Agostic Si–H bond coordination assists C–H bond activation at ruthenium in bis(phosphinobenzylsilane) complexes†

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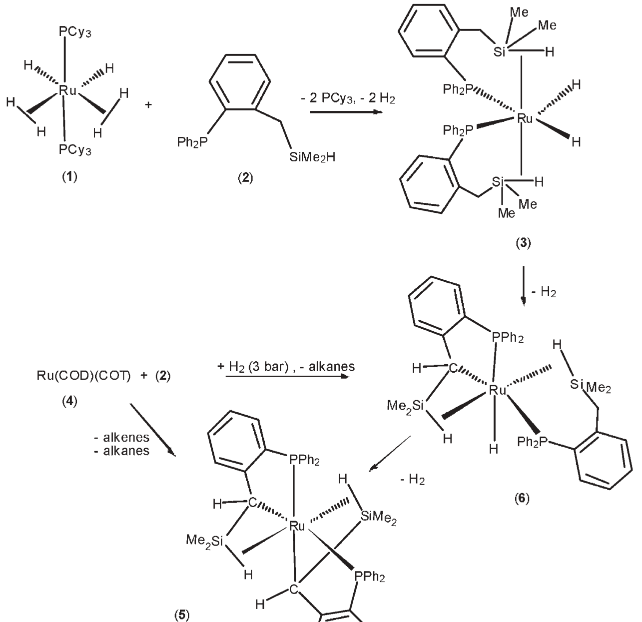
Reaction of a phosphinobenzylsilane compound with ruthenium complexes leads to C–H and/or Si–H activation. The new complex Ru{η^2-H–SiMe$_2$CH(o-C$_6$H$_4$)PPh$_2$}$_2$ (5) was isolated and X-ray, NMR and DFT studies reveal that 5 displays two agostic Si–H interactions and two carbon-metallated bonds.

Significant advances appeared concomitantly in the early 1980s in the general field of bond activation. (*i*) Bergman and Graham reported the first examples of intermolecular addition of alkane C–H bonds;[1] (*ii*) Brookhart and Green developed the concept of agostic interactions;[2] (*iii*) Kubas *et al.* established the unambiguous existence of a σ-dihydrogen complex.[3] Since these findings, the development of new systems inducing E–H bond activation (E = H, C, Si …) has witnessed tremendous growth.[4,5] Understanding E–H bond activation remains a prerequisite for progress in the field if one wants to achieve selective transformations. Moreover, tandem bond activation such as C–H/Si–H activation could offer unique properties in catalysis.[6,7] As part of our ongoing program on E–H bond activation,[8] we decided to explore the coordination of phosphinosilanes toward ruthenium complexes. We reasoned that in ruthenium chemistry, these compounds could act as bidentate hemilabile ligands through P and agostic Si–H coordination.[9,10] Furthermore, among the several strategies used to activate C–H bonds, chelating assistance by the use of substrates bearing directing groups (*e.g.* ketones, nitriles *etc.*) to promote cyclometallation is an attractive method.[11] In this contribution, we describe C–H activation derived from the reactions of RuH$_2$(η^2-H$_2$)$_2$(PCy$_3$)$_2$ (**1**) and Ru(COD)(COT) (**4**) towards the potentially chelating phosphinobenzylsilane ligand Ph$_2$P(o-C$_6$H$_4$)CH$_2$SiMe$_2$H (**2**).

Complex **1** reacts with 2 equiv. of **2** affording RuH$_2${η^2-H–SiMe$_2$CH$_2$(o-C$_6$H$_4$)PPh$_2$}$_2$ (**3**) as the main product (Scheme 1). The reaction results from the formal substitution of the two dihydrogen and the two tricyclohexylphosphine ligands in **1** by two phosphinobenzylsilane ligands, with the Si–H bonds bound to Ru in an agostic fashion. At room temperature, the ^{1}H NMR spectrum of **3** displays one broad signal in the hydride region at −7.8 ppm. Decoalescence is observed at 273 K and two broad signals in a 1 : 1 ratio can be seen at −5.2 ppm ($\omega_{1/2}$ = 40 Hz) and −10.4 ppm (AA′XX′ pattern, $\omega_{1/2}$ = 94 Hz with the two main lines separated by Δ = 30 Hz) at the low temperature limit (193 K). The observed decoalescence is attributable to the Si–H/Ru–H exchange and characterized by a $\Delta G^{\ddagger}$ of 48.2 kJ mol^{-1}, a value within the range of those previously reported for the exchange between two types of hydrides (M–(η^2-Si–H) and M–H).[12,13] The ^{29}Si NMR spectrum shows a singlet at δ = +8.3 ppm with small $J_{\text{Si–H}}$ coupling constants of 28 and 15 Hz for the agostic and classical hydrides, respectively.[14] The ^{31}P{^{1}H} NMR spectra at all temperatures show only one signal at δ = 39.2 ppm in agreement with two equivalent phosphines. As expected, **3** shows similar spectroscopic properties to those some of us previously reported for a series of bis(silane) compounds of general formula RuH$_2${(η^2-H–SiMe$_2$)$_2$X}(PCy$_3$)$_2$ (X = C$_6$H$_4$, (CH$_2$)$_2$, (CH$_2$)$_3$, OSiMe$_2$O).[15] These data lead us to propose the structure shown in Scheme 1 with a *cis* disposition of the phosphine ligands. This is also consistent with DFT calculations performed at the B3PW91 level on the model RuH$_2${η^2-H–SiMe$_2$CH$_2$(o-C$_6$H$_4$)PH$_2$}$_2$. Two



Scheme 1 Reactivity of the phosphinobenzylsilane compound **2** with ruthenium precursors. Synthesis of the bis(carbometallated) complex **5**.

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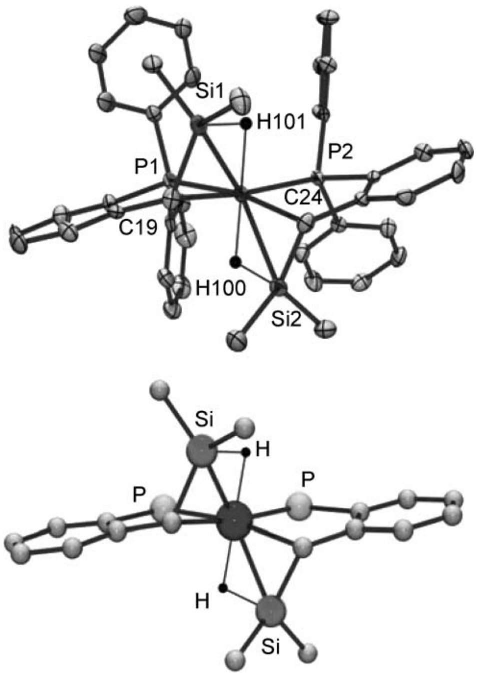

Fig. 1 X-Ray structure of **5** (top) and computed DFT/B3PW91 structure of **5b** (bottom) (non-relevant H atoms omitted for clarity). Ellipsoids in **5** are shown at the 50% probability level. Selected bond lengths (Å) and angles (°), with the DFT data in parenthesis for comparison: Ru–Si(1) 2.4587(13) (*2.454*), Ru–Si2 2.4367(13) (*2.454*), Ru–C19 2.263(4) (*2.241*), Ru–C24 2.244(4) (*2.241*), Ru–H100 1.71(4) (*1.709*), Ru–H101 1.68(4) (*1.709*), Si2–H100 1.76(4) (*1.709*), Si1–H101 1.65(3) (*1.709*), Si1–Ru–Si2 120.01(5) (*121.02*), P1–Ru–P2 107.10(4) (*102.50*), H100–Ru–H101 175.1(18) (*178.94*), Ru–H101–Si1 95.2(19) (*91.80*), Ru–H100–Si2 89.4(18) (*91.80*).

isomers (see ESI†) with the phosphorus in a *trans* (**3a**) or *cis* (**3b**) disposition were optimized. **3a** being the highest in energy (+33.6 kJ mol^{-1}).

More interestingly, when the addition of **2** was performed on Ru(COD)(COT) (**4**), the new species Ru{η^2-H–SiMe$_2$CH(*o*-C$_6$H$_4$)PPh$_2$}$_2$ (**5**) was detected as the sole product by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy, and isolated in 92% yield (Scheme 1). Its formulation as a bis(cyclometallated) species, resulting from C–H activation of the methylene groups of the starting ligand **2**, was ascertained from NMR, X-ray‡ and consistent with DFT data. The molecular structure of **5** is shown in Fig. 1. The geometry around the ruthenium centre is a bicapped pseudo-octahedron with Si atoms capping and a *cis* disposition of the other heavy atoms. Two modified phosphinobenzylsilane ligands coordinate to the metal each through a phosphorus atom, an agostic Si–H bond and a carbon atom resulting from C–H activation of the methylene group of the starting ligand. The Si–H bond lengths of *ca.* 1.70 Å, as determined from X-ray data and consistent with B3PW91 calculations on the model RuH$_2${η^2-H–SiMe$_2$CH(*o*-C$_6$H$_4$)PH$_2$}$_2$ (**5b**),[16] are typical of η^2-H–Si bonds. The metallated Ru–C bond lengths of *ca.* 2.24 Å are characteristic of Ru–C single bonds. Multinuclear NMR data highlight the unusual coordination of the ligand. In particular, the two equivalent agostic Si–H hydrides resonate as one triplet at −9.8 ppm ($J_{\mathrm{P–H}}$ = 9 Hz) with satellites due to coupling with silicon ($J_{\mathrm{Si–H}}$ = 67 Hz). The metallated C–H proton resonates as a broad singlet at 2.2 ppm, whereas the Ru–C resonance appears shielded at 24.8 ppm ($J_{\mathrm{C–H}}$ = 141 Hz) in the ^{13}C NMR spectrum. One ^{31}P{^{1}H} NMR singlet is observed at 56.9 ppm at all accessible temperatures.[17]

Complex **5** is also obtained quantitatively upon dihydrogen loss from solutions of **3**. Moreover, even under a dihydrogen atmosphere, THF, benzene or toluene solutions of **3** are not stable over a period of days and **5** is formed presumably *via* the mixed complex RuH{η^2-H–SiMe$_2$CH$_2$(*o*-C$_6$H$_4$)PPh$_2$}{η^2-H–SiMe$_2$CH(*o*-C$_6$H$_4$)PPh$_2$} (**6**) as detected spectroscopically. Independently, **6** can also be obtained as the major product from the reaction of **4** with 2 equiv of **2** under 3 bar of dihydrogen for two hours. The main NMR features of complex **6** are two ^{29}Si NMR signals at δ = 11 ppm and at δ = −13 ppm for the non-metallated and the carbometallated ligands respectively, and two ^{31}P{^{1}H} NMR doublets (δ 56.5 and 42.7 ppm, $^2J_{\mathrm{P–P}}$ 21 Hz). The three hydride resonances appear as a broad signal at δ = −6.0 ppm ($J_{\mathrm{Si–H}}$ = 76 Hz), a pseudo-triplet at −8.0 ppm ($J_{\mathrm{P–H}}$ = 21 and 27 Hz) and a doublet of doublets at −9.4 ppm ($J_{\mathrm{P–H}}$ = 24 Hz and 54 Hz). The $J_{\mathrm{Si–H}}$ value is in agreement with the presence of at least one agostic Si–H bond and a SISHA interaction.[5f] The proposed structure is consistent with the ground-state structure of **6** computed at the DFT/B3PW91 level (see ESI†).

Agostic C–H interactions preluding C–H activation are well known,[4,18] and Berry *et al.* have described tandem β-C–H activation/Si–H elimination reactions.[6] We show here that the bis(agostic) Si–H complex **3**, displaying rare high order ε-agostic Si–H interactions (to the best of our knowledge no precedent higher than δ-agostic is known) leads finally to **5**, with two β-agostic interactions as a result of C–H activations. The increased acidity of the methylene groups of the ligand in complex **3** coupled with the presence of agostic Si–H bonds, which can easily decoordinate, induce a stepwise H$_2$-loss process resulting ultimately in the formation of the stable bis(carbometallated) complex **5**. Whilst C–H activation occurring α to a heteroatom could be expected,[4] it is worth noting that in our system such a reaction proceeds with final preservation of the agostic Si–H bonds in **5** and **6**. A facile dissociation–recoordination pathway could end in the formation of the carbometallated species whilst reforming the agostic Si–H bonds in the final stable products. Although no conclusive mechanistic evidence could be found, the agostic Si–H interactions favour in some way the C–H activation process.

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16 ΔE between the structures with *trans* (**5a**) and *cis* (**5b**) phosphines is 16.4 kJ mol^{-1} at the B3PW91 level, **5b** being the most stable isomer.

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