3	1.0	97
9	DSi(OEt) ₃	3	1.0	98
10	$DSi(SiMe_3)_3^c$	16	1.0	93
11	$DSiCl(^{i}Pr)_{2}$	3	1.0	48

^{*a*} Reactions carried out in CD_2Cl_2 at 25 °C with 0.5 atm D_2 . Conversion based on integration of ¹H NMR spectra. ^{*b*} Conversion determined using ²⁹Si NMR data. ^{*c*} Reaction conducted at 50 °C with conversion based on $\nu_{Si:H/D}$ FTIR data.



Fig. 1 Free energy profile (kcal mol^{-1}) in CH₂Cl₂ of the reactivity of **1b** and **2b** with H₂.

The intermediacy of such an unstable hydride species may very well be at the origin of the H/D exchange behavior displayed by **2b**.

DFT calculations¹² resulted in the reaction profile depicted in Fig. 1. In agreement with the experiments, 1b is the more stable species. More interesting is the evolution of the reaction as indicated by the DFT calculations. While coordination of H_2 favorably occurs in the vacant coordination site of 2b (2b/H₂cis in Fig. 1) the free energy barrier connecting 2b/H₂cis to **1b** via transition state **2b/H₂cis-1b** is high (35.5 kcal mol⁻¹). Much lower, and consistent with the experimental results, is the free energy barrier (only 16.5 kcal mol^{-1}) when the addition of H₂ proceeds from 2b/H₂trans, in which the two Ir-C bonds are trans to each other.¹³ Isomer 2b/H₂trans, at 15.3 kcal mol⁻¹ above **2b** plus free H₂, is quite unstable and is a transient intermediate, since the barrier preventing it to precipitate into 1b via the 2b/H2trans-1b transition state is only 1.2 kcal/mol. The preference for 2b/H2trans-1b is explained by the preference of forming the Ir-H bond trans to the softer Cl ligand, rather than to the remaining Ir-C I^tBu' σ -bond. Once **1b** has been reached, its transformation into **4** can again occur at least via two different H₂ coordinated isomers, namely 1b/H2cis and 1b/H2trans (cis and trans indicate here the relative coordination position of H₂ and the Cl ligands). Again, the transition state presenting the forming Ir-H bond trans to the softer Cl ligand, 1b/H2trans-4 at 25.1 kcal mol⁻¹ above **1b**, is remarkably lower in energy than transition state 1b/H2cis-4, which presents the forming Ir-H bond trans to the harder H ligand.¹⁴ The high activation energy barrier in the reaction going from 1b to 4 is in stark contrast to those found for the analogous transformation from $[IrH(I^{t}Bu)(I^{t}Bu')]$ [PF₆] to $[Ir(H)_2(I^{t}Bu)_2]$ [PF₆].¹⁵ The added steric bulk of the Cl ligand in 1b within the metal coordination appears to cause significant differences in the reactivity between [IrH(I^tBu)(I^tBu')][PF₆] and [IrHCl(I^tBu)(I^tBu')] with H₂.

The DFT reaction profile is consistent with the experimental results observed in the reaction of **1b** and **2b** with H₂. As previously mentioned solutions of **2b** placed under 1 atm of H₂ were readily converted into **1b**, while in the preparation of **2b** through **1b**, H₂ must be periodically removed from the reaction mixture. The second *ortho*-metalation is calculated to be endoergonic, which is in agreement with the large H₂ overpressure required to form small amounts of **4** in solution.



Scheme 2 Model systems used in the DFT calculations.

Moving to mechanistic aspects when silanes are present, no reaction was observed when either 2b or 3b was reacted with HSiEt₃ at room temperature over the course of two days, even in the presence of a ten-fold excess of silane. Stoichiometric reactions between DSiEt₃ and the mono-hydride 1b led to mixtures of HSiEt₃ and DSiEt₃. When equimolar amounts of 1b and DSiEt₃ were reacted for 4 h, a 32% D/H exchange conversion had occurred and this slowly progressed to 70% after 5 days (see SI, Fig. S3). This suggests a possible involvement of the pendant *tert*-butyl groups of the I^tBu in the H/D exchange process. Examination of 1b in the catalytic isotopic exchange of silanes revealed it to have similar activity to that of 2b (see Table 1). This implies that reversible formal silane addition/coordination to either 2b or 1b with simultaneous de-ortho-metalation of a pendant I^tBu arm is not a viable mechanism. Further, it also suggests that a σ -CAM (σ -complex assisted metathesis) type reaction between the Ir-H bond of 1b and the silane is at least very slow under the catalytic regime. These conclusions suggest that these mechanisms are probably not operative during the H/D exchange of hydrosilanes reported in Table 1. DFT calculations are again in agreement with the experiments, since much larger free energy barriers (35.5 and 43.3 kcal mol⁻¹ for **2b** and **1b**, respectively) are indeed predicted when Me₃SiH is reacted with 2b and 1b via coordination followed by de-ortho-metalation addition (see SI, Fig. S4), and the products of Me₃SiH addition to 2b and 1b are very high in free energy (21.3 and 23.4 kcal mol^{-1} , respectively). An even higher free energy barrier, 63.2 kcal mol⁻¹, is predicted for the σ -CAM reaction between 1b and Me₃SiH.

To highlight if the unfavorable reactivity of Me_3SiH with 2b and 1b via coordination/addition or σ -CAM depends on steric or electronic factors, we investigated the reactivity of Me_3SiH with model systems 2b-xs and 1b-xs, which are model systems that minimize steric stress on the reacting atoms.

De-*ortho*-metalation of **2b-xs** by Me₃SiH is calculated to give an addition product that is 5.5 kcal mol⁻¹ more stable than **2b-xs** + free Me₃SiH, indicating that the poor reactivity of **2b** with silanes is probably driven by steric factors. Differently, the transition state for the σ -CAM reactivity between **1b-xs** and Me₃SiH is calculated at 49.7 kcal mol⁻¹, which is quite lower than that calculated for the σ -CAM reactivity between **1b** and Me₃SiH, but still extremely high in energy, which indicates that the poor σ -CAM reactivity between **1b** and silanes is probably driven by electronic factors.

In conclusion, we have highlighted the catalytic activity of complexes 1 and 2 in the H/D exchange of hydrosilanes. Reactions were found to proceed with good conversion to the corresponding deuterio-silane at ambient temperatures with catalytic loadings as low as 0.01 mol%. Preliminary

synergistic experimental and computational work allowed us to clarify the mechanism of interconversion between **2b**, **1b** and **4** in the presence of D_2 . The same work allowed to exclude a series of plausible mechanisms for the Si–H/D exchange, which suggests a more complex scenario, which is not unusual when Ir-hydride species are involved.¹⁶ Clarification of the complete mechanism as well as further investigations on the nature of the interaction between Si-H bonds and metal centers in the context of these fascinating *ortho*-metalatated complexes are currently underway.¹⁷

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- 13 The closing of the Ir–C bonds in **2b** from *trans* to *cis* is an almost barrierless process, below 2 kcal mol⁻¹.
- 14 A slightly more stable isomer of **4**, presenting a highly elongated H_2 molecule coordinated *trans* to the Cl ligand is calculated at 4.6 kcal mol⁻¹ in free energy above **2b** + 2 free H_2 molecules.
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