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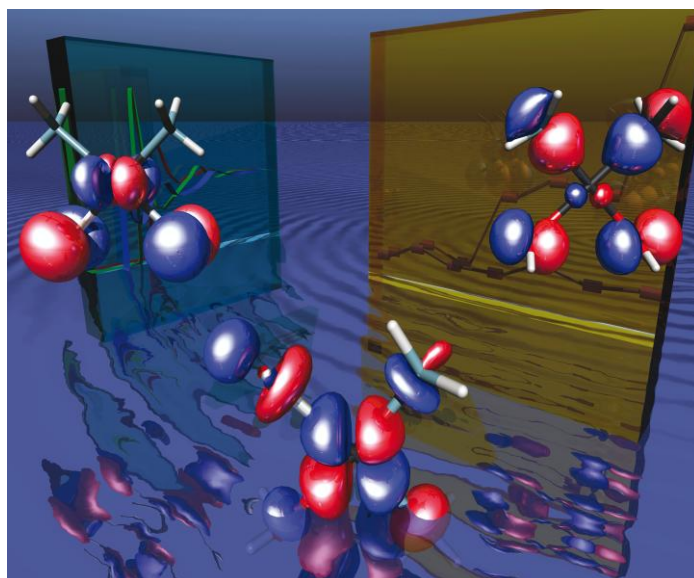


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DFT calculations of ^{29}Si -NMR chemical shifts in Ru(II) silyl complexes: Searching for trends and accurate values†

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The ^{29}Si chemical shifts in a series of closely related Ru(II) silyl complexes have been calculated by DFT methods and compared to the experimental values. The factors that lead to possible discrepancies between experimental and calculated values have been identified. It is shown that it is necessary to include the spin-orbit coupling associated with the relativistic effects of the heavy atoms for quantitative agreement with observed chemical shifts but trends are reasonably reproduced when the calculations do not include this correction. An NBO analysis of the NMR contributions from the bonds to Si and the Si core shows the greater importance of the former and a fine tuning originating from the latter.

Introduction

Nuclear Magnetic Resonance (NMR) is nowadays routinely used for structural assignment and a key source for identification when the X-ray determination of a crystal structure fails. Computational determination of nuclear magnetic shielding of various nuclei can contribute to better associate NMR measurements with detailed structure. Computational determination of NMR chemical shifts leads to good results for atoms like ^{13}C , ^{14}N , ^{29}Si , at least when these atoms are not in the vicinity of heavy atoms.^{1,2} However, calculation of NMR chemical shifts is far from routine for transition metal complexes especially for systems of large size that can be compared to experimental values. In this work, we focus on the ^{29}Si -NMR chemical shifts in a set of closely related Ru(II) silyl complexes and we compare several methods to determine those that lead to best agreement between calculations and experiment. The methods thus validated can be used in future work as additional tools for structural determination.

The importance of relativistic effects to reproduce NMR signals for various atoms has been reported in the literature.^{3–7} These effects are directly related to the high velocities of the core electrons moving around the nucleus and the coupling between the electronic motion and their spin. They become more important when a transition metal or a heavy atom is present in the molecule. The relativistic effects are categorized as scalar or spin-orbit (SO)

effects. Scalar effects are mainly due to the velocity of the core electrons and their description in the calculations could directly affect the valence electrons. SO effects are due to the coupling between the orbital motion and the electron spin, and mainly influence the valence shell.⁸ In particular, the SO coupling has been shown to be the main cause for strong variations in the calculated chemical shifts of the active nuclei in molecules containing heavy elements. This effect is substantial when the NMR active nucleus (heavy or light) is bound to a heavy atom. This is classified as heavy atom–light atom effect (HALA) or heavy atom–heavy atom (HAHA) effect. The HALA type effect is observed on the light nuclei in the vicinity of the heavy atom while the HAHA type is affected by the relativistic effects in both heavy atoms.⁹

The calculations of NMR properties by density functional theory (DFT) also depend on how the gauge origin problem is treated.¹⁰ This problem arises from the need to expand the Kohn–Sham orbitals in a finite basis set. Generally, larger basis set decreases the gauge dependency on the chemical shift. Therefore, the choice for the basis set should reflect the needed compromise between accuracy and computational time. Different computational schemes are available for overcoming this problem, among which the gauge including atomic orbitals (GIAO)¹¹ and an individual gauge of localized orbitals (IGLO)¹² are the most widespread.

To test various methodologies, we have considered a set of closely related Ru(II) silyl complexes, $\text{RuCp}(\text{PMe}_3)_2\text{SiX}_3$ ($\text{SiX}_3 = \text{SiH}_3$, SiH_2Me , SiHMe_2 , SiMe_3 , SiH_2Cl , SiHMeCl , SiHCl_2 , SiMeCl_2 , SiPhCl_2 , SiMeCl_2 and SiCl_3 and $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$). These complexes, shown on Fig. 1, have been synthesized and characterized by Lemke *et al.* and, a detailed NMR study of the ^{29}Si chemical shift is available.^{13–15} The influence of the phosphine ligand was also studied.¹⁶

The ^{29}Si -NMR signals in these Ru silyl complexes appear between -56.7 and 92.2 ppm. Since all complexes have the same $\text{RuCp}(\text{PMe}_3)_2$ part the changes in the ^{29}Si chemical shifts should be

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† Electronic supplementary information (ESI) available: Computational details including full list of coordinates and energy for all optimized structures. Tables and graphs on the effects of functional on the ^{29}Si chemical shifts. Table of chemical shieldings for all systems associated with Fig. 4a. See DOI: 10.1039/c1dt11135c

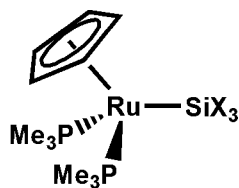


Fig. 1 $\text{RuCp}(\text{PMe}_3)_2\text{SiX}_3$ ($\text{SiX}_3 = \text{SiH}_3, \text{SiH}_2\text{Me}, \text{SiHMe}_2, \text{SiMe}_3, \text{SiH}_2\text{Cl}, \text{SiHMeCl}, \text{SiHCl}_2, \text{SiMeCl}_2, \text{SiPhCl}_2, \text{SiMe}_2\text{Cl}$ and SiCl_3 and $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$).

directly related to the silyl ligands as well as its interaction with the Ru fragment. Lemke *et al.* have established a linear relationship between ^{29}Si -NMR chemical shift and the electron withdrawing ability of the substituents on the silyl group. A similar relationship has been also established for the ^1H and ^{13}C -NMR of the silyl group in the same Ru complexes. Interestingly, the replacement of H or Me by Cl on Si moves the silicon signal upfield. This effect was called “the chloride effect” by the authors. It was suggested that the presence of a strongly electronegative atom such as Cl increases the back-donation from Ru to the Si-X σ^* orbital.¹⁴ It was also shown that the change of phosphine from PMe_3 to PMe_2Ph and PPh_2Me has a negligible influence on the ^{29}Si chemical shift.¹⁶ The list of experimentally determined ^{29}Si chemical shifts is shown in Table 1.

The ^{29}Si -NMR resonance spectrum covers a wide range of 150 ppm, which is an ideal situation for validating a computational method aimed at reproducing the silicon chemical shift in a quantitative manner. This paper presents the results for various levels of DFT calculations and highlights the role of the relativistic effects.

Computational details

A. Geometry optimization

The $\text{RuCp}(\text{PMe}_3)_2\text{SiX}_3$ ($\text{SiX}_3 = \text{SiH}_3, \text{SiMe}_2\text{H}, \text{SiMe}_2\text{H}, \text{SiMe}_3, \text{SiH}_2\text{Cl}, \text{SiHMeCl}, \text{SiMe}_2\text{Cl}, \text{SiHCl}_2, \text{SiCl}_2\text{Me}$, and SiCl_3) geometries were optimized in vacuum using the DFT (B3PW91) functional^{17,18} with the Gaussian 03 package.¹⁹ All electron basis sets for C, H (6-31G(d,p))^{20,21} and Si (cc-pvtz)²² and Stuttgart/Dresden (SDD) quasi-relativistic effective core potentials (ECPs)^{23–25} for Ru, P and Cl, with associated basis sets and additional polarization functions on the two latter atoms were used.²⁶ The optimized geometries of all complexes are given in the

Table 1 Experimental ^{29}Si NMR chemical shifts (ppm), relative to tetramethylsilane, in $\text{CpL}_2\text{RuSiX}_3$ measured in dichloromethane

SiX_3	^{29}Si -NMR δ ($\text{L} = \text{PMe}_3$)	^{29}Si -NMR δ ($\text{L} = \text{PMe}_2\text{Ph}$)	^{29}Si -NMR δ ($\text{L} = \text{PPh}_2\text{Me}$)
SiH_3	−56.7 ¹⁴	−53.9 ¹⁶	—
SiH_2Me	−13.7 ¹⁴	−14.3 ¹⁶	—
SiHMe_2	13.8 ¹⁴	—	—
SiMe_3	19.6 ¹⁴	18.4 ¹⁶	—
SiH_2Cl	36.4 ¹⁴	37.0 ¹⁶	35.5 ¹⁶
SiHMeCl	57.2 ¹³	68.4 ¹⁶	—
SiMe_2Cl	87.3 ¹³	—	—
SiHCl_2	66.8 ¹³	68.5 ¹⁶	65.8 ¹⁶
SiMeCl_2	92.2 ¹³	—	89.1 ¹⁶
SiPhCl_2	76.8 ¹⁵	—	—
SiCl_3	42.1 ¹³	44.1 ¹⁶	41.2 ¹⁶

ESI†. Single point calculations on B3PW91 optimized geometries were performed to evaluate the influence of the functional, basis sets and relativistic effects.

B. NMR calculations

Standard NMR chemical shifts were calculated with the GIAO approximation using the Gaussian 03 package. The calculations were performed with the same level of theory and basis sets used for the geometry optimization. Solvation effects were computed *via* PCM²⁷ single point calculations using dichloromethane (DCM) as solvent to reproduce the experimental conditions (see ESI† for full details).

Scalar relativistic effects were evaluated using the Douglas–Kroll–Hess (DKH),^{28–30} the Zeroth-Order Regular Approximation (ZORA),^{31,32} the Infinite-Order Regular Approximation (IORA)^{33,34} and the IORA mm (modified metric) approximations with the ORCA program.³⁵ The IGLO approximation was used for computing the chemical shifts. The same functional than this used for the geometry optimization was employed. An all-electron basis set for all atoms has been used.³⁶

Scalar and spin-orbit relativistic effects were calculated with the ZORA³¹ approximation and the ADF code.³⁷ Calculations were performed using PBE0 functional and all-electron triple- ζ polarized (TZVP)³⁸ basis set for all atoms.

Finally, the spin-orbit correction was computed by perturbation theory.^{39,40} This correction is computed using SO ECPs^{24,41} for Ru, Cl and Koseki SO effective charge approximation for C, H, P and Si by the MAG code.^{42,43} The basis sets were: SDD with ECPs for Ru and Cl, 6-31G(d,p) for H, C and P and dzvp³⁸ for Si. The resulting correction is added to the ^{29}Si shielding σ computed with Gaussian 03.

Calculated absolute chemical shieldings σ were converted to relative shifts δ using the reference tetramethylsilane (TMS) at the same level of theory. The calculated chemical shieldings are given in tables S5 and S6†.

The natural chemical shielding (NCS) analysis was performed with the natural bond orbital (NBO) program.^{44,45}

Results

A. Structural parameters

The X-ray structures of $\text{RuCp}(\text{PMe}_3)_2\text{SiX}_3$ ($\text{SiX}_3 = \text{SiCl}_3, \text{SiMeCl}_2$ and SiPhCl_2) and $\text{RuCp}(\text{PPh}_2)_2\text{SiCl}_3$ showed that the complexes adopted a three-legged “piano-stool” geometry with a Ru–Si distances of 2.28–2.31 Å consistent with a single bond and Si–Cl distances longer than in free chlorosilane (2.11–2.15 Å vs. 2.02 Å).¹⁶ The optimized geometries faithfully reproduce the structural features but give slightly longer distances at the silicon atom with Ru–Si ranging from 2.31 to 2.40 Å and Si–Cl between 2.13 and 2.17 Å. The experimental structures show that the silyl substituents adopt a staggered conformation at the Ru–Si bond with the Cp and Cl in an anti relationship. In the case of SiH_2Me , SiHMe_2 , SiH_2Cl , SiHMeCl , SiMe_2Cl , SiHCl_2 , and SiMeCl_2 , a conformational search gave the most stable staggered isomer. The results of this conformational search are shown in Fig. 2. In the most stable structure the chloride substituent is located between

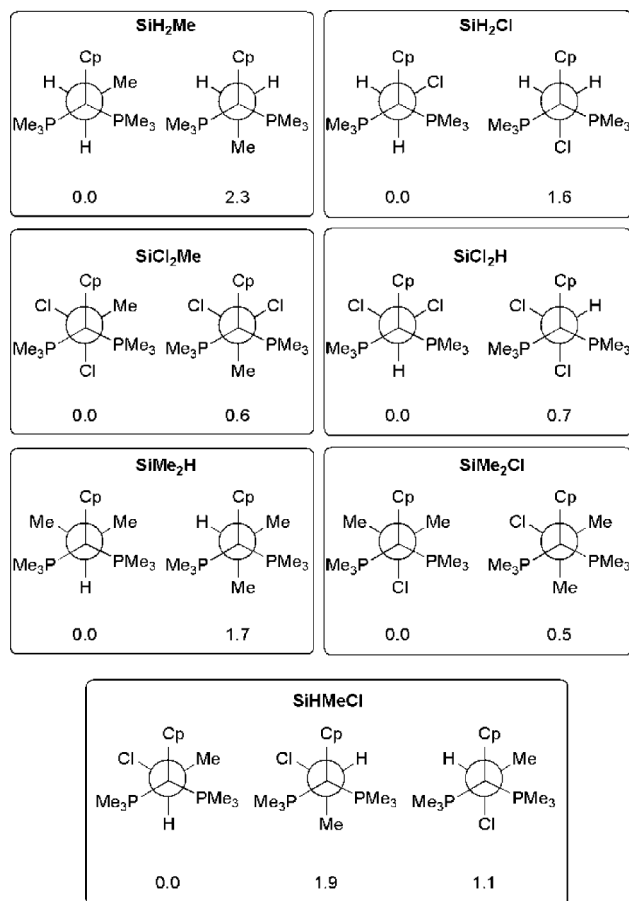


Fig. 2 Conformations of $\text{RuCp}(\text{PMe}_3)_2\text{SiX}_3$ ($\text{SiX}_3 = \text{SiH}_2\text{Me}$, SiHMe_2 , SiH_2Cl , SiHMeCl , SiMe_2Cl , SiHCl_2 , and SiMeCl_2) with energies in kcal mol^{-1} .

the Cp and one of the phosphine ligands. The difference in energy between conformers is less than $2.3 \text{ kcal mol}^{-1}$.

B. Computation of chemical shifts, δ

B.1. Choice of methodology. DFT methods have been used successfully to calculate NMR chemical shifts for organic and inorganic molecules. Good results have been obtained with hybrid-GGA functional (e.g. B3LYP, PBE0, B3PW91...), and no functional or basis-set appears to give an especially better performance.^{46,47} In the present case, these non-SO corrected using quasi-relativistic ECPs calculations of the ^{29}Si -NMR chemical shifts of $\text{RuCp}(\text{PMe}_3)_2\text{SiX}_3$ complexes were carried out using the hybrid-GGA B3PW91 functional. The computed chemical shifts are too high (deshielded) by at least 15 ppm. The overestimation of the signal does not depend on the functional or the basis set used on the Si atom. Other functionals gave similar results (see table S1 and graph S1†) and the calculated signal did not change by more than 3 ppm when an all-electron-basis-set igloIII, commonly used for calculating NMR responses, was used for Si (see table S2†).⁴⁸ Clearly, other factors are responsible for the discrepancy between the calculated and the experimental values. The need to include relativistic effects linked to the presence of heavy elements, notably Ru, clearly appears.⁴⁷ The σ -character of the Ru–Si bond could be particularly affected by the relativistic effects.

Table 2 Computed ^{29}Si -NMR chemical shifts in ppm relative to TMS for $\text{RuCp}(\text{PMe}_3)_2\text{SiH}_3$ and $\text{RuCp}(\text{PMe}_3)_2\text{SiMe}_3$ complexes

System	$\delta_{\text{expt}}^{14}$	δ_{scalar}	δ_{zora}	δ_{full}
$\text{RuCp}(\text{PMe}_3)_2\text{SiH}_3$	−56.7	−34.7	−67.8	−52.9
$\text{RuCp}(\text{PMe}_3)_2\text{SiMe}_3$	19.6	41.1	29.6	21.1

δ_{expt} : experimental chemical shift, δ_{scalar} : chemical shift calculated with scalar relativistic effects only, δ_{zora} : chemical shift including the zora SO correction and δ_{full} : chemical shift including the SO correction from perturbation theory.

Therefore, $\text{RuCp}(\text{PMe}_3)_2\text{SiMe}_3$ and $\text{RuCp}(\text{PMe}_3)_2\text{SiH}_3$ were used to investigate the various ways to take into account both, scalar and SO, relativistic effects in the ^{29}Si chemical shift.

The key need for including scalar relativistic effects was assessed by performing all-electron non-relativistic calculations. As expected, this did not lead to an improvement of the results which in fact worsened. In particular, valence electrons are no longer correctly represented and this leads to a poor description of the bonds in the molecule. Scalar relativistic effects evaluated by various methods (DKH, ZORA, IORA and IORA mm) were then considered. In all cases, the results were within 1 ppm from those obtained with the SDD ECPs (see table S3†). Therefore, scalar relativistic effects at Ru will be included *via* the SDD ECP.

Spin-orbit effects on the chemical shift were then considered. In a first set of calculations, the ZORA approximation was considered for both, scalar and SO effects.³¹ This led to a significant improvement in the results. The computed chemical shifts (−67.8 ppm for $\text{RuCp}(\text{PMe}_3)_2\text{SiH}_3$ and 29.6 ppm for $\text{RuCp}(\text{PMe}_3)_2\text{SiMe}_3$) are quite different from the values calculated in absence of spin-orbit effect (−34.7 and 41.1 ppm, respectively) and closer to the experimental values (−56.7 and 19.6 ppm, respectively).¹⁴ In a second set of calculations, SO correction was calculated by perturbation theory^{39,40} and led to even better agreement with experiment (−52.9 ppm for $\text{RuCp}(\text{PMe}_3)_2\text{SiH}_3$ and 21.1 ppm for $\text{RuCp}(\text{PMe}_3)_2\text{SiMe}_3$) (Table 2).

B.2. Calculations for the full series. Following the good results obtained for $\text{RuCp}(\text{PMe}_3)_2\text{SiH}_3$ and $\text{RuCp}(\text{PMe}_3)_2\text{SiMe}_3$ with inclusion of the spin-orbit effects calculated by perturbation theory, the same methodology was used for $\text{RuCp}(\text{PMe}_3)_2\text{SiX}_3$ ($\text{SiX}_3 = \text{SiH}_3$, SiH_2Me , SiHMe_2 , SiMe_3 , SiH_2Cl , SiHMeCl , SiMe_2Cl , SiHCl_2 , SiMeCl_2 , and SiCl_3). SO corrections, SO_{corr} , and the resulting computed chemical shift, δ_{full} , are shown in Table 3. This table also reports the experimental, δ_{expt} ,^{13,14} and the ^{29}Si -NMR shifts calculated with scalar relativistic effects, δ_{scalar} . The ^{29}Si chemical shifts δ for $\text{SiX}_3 = \text{SiH}_2\text{Me}$, SiHMe_2 , SiH_2Cl , SiHMeCl , SiMe_2Cl , SiHCl_2 , and SiMeCl_2 , have been calculated for the most stable isomer. It has been verified that the contribution of the less stable isomers has a negligible influence at our level of accuracy.

The agreement between computed and experimental data is significantly improved for the entire series when the SO corrections are included (Fig. 3). For $\text{RuCp}(\text{PMe}_3)_2\text{SiH}_3$, $\text{RuCp}(\text{PMe}_3)_2\text{SiH}_2\text{Me}$ and $\text{RuCp}(\text{PMe}_3)_2\text{SiMe}_3$ systems, the computed chemical shifts differ from the experimental values by only 3.8, 2.3 and 1.5 ppm, respectively. While the agreement is very good for the alkylsilyl groups, the calculations give poorer results for chlorosilyl groups (Fig. 3).

Table 3 Computed ^{29}Si NMR chemical shifts in ppm relative to TMS for $\text{RuCp}(\text{PMe}_3)_2\text{SiX}_3$ shown in Fig. 1

SiX_3	δ_{expt}	δ_{scalar}	SO_{corr}	δ_{full}
SiH_3	-56.7 ¹⁴	-34.7	18.2	-52.9
SiH_2Me	-13.7 ¹⁴	3.7	19.7	-16.0
SiHMe_2	13.8 ¹⁴	34.1	17.2	16.9
SiMe_3	19.6 ¹⁴	41.1	20.0	21.1
SiH_2Cl	36.4 ¹⁴	77.9	21.7	56.2
SiHMeCl	57.2 ¹³	108.4	21.7	86.7
SiMe_2Cl	87.3 ¹³	126.9	24.3	102.6
SiHCl_2	66.8 ¹³	127.5	30.3	97.2
SiMeCl_2	92.2 ¹³	147.1	33.4	113.7
SiCl_3	42.1 ¹³	119.9	35.4	84.5

δ_{expt} : experimental values; δ_{scalar} : computed values including scalar relativistic effects; SO_{corr} : calculated SO corrections by perturbation theory and δ_{full} : computed values including scalar and SO effects. δ_{full} is obtained by subtracting the SO correction from the δ_{scalar} .

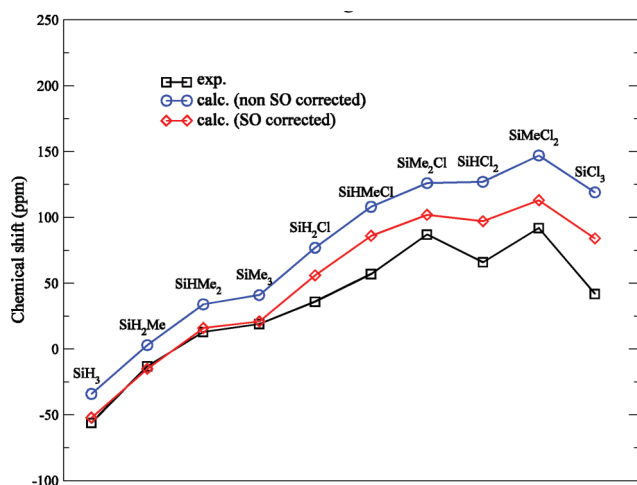


Fig. 3 Experimental and computed ^{29}Si -NMR chemical shifts for $\text{RuCp}(\text{PMe}_3)_2\text{SiX}_3$ ($\text{SiX}_3 = \text{SiH}_3, \text{SiH}_2\text{Me}, \text{SiHMe}_2, \text{SiMe}_3, \text{SiH}_2\text{Cl}, \text{SiHMeCl}, \text{SiMe}_2\text{Cl}, \text{SiHCl}_2, \text{SiMeCl}_2, \text{and SiCl}_3$) species. Black curve (squares): experimental values; blue curve (circles): calculated values with scalar relativistic effects and red curve (diamonds): calculated values including scalar and SO relativistic effects.

The same calculations were also run using the zora SO correction (see table S4†). These two methods give thus similar ^{29}Si -NMR chemical shifts.

The inclusion of the solvent effects (dichloromethane) using PCM calculations does not modify the computed trends (see tables S5 and S6†). Consequently, solvation is not at the origin of the discrepancies between the experimental and the computed values.

Interestingly, while accurate values are difficult to reach (compare the red (diamonds) and black (squares) curves in Fig. 3), a relatively good trend is obtained even in the absence of SO correction (blue -circles- in Fig. 3). As already mentioned, similar trends were obtained when different methods of including the SO correction were used.

Discussion

In order to better understand the origin of the influence of substituents of the silicon atom on the ^{29}Si -NMR chemical shifts an analysis of the shielding (NCS) in terms of natural bond orbitals

(NBOs) contributions was carried out (Fig. 4). For this analysis the SO correction is not included. The values for the experimental chemical shieldings were obtained by using the calculated value of the shielding for ^{29}Si in TMS. The experimental and calculated chemical shieldings are shown in Fig. 4a. The NBO analysis gives the contribution of each natural orbital to the total shielding. The contribution coming from the three Si–X bonds (in the case of $\text{X} = \text{Cl}$, the small contribution of the lone pairs was also included) and the Ru–Si bond were added. They represent to the contribution of the valence electrons (Si–L₄, Fig. 4b). The contribution from the Si core is shown in Fig. 4c. Numerical values are reported in table S7†.

As was already apparent in Fig. 3 for the chemical shifts, the experimental and calculated shieldings follow similar trends (black (squares) and blue (circles) curves of Fig. 4). The positive values of the shieldings come from the contribution of the core (Fig. 4c). Comparing the blue (circles) curve of Fig. 4a with those of Fig. 4b, it appears that the contributions from the Si–X bonds determine the global behaviour of the total shielding since they both vary in the same direction and by globally the same amount. From SiH_3 to SiCl_3 , the total shielding and the contribution from the valence electrons become more negative (from 353 to 198 ppm and from -274 to -447 ppm, respectively). The core contribution varies by 60 ppm which is less than the variation of the contribution of the valence electrons. Exchanging H for Me decreases the shielding from the core; from SiH_3 to SiMe_3 , the core contribution decreases from 645 to 592 ppm. In contrast, exchanging H for Cl has essentially no influence on the core contribution (from SiH_3 and SiCl_3 the core contribution varies from 645 to 657 ppm). Thus, the contribution from Si core electrons cannot be considered as constant since it significantly modifies the chemical shifts commended by the valence electrons. The influence of the core and valence electrons was also reported by Autschbach for a series of LaX_3 ($\text{X} = \text{F}, \text{Cl}, \text{Br}$ and I) complexes.⁴⁹ In this case also, the core contribution was not constant.

The substitution of a hydrogen for a chloride or a methyl ligand has a different influence on the contributions from the valence and core electrons. Exchanging H for Cl in SiH_3 lowers the shielding which becomes more negative by around 100 ppm. Substituting the second and third hydrogen of SiH_3 by a chlorine has a smaller effect. In contrast, the substitution of hydrogen by a methyl group lowers the shielding by no more than 12 ppm. The influence on the core is different. Replacing H for Cl decreases the shielding of the Si core by 10 ppm while replacing H for Me decreases the Si core by 20 ppm.

The reasons why exchanging H for Me and Cl has a different influence on the valence and core electrons are not easy to assign. Some contributing effects can be the following. Changing H for Me, can make the Si orbital more diffuse, which would decrease the shielding. In contrast, exchanging H for Cl lowers the energy of 2p orbitals, which should lead to more contracted orbitals (see table S7†). This factor contributes to increase the contribution to the shielding from the core. Tossell *et al.*⁵⁰ also reported that the Si 2p orbital can increase the Si shielding. We could not attribute the variation of the valence electrons to any specific property of H and Cl substituents on Si.

It is thus not easy to understand qualitatively the influence of substituent on the valence shell and on the core electrons. Lemke *et al.* have found a correlation between the chemical shifts and an electronegativity property of the substituent X (Tolman electronic

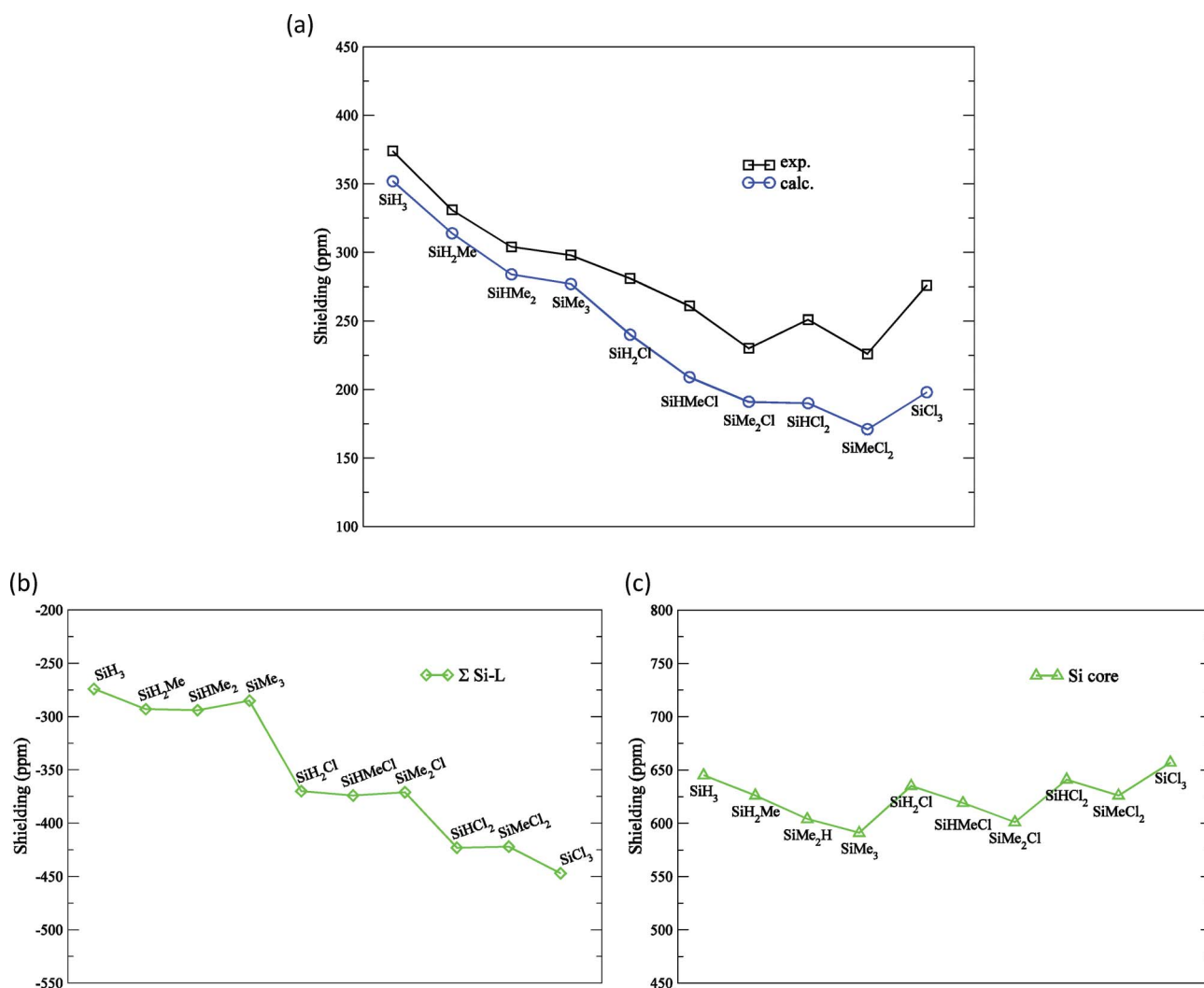


Fig. 4 (a) Experimental (black-squares) shieldings calculated using calculated TMS and computed shieldings (blue-circles), in ppm, for RuCp(PMe)₃SiX₃ (SiX₃ = SiH₃, SiH₂Me, SiHMe₂, SiMe₃, SiH₂Cl, SiHMeCl, SiMe₂Cl, SiHCl₂, SiMeCl₂, and SiCl₃). Contributions to the shielding from (b) Σ Si-L bonds compositions and (c) the Si core were calculated by NCS-NBO.

parameter, χ_i). The sum of χ_i was used to assign the donating power of PX₃ as measured by the A₁ ν_{CO} stretching frequencies of Ni(CO)₃(PX₃).⁵¹ However, good correlations were also reached by constructing separate correlation lines between the silyl groups with and without chlorine atoms. Lemke invoked the back-donating from the lone pair of Ru to the $\sigma^*_{\text{Si-Cl}}$. The magnitude of this effect could not be established by the NBO analysis done in this study. Our present approach is rather different since it enables to link the NMR shielding to the bonds and core of the NMR active nucleus *via* an NCS analysis. This analysis highlights a different effect on the valence and core electrons if an H is substituted by Me or Cl. However, more studies and in particular calculations of different chemical systems are needed to establish the generality of our results and better understand their origin.

Conclusions

DFT calculations have reproduced the ²⁹Si-NMR chemical shifts for a set of ruthenium silyl complexes, RuCp(PMe)₃SiX₃ (SiX₃ = SiH₃, SiH₂Me, SiHMe₂, SiMe₃, SiH₂Cl, SiHMeCl, SiMe₂Cl,

SiHCl₂, SiMeCl₂, and SiCl₃) with good to fair accuracy. Different approaches were used to obtain a better insight into NMR chemical shifts. The results show that the relativistic effects and notably the spin-orbit correction becomes decisive for obtaining a good agreement between experiment and computed results. This is most likely due to the fact that Si is directly bound to Ru. However, trends are reproduced in an acceptable manner with a level of calculation used for calculating structural properties as long as a quasi-relativistic ECP is used for the heavy atoms. However, discrepancies between calculations and experiment are fairly large for chlorosilyl groups.

An NBO analysis of the contributions of the chemical shielding of the bonds at Si and of the Si core show influences which are different for H and Me on one hand, and Cl on the other hand. Additional studies are needed to establish the generality of these findings and obtain a better understanding of the effect of substituent on heavy atom NMR chemical shifts. However, a key result of this study is the need to include the spin-orbit correction when the active nucleus is next to a transition metal centre.

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