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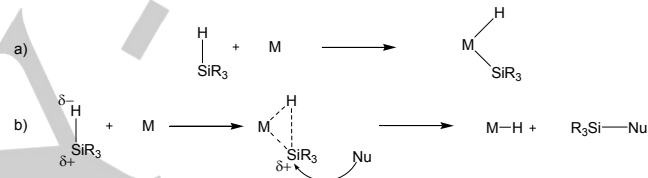
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Is the R_3Si Moiety in Metal-Silyl Complexes a Z ligand ? An Answer from the Interaction Energy

Dang Ho Binh^[a], Milan Milovanović^{[a], [b]}, Julia Puertes-Mico^[a], Mustapha Hamdaoui^[a], Snežana D. Zarić^{[b], [c]} and Jean-Pierre Djukic^{[a],*}

Abstract: The computation of metal-silyl interaction energies indicates the existence of situations where the silyl group behaves as a Z-type ligand according to Green's covalent bond classification method. It is shown that a scale of relative intrinsic silylicity \mathcal{I} , defined as the ratio of the intrinsic silyl-to-triflate interaction energy of a silyltriflate taken as reference compound and that of the silyl-to-metal interaction of given complex, can reveal in a straightforward manner the propensity of SiR_3 groups to behave chemically as metal-bound "silyliums" $[SiR_3]^+$. Emblematic cases of the literature, either taken from the Cambridge Structural Database or constructed for the purpose of this study, were also investigated under the lights of ETS-NOCV and QTAIM analyses. It is shown in one case, i.e. POBMUP the iridium-POCOP complex isolated by Brookhart *et al.*, how slight variations of molecular charge and structure can affect drastically the relative intrinsic silylicity of the $SiEt_3$ group that is weakly bonded to the hydrido-iridium motif.

variants were proposed: the so-called "two-silicon" proposal^[4], the "modified Chalk-Harrod"^[5], the "Glaser-Tilley"^[6], the "Ojima"^[7], the "Zheng-Chan"^[8] and the "Hofmann-Gade"^[9] mechanisms. The " σ -bond metathesis"^[10] mechanism does not involve explicitly an oxidative-addition step. In summary, the complex electronic situation of the metal-bound silane has indeed fuelled a range of reports that dwelt with the electronic relationships within the $M(H)(SiR_3)$ unit^[2, 11], some authors considering that any metal-silane adduct wherein some Si-H interaction persists should be considered as an "arrested intermediate" of an aborted ideal oxidative-addition^[11g].



Scheme 1. The two main modes of activation of silanes : a) oxidative addition; b) heterolytic polar "electrophilic" activation of the Si-H bond.

Introduction

In a recent article, Tilley and co-workers extensively reviewed the vast research on the catalysis of organic transformations that entail the metal promoted activation of silane's Si-H bond^[1]. This update of the most salient research in the field completes other comprehensive reviews^[2] that already demonstrated the diversity of the structural features of metal-silane complexes that can be encountered along the whole series of *d*-block transition metal complexes. Moreover, Tilley's review made an important emphasis on the variety of mechanisms that metal-catalyzed hydrosilylation reactions could entail like the heterolytic Si-H bond cleavage giving rise in most cases to a key "silylium" type of reactivity of the putative catalytic intermediates (Scheme 1). This mode of activation of silanes constitutes an important alternative to the conventional Chalk-Harrod mechanism^[3] that entails the oxidative-addition of the silane's Si-H bond at a metal centre for which a number of

The historical Chalk-Harrod mechanism^[3a] considers the initial reaction of a silane of general formula R_3SiH (R = aryl, alkyl, halido and hydrogen) with a metal centre as an oxidative-addition, leading logically to the formal oxidation of the metal centre and the creation of two new M-H and M- SiR_3 bonds; the latter ligands being considered as of the X-type according to the *covalent bond classification* formalism (abbr. CBC)^[12]. In fact, this view of the reaction of a silane with a metal centre may be misleading for two reasons. First of all, if the oxidative addition scenario is valid, categorizing univocally the H and SiR_3 ligands as X may be too reductionistic because H and Si may be mutually attractively interacting and the H-Si bonding interaction may well not be fully disrupted^[2, 11]. Second, the pre-existing polarization of the Si-H bond may give rise to another scenario^[13] where, instead of a supposedly concerted oxidative-addition step (termed metal activation according to Tilley), a formal hydride transfer to the metal may operate with either a concerted or non concerted transfer of a formal silylium to the metal^[13-14], to a neighboring group or to the organic substrate (termed ionic activation by Tilley *et al.*). Oestreich *et al.* made recently use of this faculty of a thio group bonded to the ruthenium centre of a catalyst in their recent work^[15]. In this second scenario, whether the silyl group holds a X or Z character becomes the central question, which conditions one's understanding of the capabilities of a given catalyst. In other words, these two modes of addition of silanes to metal centres are expected to have different consequences on the electronic structure of the $M(H)(SiR_3)$ motif.

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As can be figured out readily from the literature, not all metal-silyl compounds display catalytic activity or even possess propensity to release the SiR_3 moiety readily by a chemical reaction. As a consequence, neither the chemical properties nor the reactivity of known cases of M-SiR_3 complexes are comprehensively documented. In the cases of reactive M-H-SiR_3 intermediates -or silane-metal adducts- for which strong evidence exists for their central intervention in key catalytic events, reactivity studies of such intermediates are sparse perhaps because of the difficulty of isolating^[13, 16] and using them as reactants in stoichiometric reactions.

The central question treated here is: can one readily infer the nature of a metal-bound silyl from a straightforward descriptor of bonding that could distinguish electrophilic silyl ligands -or "silyliums"- Z ligands (Figure 1) from other situations, in a way highly suggestive of the properties of a given catalyst in terms of reactivity and associated mechanism of action?

In the absence of any experimental information on the actual reactivity of a considered metal-silyl fragment, the typology of the R_3Si ligand is ambiguous because, depending on the extent of the interaction with the metal centre, it can be considered either as a Z ligand^[17] (a Lewis type acceptor, namely here $[\text{SiR}_3]^+$), or somewhat as a X ligand (Figure 1). In some cases though, the silane's Si-H σ bond is even assimilated to a L ligand^[2].

In the CBC typology of ligands^[12a-c], the Z class corresponds to Lewis acids or acceptors, either neutral (BR_3 for instance) or charged ($[\text{SiEt}_3]^+$ for instance^[13]), which do not interfere with the formal oxidation state of the metal and its valence electron bookkeeping. A Z-type ligand should be, in principle, displaceable by a Lewis base stronger than the bound metal. Experimental information should hence provide a good indication of the character of the metal-silyl interaction that theory could validate.

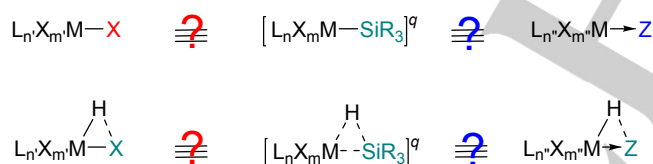


Figure 1. How to best formulate a metal-silyl/silane complex?

In this report, our aim is to outline the usefulness of some established tools of the density functional theory that can help rationalizing Lewis formulations so that they eventually match experimental observations and particularly contribute to clarify the mechanisms and concepts lying behind hydrosilylation reactions where electrophilic silyls are involved. Although the trigonal planar silylium^[18] cannot exist as such in solution^[19], several articles have brought evidence that molecular complexes of electrophilic silyl groups may form in solution with one or two Si-bound donor molecules depending on the substitution pattern in R_3 ^[20]. The solvent is often a privileged partner of the silylium cation^[21] as well as any other significant Lewis base or reactant of a hydrosilylation reaction that contains a Lewis-basic site^{[22] [23]}. Our main goal is to propose a simple approach for the evaluation of the "relative intrinsic silylicity" of a metal-silyl complex, that is its capability to undergo the

heterolytic cleavage of a M-Si bond to produce a formal Lewis acidic silylium^[24] $[\text{SiR}_3]^+$ fragment.

One ready way this may be achieved is by performing a systematic fragment interaction energy analysis of the silyl to metal interaction based on the energy decomposition analysis (EDA) framework^{[25][26]}. By confronting the corresponding interaction energies to experimental information, matching trends and correlations might emerge providing unambiguous information. This report does not intend to cover comprehensively all situations encountered in the literature but rather to illustrate the simplicity of EDA that may readily provide a sound hint on the expected properties of silyl groups based on the "reputation analysis" of published experimental information on the topic. In analogy with *hydricity*^[26] we propose the notion of *silylicity* to characterize the capability of a given metal-silyl complex to release/transfer a "silylium" group. Note that the SiMe_3 -specific TMSA (trimethyl silyl affinity) was introduced by Villingier et al.^[27] for the computation of thermodynamic parameters of model reactions implying the formation of molecular complexes of the trimethylsilylium cation. In the present article, we rather focus on intrinsic properties of the complexes and introduce the "relative intrinsic silylicity" descriptor \mathcal{I} . For convenience, we will use the term "silylium" as a synonym of "electrophilic silyl" throughout this article.

Results and Discussion

Material

Several criteria were applied (see below) to select the structures that were optimized *in vacuo* using a DFT method that performs notoriously well with transition metal complexes, that is the dispersion-corrected PBE-D3(BJ) GGA functional^[28]. It is important to state here that control calculations carried out with the hybrid PBE0 functional^[29] gave results consistent with those produced by the latter GGA functional. The PBE-D3(BJ) functional was associated to all-electron triple- ζ basis sets containing one polarization function within the scalar Zeroth Order Relativistic Approximation (ZORA)^[30], which produced little basis set superposition error (BSSE) bias (about less than 3 % of the interaction energy, see Table 1)^[31]. BSSE was accounted for in the computation of \mathcal{I} as shown in Table 1. In this study geometries taken from the Cambridge Structural Database (CSD) or those constructed from structural data of differently substituted compounds at the silyl group produced optimized geometries in the gas phase in good match with the main features of crystallographic data (Figure 2 and 3).

The chosen compounds were either: 1) established or tangible intermediates in a catalytic cycle, 2) established silane-metal reaction adducts where the silyl group is considered as a X-type ligand, 3) other silyl-metal complexes wherein the silyl group is notoriously considered as a X-type ligand and 4) established forms of metal bound silylides $[\text{R}_3\text{Si}]^-$.

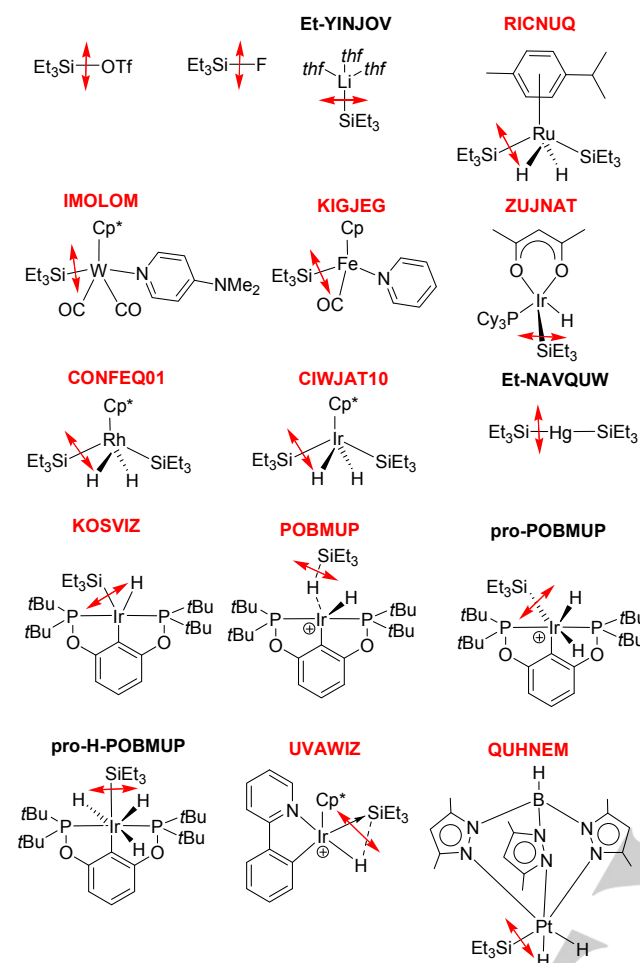
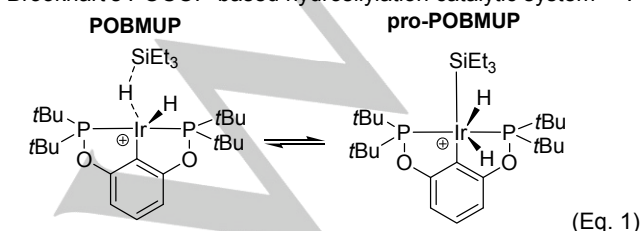


Figure 2. Developed formulas of the metal-triethylsilyl complexes considered in this study with their CSD *refcodes* (red-coloured six-letter codes). Other codes are associated to models reconstructed from models of the CSD either with different substitution patterns or from putative reaction intermediates. Red double arrows indicate which bond is cleaved in the fragmentation scheme implying the separation of the “prepared” silylium fragment from the associated metal complex residue (either negatively charged or neutral).

In this study we limit our coverage to four silyl groups, namely Et_3Si , Ph_3Si and PhR_2Si ($\text{R} = \text{H}$ or Me) for which numerous structural data of metal complexes can be found or built from similar structures downloaded from the Cambridge Structural Data Base (CSD). For the sake of conciseness we limited the study to cases where the silyl group exclusively binds the metal except in one case, i.e. POBMUP (Figure 2), which holds a special place as a rare case of so-called iridium-(η^1 -silane) adduct of the type $\text{R}_3\text{Si-H-Ir}$ that plays a central role in Brookhart’s POCOP-based hydrosilylation catalytic system^[32].



complex could be found, that is UVAWIZ, POBMUP, and LUWNAS (Figure 2 and 3). pro-POBMUP, which is the assumed isomer of cation POBMUP that coexists dynamically in solution (Eq. 1) according to Brookhart et al., was computed and considered for comparison of its properties.

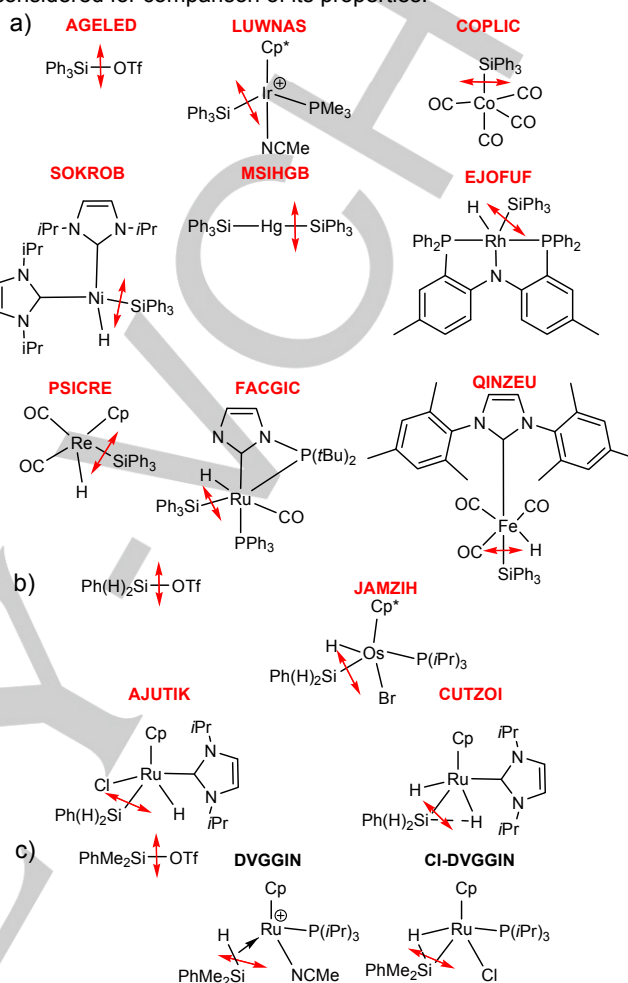


Figure 3. Developed formulas of the metal-triphenylsilyl (a), -phenylsilyl (b) and -dimethylphenylsilyl (c) complexes considered in this study with their CSD *refcodes* (red-coloured six-letter codes exclusively). DVGGIN is a putative reaction intermediate of interest, it is formulated here according to the authors first proposal^[33]. Red double arrows indicate which bond is cleaved in the fragmentation scheme implying the separation of the “prepared” silylium from the associated metal complex residue (either negatively charged or neutral).

For comparison purposes, the neutral analogue of pro-POBMUP, that is the trisilido complex pro-H-POBMUP constructed computationally by Oestreich et al.^[34] is also accounted for here. Finally one case of a key catalytic species responsible for the hydrosilylation of nitriles postulated by Gutsulyak and Nikonov^[33], named here for convenience as DVGGIN (Figure 3) and containing the SiMe_2Ph moiety, was also considered. The latter authors proposed that this intermediate formulated as a $\text{Ru}-(\eta^2\text{-silane})$ species could undergo the displacement of an implicit silylium moiety, e.g. $[\text{PhMe}_2\text{Si}]^+$ by interaction with an aryl nitrile. It is shown farther that the formulation of DVGGIN and of some other metal-silane complexes requires revision in view of the data produced here.

With complexes containing the PhH_2Si moiety, only neutral complexes were found in the CSD, whereas with two other types of silyls (SiEt_3 and SiPh_3) few cases of cationic metal-silyl

Method

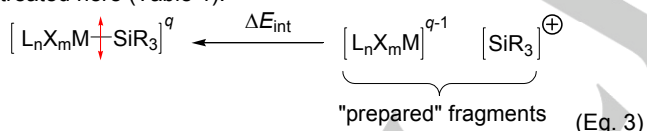
As stated above interaction energies were obtained from EDA^[25], which was carried out using the protocol implemented in the SCM-Amsterdam Density Functional suite of its 2016 version^[35]. The EDA requires the formal fragmentation of a molecule into two fragments, the geometries of which are kept identical to those in the molecule under scrutiny: for convenience, those geometries of the fragments are termed “prepared” as they are geometrically prepared to give rise to the final molecule in its relaxed geometry without deformation. In this article, all fragments and molecules have a singlet closed-shell electronic structure. The EDA, according to Ziegler and Rauk^[25], produces a dichotomy of the inter-fragment interaction energy partitioned into Pauli repulsion, electrostatic attractive, orbital attractive and, with dispersion corrected functionals, dispersion attractive interaction energy terms. This dichotomy into repulsive and attractive energetic contributions is a very powerful tool for the analysis of the nature of chemical bonds^[36] (Eq. 2). The latter dispersion term corresponds to the first-principle-based semi-empirical contribution to the inter-fragment interaction of the correction introduced by Grimme for mid to long range London force^[37], which does not include local electron correlation terms since the latter is treated by the native functional, a cut-off to the London force^[38] correction being operated by a Becke-Johnson type damping function^[39]. For the sake of conciseness, only the ΔE_{int} and ΔE_{d} are listed in Table 1.

$$\Delta E_{\text{int}} = \Delta E_{\text{p}} + \Delta E_{\text{e}} + \Delta E_{\text{o}} + \Delta E_{\text{d}}$$

ΔE_{p} : Pauli repulsion; ΔE_{e} : attractive electrostatic; ΔE_{o} : attractive dispersion; ΔE_{d} : attractive orbital

(Eq. 2)

Large and extended R groups at R_3Si will forcibly have a non-negligible impact onto the interaction energy, for the London force opposes Pauli repulsion particularly in sterically cluttered structures^[40]. It is important to mention that ΔE_{d} contributes attractively up to ca. 10 % of the value of ΔE_{int} in all cases treated here (Table 1).



The considered fragmentation scheme entails the disruption of a formal “silylium” fragment and the charged or neutral organometallic counterpart in their unrelaxed geometries (Eq. 3), this notwithstanding the “chemical realism” of the fragmentation scheme (Eq. 3). Indeed, in the case of Et-YINJOV (Figure 2, structure constructed with Et groups instead of *t*Bu groups from ref.^[41]) it is obvious that the fragmentation is not realistic from a chemical point of view, for in reality the Et_3Si group displays a silylide $[\text{Et}_3\text{Si}]^-$ character. The associated interaction energy nonetheless gives reasonable information on the strength of the binding and provides a non-ambiguous limit case that may help categorizing other Si-M bonds. To define a scale of “relative intrinsic silylicity” we chose silyl triflates as reference compounds.

In a previous report, we showed that the triflate ion, which is considered as one of the weakest Lewis bases and one of the best nucleofuges^[42], nonetheless was capable of capturing the Et_3Si group of UVAWIZ^[13] (Figure 2), suggesting that in the latter cation the iridium centre was rather weakly bonded to the silicon atom. It appeared to us that comparing metal-silyl

complexes to silyl triflates was the best choice to identify situations like UVAWIZ where the silyl group obviously behaves like a Z ligand^[13].

Therefore, we define the “relative intrinsic silylicity” Π (the greek letter Π was chosen for it is the initial of the Greek word $\pi\upsilon\rho\iota\tau\iota\omicron$ that means “elemental silicon”) as the ratio of the inter-fragment interaction energy of the triflate with the “silylium” of TfO-SiR_3 and the interaction energy of the metal fragment with the same formal “silylium” in a metal- SiR_3 compound (Eq. 4). For POBMUP (Figure 2) only this ratio is associated with the dissociation of the Si-H bond in the Ir-bound Et_3SiH complex, since it is crystallographically established that the Si atom does not interact directly with the Ir centre.

$$\Pi = [\Delta E_{\text{int}}(\text{R}_3\text{Si-OTf})] / [\Delta E_{\text{int}}(\text{R}_3\text{Si-M})] \quad (\text{Eq. 4})$$

The M-Si bond disruption model considered here serves as a probe of the potential propensity to release a “silylium” moiety. Given the fact that we exclusively consider unrelaxed “prepared” geometries of fragments that do not imply planar silyliums but pyramidalized ones, we consider in a first approximation that all ΔE_{int} values are directly comparable.

Our formal considerations do not aim at revising *per se* the mechanisms of silylium transfer that imply for instance a $\text{S}_{\text{N}}2$ type attack of the Si centre by a potential nucleophile that is often thought to imply a 5-coordinate-at-Si-atom transition state^[14, 43]. The relative intrinsic silylicity Π is a descriptor of the Lewis acidic (electrophilic) character of a given SiR_3 moiety, where values <1 characterize low “silylium” releasing ability and values >1 high releasing ability.

Table 1. Energetic (ΔE_{int} , IT , ΔE_d) and electronic properties of $R_3\text{Si-M}$ bonds, and their reactivity "reputation".

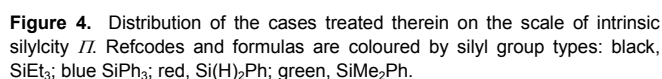
| entry | cmpd REFCODE | ΔE_{int} (BSSE) ^[a] (kcal/mol) | IT | ΔE_d | Wbi (M-Si) ^[b] | $d(\text{Y-Si})$ cptd(exptl) (Å) ^[c] | $q^{[d]}$ | $q(\text{Si})$ (NPA) | « silylium » reactivity ? ^[e] | refs |
|-------------------------------------|--------------------------------------------------|---------------------------------------------------------------|------|--------------|---------------------------|-------------------------------------------------|-----------|-------------------------|---------------------------------------------|-----------------------------------|
| R= Et | | | | | | | | | | |
| 1 | [Et ₃ Si] ⁺ ^[f] | - | - | - | - | - | +1 | +1.8 | yes | [19, 20c, 20e-h, 21, 23, 24d, 44] |
| 2 | Et ₃ SiH ^[f] | -240 (-3.8) | 0.70 | -0.2 | 0.78 | 1.507 | 0 | +1.2 | no (radical) | [45] |
| 3 | Et ₃ SiOTf ^[f] | -167 (-1.3) | 1 | -4.8 | 0.51 | 1.768 | 0 | +1.7 | yes | [46] |
| 4 | Et ₃ SiF ^[f] | -238 (-10.2) | 0.73 | -0.5 | 0.57 | 1.644 | 0 | +1.8 | moderate | [47] |
| 5 | Et-YINJOV ^[f] | -252 (-6.4) | 0.67 | -9.2 | 0.25 | 2.659 | 0 | +0.5 | no | [41] |
| 6 | RIQNUC | -222 (-1.8) | 0.75 | -12.6 | 0.50 | 2.425 (2.400) | 0 | +1.4 | no evidence | [48] |
| 7 | IMOLOM | -222 (-2.2) | 0.75 | -12.5 | 0.52 | 2.667 (2.635) | 0 | +1.3 | no evidence | [49] |
| 8 | QUHNEM | -228 (-1.9) | 0.73 | -11.4 | 0.58 | 2.379 (2.325) | 0 | +1.3 | sluggish | [50] |
| 9 | KIGJEQ | -222 (-2.4) | 0.75 | -10.8 | 0.51 | 2.340 (2.303) | 0 | +1.3 | no evidence | [51] |
| 10 | ZUJNAT | -233 (-2.4) | 0.72 | -14.3 | 0.70 | 2.332 (2.307) | 0 | +1.4 | no | [52] |
| 11 | CONFEQ01 | -216 (-1.5) | 0.78 | -12.9 | 0.43 | 2.405 (2.379) | 0 | +1.3 | sluggish | [53] |
| 12 | CIWJAT10 | -226 (-1.9) | 0.74 | -12.9 | 0.50 | 2.420 (2.390) | 0 | +1.3 | no ^[g] | [54] |
| 13 | Et-NAVQUW ^[f] | -209 (-2.9) | 0.81 | -3.2 | 0.43 | 2.550 | 0 | +0.8 | no | [55] |
| 14 | UVAWIZ | -119 (-2.0) | 1.41 | -14.4 | 0.37 | 2.547 (2.501) | +1 | +1.4 | yes | [13] |
| 15 | KOSVIZ | -215 (-2.1) | 0.78 | -15.2 | 0.46 | 2.482 (2.434) | 0 | +1.2 | no | [34] |
| 16 | POBMUP | -92 (-1.5) | 1.84 | -12.8 | 0.6 ^o | 3.299 (3.346) | +1 | +1.4 | yes | [56] |
| 17 | pro-POBMUP ^[f] | -120 (-2.4) | 1.41 | -16.2 | 0.15 | 2.434 | +1 | +1.3 | yes | [56] |
| 18 | pro-H-POBMUP ^[f] | -214 (-2.1) | 0.78 | -15.7 | 0.35 | 2.529 | 0 | +1.3 | no evidence | [34] |
| R= Ph | | | | | | | | | | |
| 19 | AGELED | -152 (-1.3) | 1 | -5.7 | 0.52 | 1.746(1.740) | 0 | +1.7 | yes | [57] |
| 20 | LUWNAS | -150 (-2.7) | 1.02 | -21.2 | 0.55 | 2.437 (2.411) | +1 | +1.3 | sluggish | [58] |
| 21 | COPLIC | -153 (-1.9) | 1 | -9.9 | 0.30 | 2.418 (2.381) | 0 | +1.3 | no evidence | [59] |
| 22 | SOKROB | -259 (-5.3) | 0.59 | -16.3 | 0.45 | 2.231 (2.202) | 0 | +0.9 | no evidence | [60] |
| 23 | MSIHGB | -176 (-1.9) | 0.87 | -4.7 | 0.43 | 2.513 (2.494) | 0 | +0.8 | no evidence | [61] |
| 24 | EJOJUF | -215 (-2.9) | 0.71 | -27.1 | 0.46 | 2.330 (2.315) | 0 | +1.3 | no evidence | [62] |
| 25 | PSICRE | -199 (-2.5) | 0.77 | -11.8 | 0.49 | 2.515 (2.487) | 0 | +1.2 | no evidence | [63] |
| 26 | QINZEU | -205 (-2.4) | 0.74 | -12.2 | 0.33 | 2.372 (2.349) | 0 | +1.2 | no | [64] |
| 27 | FACGIC | -246 (-3.1) | 0.62 | -22.7 | 0.45 | 2.366 (2.409) | 0 | +1.2 | no evidence | [65] |
| R ₃ = Ph(H) ₂ | | | | | | | | | | |
| 28 | Ph(H) ₂ SiOTf ^[e] | -175 (-0.9) | 1 | -3.2 | 0.55 | 1.740 | 0 | +1.7 | yes | [66] |
| 29 | JAMZIH | -260 (-2.0) | 0.67 | -11.9 | 0.62 | 2.415 (2.398) | 0 | +0.7 | no evidence | [67] |
| 30 | AJUTIK | -222 (-1.7) | 0.79 | -12.6 | 0.46 | 2.433 (2.419) | 0 | +0.8 | no evidence | [68] |
| 31 | CUTZOI | -265 (-1.6) | 0.66 | -11.6 | 0.53 | 2.365 (2.328) | 0 | +0.8 | no evidence | [69] |
| R ₃ =PhMe ₂ | | | | | | | | | | |
| 32 | Ph(Me) ₂ SiOTf ^[e] | -160 (-1.2) | 1 | -4.1 | 0.51 | 1.769 | 0 | +1.7 | yes | [70] |
| 33 | DVGGIN ^[e] | -113 (-1.9) | 1.43 | -12.4 | 0.34 | 2.527 | +1 | +1.3 | yes | [33, 71] |
| 34 | Cl-DVGGIN ^[e] | -210 (-2.1) | 0.73 | -11.6 | 0.46 | 2.469 | 0 | +1.3 | no evidence | [f] |

^[a] raw ΔE_{int} and the associated computed energy related to basis set superposition error (BSSE); all values of IT are based on corrected values of ΔE_{int} . ^[b] Wiberg bond index. ^[c] distance in the computed model and in the X-ray diffraction established structure; Y= metal for organometallic compounds, H for POBMUP, OTf for $R_3\text{SiOTf}$ compounds, F for Et_3SiF . ^[d] charge of the complex. ^[e] considerations based on the content of the seminal paper(s) wherein the synthesis and properties of a given compound were reported: the term "sluggish" means that drastic conditions were used to induce reactivity. ^[f] geometries computed from a reconstructed model inspired by a published CIF or another model (see Figure 2 and 3). ^[g] this study.

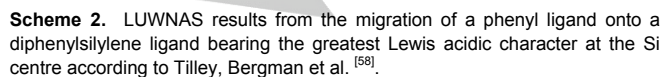
A minor number of complexes displays ΔE_{int} values close to 1 related to a significant electrophilic character of the silyl fragment at least similar to that of the associated triflate. These are essentially compounds containing the SiPh_3 fragment for which little information on their reactivity is available in the original published reports. For instance, LUWNAS^[58] can be formulated as a formal cationic Ir(I) complex bearing a pentamethylcyclopentadienyl ligand and two 2-electron donor ligands (MeCN and PMe_3). This formulation is consistent if one considers the manner LUWNAS was reportedly synthesized in the original publication. LUWNAS results from the $\text{Na}[\text{BARF}_{24}]$ -promoted migration of a phenyl X ligand onto a silylene intermediate^[58] (scheme 2) followed by the coordination of a molecule of acetonitrile. The compound was mainly characterized by X-ray diffraction analysis^[58]. Its CBC formula can be reduced to ML_4XZ where Z stands for $[\text{SiPh}_3]^+$. If one considers that the intermediate silylene is indeed a strong Lewis acid at Si atom, like documented by Tilley, Bergman et al., one reasonable CBC formulation of the $[\text{SiPh}_2]^+$ silylene ligand is the (XZ) combination^[12b], which gives to the intermediate complex the equivalent $\text{ML}_2\text{X}_3\text{Z}$ formula where the Ir bears now a formal +III oxidation state. Consequently the migration of the phenyl group onto the silylene may then be assimilated to an intramolecular reductive-elimination from the $\text{ML}_2\text{X}_3\text{Z}$ silylene complex producing cation LUWNAS, i.e ML_4XZ . That the SiPh_3 group behaves as a potential Z ligand $[\text{SiPh}_3]^+$ is not only strongly suggested by the value of ΔE_{int} listed in Table 1 (entry 20) but also by hints on the reactivity given in the seminal paper of Tilley, Bergman et al.^[58]. Indeed the Ir cation LUWNAS is said to undergo at high temperature a major transformation wherein the SiPh_3 group migrates to the N atom of the vicinal Ir -bound MeCN ligand that subsequently undergoes a C-C bond cleavage leading to a new Ir triphenylsilylisocyanide complex. If this electrophilic migration of SiPh_3 is strongly informative of the Lewis acidic character of this group, there is however no other available information to confirm it further.

COPLIC (Table 1, entry 21)^[59], if one refers to the associated value of Π , can be formally considered as a cobalt (I) complex bearing four carbonyl ligands that may contribute in weakening the Co-Si bond. Published data depict this complex as a stable and manageable species displaying the longest known Co-Si bond distance, which supports the classification of the SiPh_3 as X ligand. Worthy to note, the synthesis of COPLIC is reportedly requiring the thermolysis of $\text{Co}_2(\text{CO})_8$ in the presence of $(\text{Ph}_2\text{HSi})_2$. The reaction leading to COPLIC implies a number of rearrangements and a phenyl group transposition with evidence of formation of paramagnetic species such as $[\text{Co}(\text{CO})_4]$. We thus speculate that COPLIC might be a limit case, which warrants not to categorize the silyl group as a Z type ligand.

A third class of compounds that possess Π values greater than 1 gathers in almost all cases catalytic intermediates, the reactivity of which were already documented as that of labile sources of electrophilic $[\text{SiEt}_3]^+$ [1, 13, 34, 56]. UVAWIZ has been reported recently by us and formulated as a donor-acceptor $(\text{Ir}-\text{H})\rightarrow[\text{SiEt}_3]^+ \text{Ir(III)}$ complex [13] wherein the donor-acceptor interaction is delocalized, with electron density donation operating unequally from both the Ir centre and the hydrido ligand. POBMUP, which in the Π scale outperforms all metal-silyl complexes, is the peculiar intermediate isolated and structurally characterized by Brookhart et al.. According to latter



In the π scale (Figure 4) the first situation corresponds to values spanning 0.59-0.87 related to established forms of silylides (values around 0.67) and what one could consider as classical X-type metal silyl complexes with no “silylium” character. CIWJAT10^[54] (Table 1, entry 12), which was synthesized by us for the purpose of the present study according to the procedure reported by Maitlis et al.^[72] did not display any reactivity towards weak and strong Lewis bases such as TfO⁻ and 4-*N,N*-dimethylaminopyridine (DMAP) and remained unchanged. The SiEt₃ moiety in CIWJAT10 is most certainly a X-type ligand and a formal +V oxidation state can be assigned to the Ir centre. SOKROB^[60] that features a π value of 0.59 appears here as a limit case of low silylicity similar to the value determined for FACGIC^[65], both bearing two to three strong electron donating L-type ligands (N-heterocyclic carbenes and phosphines) that may contribute in enriching the metal centre and in consolidating the bond with the Si centre. QUINZEU^[64], which was described as a model of catalytic key intermediate of the Fe(0)-promoted reduction of esters into aldehydes under UV-light irradiation, reportedly displays no catalytic activity at all. The minor number of complexes with $\pi < 1$ reported to show some sluggish reactivity (Table 1) of the silyl moiety were essentially brought to forced conditions wherein the very fate of the complex was not clear enough to deem reliable any information on the silyl group's reactivity.



authors it may exist under two equilibrating forms, that is POBMUP and pro-POBMUP^[56] (Eq. 2). It appears here that the difference of ΔE_{int} values of the two isomers makes of POBMUP the most likely "silylium" source in a catalytic transformation, which is consistent with the information published by Brookhart et al.^[56] as well as by further studies by Oestreich et al.^[34]. Quite interestingly, the neutral analogue of pro-POBMUP that was considered by Oestreich in a computational study, i.e. pro-H-POBMUP^[34] (Figure 3, Table 1, entry 18) displays half the silylicity of its cationic parent, which compels to consider its silyl group as a X-type ligand rather than a Z-type one.

This observation tends to suggest that the "silylium" character can be tuned by a significant modification of both the ligand retinue and the charge of the complex giving rise to a peculiar polarisation change -or silicon-centred "umpolung effect". If all the maps of coulombic potential (MCP) (MCPs not shown here) of the complexes considered in Table 1 reveal that the largest depletion of charge density is located at the Si atom (cf Table 1 natural partial charge at Si, i.e. $q_{\text{NPA}}(\text{Si})$), this is however not a sufficient condition for a complex to chemically express a "silylium"-source reactivity though. All complexes of ΔE_{int} value > 1 are cations, which raises the question of the way the charge density unbalance existing in such complexes may lead to "silylium"-type behavior in chemical reactions.

The case of POBMUP and related molecules

Pro-H-POBMUP and pro-POBMUP offer here an opportunity to address the peculiar "umpolung"^[73] effect that apparently operates at the SiEt_3 group upon formal removal of one axial hydrido ligand at the Ir centre of the former complex (Figure 5). As a preliminary hint, the removal of one axial hydrido ligands causes the Ir-Si Wiberg bond indice^[74] (abbr. Wbi) to decrease by half of its value on going from pro-H-POBMUP (Wbi = 0.35, entry 18, Table 1) to pro-POBMUP (0.15, entry 17 Table 1), which is rather consistent with the difference of ΔE_{int} computed for those two compounds. Concomitantly, major changes also occur in the near vicinity of the SiEt_3 group, which is a raise from 0.27 to 0.55 of the Wbi of the interaction of the Si centre with the vicinal hydrido ligand. This significant change can be rationalized as a shift from a delocalized (Ir-H_{Si})... SiEt_3 interaction in pro-H-POBMUP ($d(\text{H}_{\text{Si}}-\text{Si}) = 2.037 \text{ \AA}$, $d(\text{Ir}-\text{H}_{\text{Si}}) = 1.633 \text{ \AA}$, $d(\text{Ir}-\text{Si}) = 2.529 \text{ \AA}$) to a more localized interaction in pro-POBMUP where the $\text{H}_{\text{Si}}-\text{Si}$ interaction ($d(\text{H}_{\text{Si}}-\text{Si}) = 1.643 \text{ \AA}$, $d(\text{Ir}-\text{H}_{\text{Si}}) = 1.723 \text{ \AA}$, $d(\text{Ir}-\text{Si}) = 2.867 \text{ \AA}$) dominates. The abstraction of the axial hydrido ligand H_{trans} bound to Ir with a Wbi of 0.33 also results in the major raise of the Wbi of the Ir-H bond trans to it from 0.34 to 0.69 (Figure 5), with the collapse of the Wbi of the $\text{H}-\text{H}_{\text{Si}}$ interaction between the two vicinal hydrido ligands. The QTAIM analysis^[75] of pro-POBMUP (Table 2) indicates the absence of bond critical point (3,-1) and path for a Ir-Si interaction. In turn it reveals the existence of a BCP(3,-1) and bond path for the interaction of the Si centre with the proximal hydridic hydrogen.

Natural population analysis (NPA) provides natural charges at atoms^[76]. In directly related cases variations of natural atomic charges can be cross-correlated with the variations of charge density, which makes of NPA natural charges a convenient tool to study the impact of slight structural changes on the charge density distribution^[77]. For instance it is found that the total natural charge borne by the SiEt_3 moiety in neutral pro-H-POBMUP and in cationic pro-POBMUP is +0.05 and +0.34

respectively. This suggests that upon the virtual removal of the axial hydrido ligand H_{trans} the resulting positive charge build up is delocalized by ca. 30 % on the SiEt_3 moiety alone; the rest being distributed over the POCOP ligand-bound dihydrido-iridium fragment of pro-POBMUP. Equivalent CBC formulas are proposed in Figure 5.

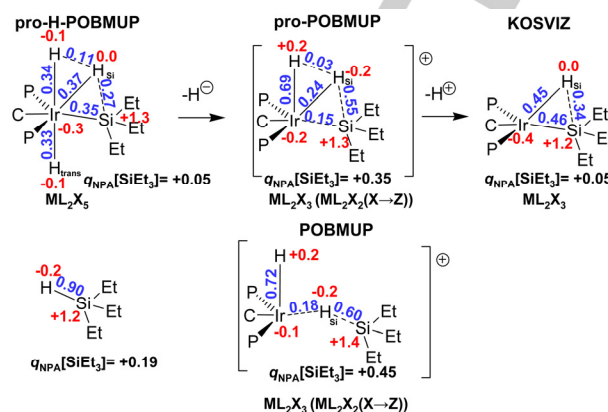


Figure 5. Wiberg bond indices (blue colored fonts) and natural atomic charges (NPA, red colored fonts) at the Ir-H-Si motif and its vicinity. The total natural charge borne by the SiEt_3 moiety was obtained by summing up the atomic natural charges of the fragment.

Pro-POBMUP and POBMUP differ by the complete loss of Si-Ir interaction in the latter ($d(\text{Ir}-\text{Si}) = 3.299 \text{ \AA}$, $d(\text{Ir}-\text{H}_{\text{Si}}) = 1.805 \text{ \AA}$, $d(\text{H}_{\text{Si}}-\text{Si}) = 1.593 \text{ \AA}$). They also differ by the larger natural positive charge borne by the SiEt_3 moiety of +0.45 in POBMUP according to NPA. Worthy to note, KOSVIZ, that is the structure resulting formally from the abstraction of a proton from pro-POBMUP displays a low ΔE_{int} value similar to that of pro-H-POBMUP (Table 1, entry 15), which suggests that the SiEt_3 moiety is rather a X-type ligand.

Very similar is also the natural charge of +0.05 borne by the SiEt_3 moiety in KOSVIZ (Figure 5). The main consequence of the formal abstraction of one proton from pro-POBMUP is the increase of the Wiberg bond indice of the Ir-Si and Ir-H_{Si} bonds and the decrease of the bond indice of the $\text{H}_{\text{Si}}-\text{Si}$ interaction. The QTAIM analysis of KOSVIZ (Table 2 and Figure 6) confirms the absence of bond critical point and bond path for this interaction. Quite consistently, the SiEt_3 moiety in KOSVIZ was not reported to have a peculiar reactivity towards Lewis bases.

POBMUP was reportedly presented as a Lewis complex where the monohydrido-iridium POCOP moiety plays the role of the acceptor and the silane that of the donor^[56]. If this representation might be valid in the early stages of the interaction of HSiEt_3 with the Ir centre^[78], in POBMUP the fact is that the Si-H_{Si} bond is greatly weakened and can be disrupted very readily by a weak Lewis base such as Et_2O ^[16]. The Si-H_{Si} Wbi of 0.6 contrasts with the value of 0.9 computed for HSiEt_3 and this difference translates into a difference of ΔE_{int} of around 150 kcal/mol between the free silane (Table 1, entry 2) and POBMUP (Table 1, entry 16).

Table 2. QTAIM selected features for POBMUP-related structures: list of selected electron density values and Laplacians at bond critical points (3,-1) in the coordination sphere of the Ir centre of a series of POCOP complexes (refer to Figure 6 for associated plots of the density Laplacians).

| cmpd | interaction | ρ (a.u.)@BCP (3,-1) | $\nabla^2\rho$ (a.u.)@BCP(3,-1) |
|---------------------|-----------------------|--------------------------|---------------------------------|
| pro-H-POBMUP | Ir-Si | 0.072 | -0.420 |
| | Ir-H _{Si} | 0.139 | 0.078 |
| | Ir-H | 0.137 | 0.075 |
| | Ir-H _{trans} | 0.137 | 0.085 |
| pro-POBMUP | Ir-H _{Si} | 0.102 | 0.201 |
| | Si-H | 0.083 | 0.032 |
| | Ir-H | 0.142 | -0.038 |
| | Ir-Si | no BCP | |
| KOSVIZ | Ir-Si | 0.077 | -0.043 |
| | Ir-H | 0.142 | 0.102 |
| | H-Si | no BCP | |
| POBMUP | Ir-H _{Si} | 0.076 | 0.206 |
| | Ir-H | 0.176 | -0.051 |
| | H-Si | 0.086 | 0.055 |

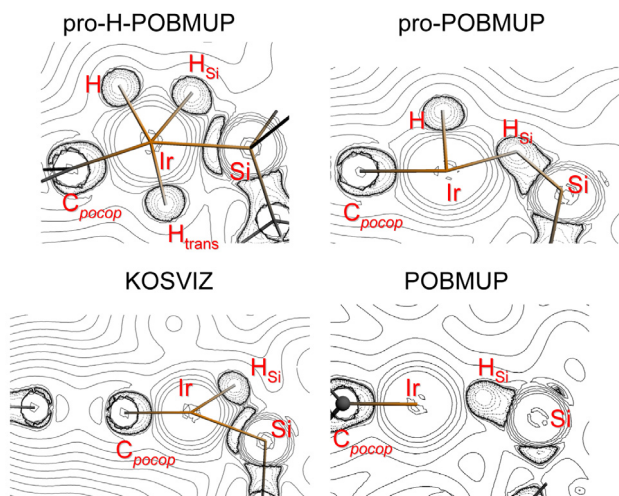


Figure 6. Contour plots of the Laplacian of the density $\nabla^2\rho(r)$ in the Ir-H_{Si}-Si plane for POBMUP and three other related molecules, where H_{Si} is the hydrogen atom in close vicinity to the Si atom (ZORA-PBE0/all electron TZP level). Dashed contour lines correspond to $\nabla^2\rho(r) < 0$.

In other words the strong \mathcal{H} value of POBMUP commands a revision of its chemical formulation as that of a μ -hydrido bridged complex; a limit formulation of the Ir-H_{Si}-Si motif consistent with its reactivity being Ir-H_{Si}→Z (Z= [SiEt₃]⁺). The large Ir-H_{Si} distance of ca. 1.8 Å is in the domain of distances observed in other μ -hydrido bridged bis-iridium complexes^[13, 80]. QTAIM analysis further confirms that BCPs (3,-1) and bond paths can be located for the Ir-H_{Si} and the H_{Si}-Si interactions.

The DVGGIN case

To the latter category of compounds displaying $\mathcal{H} > 1$ can be added the cationic intermediate DVGGIN (Table 1, entry 33), which was reportedly detected by NMR spectroscopic means by Nikonov et al.^[33, 71]. It is plausibly the key catalytic species in the hydrosilylation of nitriles for it is supposed to readily transfer the [PhMe₂Si]⁺ moiety to the nitrogen atom of the attacking nitrile giving rise to an activated nityrium cation that can further undergo hydride transfer from a ruthenium-hydrido intermediate. DVGGIN displays a value of \mathcal{H} (Table 1, entry 33) very similar to that of UVAWIZ (Table 1, entry 14). In a first approximation, it may be considered as a donor-acceptor complex of a Ru (II) complex formulated ML₄X₂Z. The values of Wbi within the Ru-H-Si motif ((Ru-H) = 0.40, (Ru-Si) = 0.34, (H-Si) = 0.34) suggest indeed a significantly weak Si-H interaction that pleads in favor of a delocalized interaction between the three atomic centres. In the computed model, the H-Si distance (1.815 Å) is similar to that in the computed model of UVAWIZ^[13]; the Ru-H (1.623 Å) and Ru-Si (2.533 Å) distances displaying standard values not greatly different from the Ir-H and Ir-Si distances in UVAWIZ. Applying the fragmentation scheme used to compute ΔE_{int} in Table 1, extended transition state-natural orbitals for chemical valence (ETS-NOCV) analysis^[81] reveals a trend already reported for UVAWIZ previously. The strongest orbital interaction obtained from the ETS-NOCV breakout into symmetry-related orbital interactions is depicted in Figure 7. The deformation density isosurface plot $\Delta\rho_1$ suggests that the donation of electron density operates from Ru-centred orbitals (red-colored isosurfaces) but also from the Ru-H σ bond (1.623 Å at the ZORA-PBE0-dDsC/all electron TZP level) to populate a wide area (blue-colored isosurface) located in the inter-atomic space separating the Ru-H bond from the Si centre.

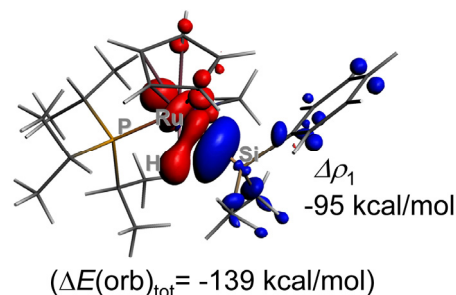


Figure 7. Plot of the density deformation isosurface (0.005 e/bohr³) associated with the highest orbital interaction energy arising from the ETS-NOCV analysis of DVGGIN. The original singlet ground state geometry of the latter was optimized at the ZORA-PBE0-dDsC/all electron TZP level and analyzed at the PBE0 level. The total orbital interaction energy in parentheses was computed by a standard EDA procedure.

This isosurface materializes the delocalized bonding (Ru-H)→Si interaction. QTAIM further indicates that a bond critical point (abbr. BCP) (3,-1) related to a H-Si bond path does exist within the Ru-H-Si plane, localized slightly away from the H_{Ru}-Si segment. Worthy to note, the Si atom of the trigonal pyramidal PhMe₂Si moiety does not point towards the hydridic hydrogen but rather towards the middle of Ru-H bond, the latter bond being properly characterized by a BCP(3,-1) and a bond path. According to the plot of the Laplacian of the density (Figure 8a), the BCP (3,-1) in the H-Si bond path appears at the border of a

region of charge density build-up (dashed contour lines) where the exact localization of a BCP seems to be somewhat inaccurate owing to the low density involved. Indeed, whereas computation of the density Laplacian of a geometry relaxed at the GGA ZORA-PBE-D3(BJ)/all electron TZP level produced a $\nabla^2\rho$ plot displaying the same topology, the corresponding QTAIM analysis localized a BCP(3,-1) within a Si-Ru bond path instead, and no BCP (3,-1) or bond path related to a H-Si interaction. This discrepancy^[82] is putatively attributed to the delocalized character of the (Ru-H)-to-Si interaction^[11] and to the low electron density involved therein. All things considered, the alignment of the Si atom with BCP #1 and BCP #2 (Figure 8a) supports the hypothesis of a delocalized weak (Ru-H)→Si interaction. The NCI region plot (cf. Supporting information for Figure S1 for a NCI plot) reveals a situation that resembles that encountered in UVAWIZ with a ring of attractive NCI isosurface (red colored) surrounding the (Ru-H)→Si interaction.

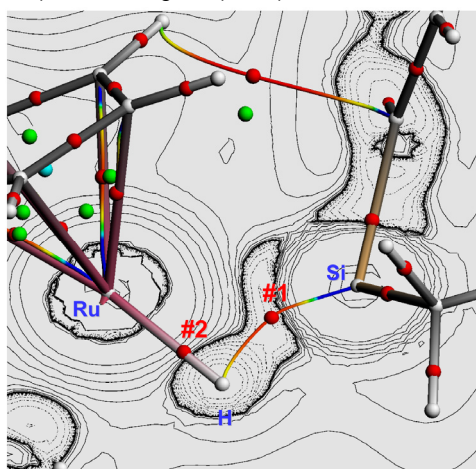


Figure 8. Contour plot of the Laplacian of the density^[79] for DVGGIN (ZORA-PBE0/all electron TZP level, dashed contours correspond to $\nabla^2\rho(r) < 0$) determined in the Ir-Si-H plane, overlaid with a 3D representation of the QTAIM analysis displaying bond critical points (red dots), ring critical points (green dots) and bond paths (coloured by density). BCP (3,-1) #1: $\rho = 0.072$ a.u., $\nabla^2\rho = -0.0556$ a.u. BCP(3,-1) #2: $\rho = 0.1259$ a.u., $\nabla^2\rho = 0.198$ a.u. (cf. Supporting information for Figure S1 for a NCI plot). Interatomic distances (Å): Ru-Si 2.535, Ru-H 1.623, H-Si 1.815.

It is also worthy to note that the bean-shaped area of charge concentration $\nabla^2\rho(r) < 0$ is located within the inter-atomic space separating Ru and H atoms from Si in a way similar to that reported for UVAWIZ^[13] (Figure 8, cf. dashed contours around the hydridic H centre spreading towards the Ru-Si segment). It is worthy to note that a similar topology of $\nabla^2\rho(r)$ seemingly characteristic of a delocalized 3 centre bond in a Mn-H-Si motif was also observed by Scherer et al. for two presumed (η^2 -H-SiRPh₂)Mn(MeCp)(CO)₂ complexes, the charge density of which was determined from multipolar high resolution X-ray diffraction experiments and corroborated by theory^[83]. It is thus tempting to state that the SiMe₂Ph moiety maintains in DVGGIN the same type of interaction with the hydrido-metal unit as in UVAWIZ^[13]. QTAIM analysis suggests that the formulation of DVGGIN cannot univocally be that of a coordinated η^2 -metal bound silane like suggested by Nikonov et al.^[33, 71]

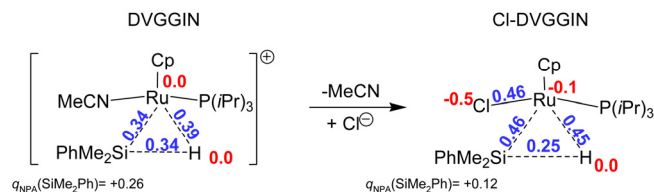


Figure 9. The electronic consequences of the fictitious replacement of the MeCN ligand by a chlorido: Wiberg bond indices are printed in blue, natural (NPA) charges are printed in red.

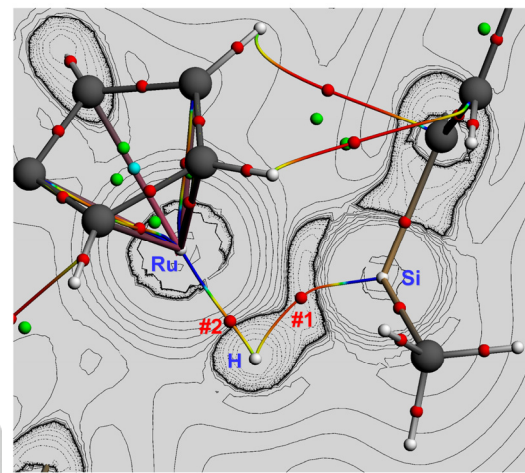


Figure 10. Contour plot of the Laplacian of the density^[79] for Cl-DVGGIN (ZORA-PBE0/all electron TZP level, dashed contours correspond to $\nabla^2\rho(r) < 0$) determined in the Ir-Si-H plane, overlaid with a 3D representation of the QTAIM analysis displaying bond critical points (red dots), ring critical points (green dots) and bond paths (coloured by density). BCP (3,-1) #1: $\rho = 0.0740$ a.u., $\nabla^2\rho = -0.0482$ a.u. BCP (3,-1) #2: $\rho = 0.1239$ a.u., $\nabla^2\rho = 0.2044$ a.u. The singlet ground state geometry of Cl-DVGGIN was optimized at the ZORA-PBE0-dDsC/all electron TZP level (cf. Supporting information for Figure S2 for a NCI plot). Interatomic distances (Å): Ru-Si 2.486, Ru-H 1.626, H-Si 1.888.

For the purpose of comparison, a neutral analogue of DVGGIN, i.e. Cl-DVGGIN a parent of AJUTIK (Figure 3), was constructed by replacing the acetonitrile ligand by a chloride and optimized. The resulting \mathcal{I} value of 0.73 (Table 1, entry 34) indicates in this case that the charge of the species and a minor change of ligand at the metal impacts directly the cohesion of the Ru-Si bond. The Wbi value of the latter interaction rises from 0.34 to 0.46 (Figure 9) and the natural charge borne by the SiMe₂Ph moiety drops from +0.26 in DVGGIN to +0.12 in Cl-DVGGIN. On going from the cationic to the neutral species the Ru-H and Ru-Si interactions consolidate and the Si-H interaction, albeit still significant, slightly weakens. The QTAIM analysis of Cl-DVGGIN and the Laplacian of the density (Figure 10) are very similar to those of DVGGIN for the Ru-H-Si motif; both analyses point to a delocalised Ru-H-Si interaction (Figure 10). The NCI region plot of Cl-DVGGIN (cf. Supporting information for Figure S2 for a NCI plot) contains a reduced attractive NCI isosurface around the (Ru-H)-Si interaction as compared to that materialized for DVGGIN.

Conclusions

In recent reports we merely suggested to qualify the bonding relationship existing between the metal centre and a particularly labile SiR_3 moiety in intermediates resulting from the reaction of an Ir(III) centre with a silane^[13, 84] on the basis of the value of the interaction energy between a fictitious "silylium" and the remaining metal centred fragment of a complex. We now show that applying this simple method to a wide range of metal-silane adducts and other metal-silyl complexes where there seems to be a consensus on the X character of the silyl ligand is very informative. It reveals a net separation between cases where the Z character of the silyl moiety is pronounced and those pertaining to "classical" situations where the X character dominates (established cases of $(\eta^2\text{-silane})\text{metal complexes}$ ^[85]^[86] were not addressed in the present report). Our present contribution reveals the consistent relationship existing between high values of the relative intrinsic silylicity parameter \mathcal{I} and experimental recensions of the reactivity of the same compounds as potential silylium sources. The highest \mathcal{I} values are those of cationic species displaying established catalytic properties.

This study also shows that the treatment of M-Si interactions should rely on documented experimental information. The main difficulty in establishing a Lewis formulation of the bonding in a new "metal-silane" adduct is to verify whether the principle of microscopic reversibility^[87] is obeyed, which entails that the integrity of the metal-bound ligand^[88] is preserved. In the case of POBMUP and DVGGIN, the initial formulations suggested that the silane was basically a 2 electron donor ligand L, which consequently should be displaceable by any donor ligand without loss of silane's integrity like reported in other cases of the literature^[85]. The reality is that donor ligands do not displace the silane but rather react with the silyl moiety, which is a rather good indication that the integrity of the "bonded silane" ligand is strongly and irreversibly altered in the initial interaction of the silane with the metal centre.

We speculate that for metal-silane adducts that possess a relative intrinsic silylicity lower than 1, an appropriate change of the structure by way of ligand replacement or a change of the oxidation state at the metal may switch on high "silylicity". It is already known that charge can induce major changes in the intrinsic enthalpies of metal-methyl bonds within the same series of transition metals^[89]; those changes were not systematically investigated for metal silyl complexes to the best of our knowledge^[90]. In other terms, it appears that the M-H-Si motif is highly sensitive and responsive to major electronic changes occurring in the metal's ligand retinue. Most importantly and in agreement with Tilley's recent observations^[1], the strongest shift of reactivity of the M-H-Si motif occurs with molecular cations, where the silyl group tends to enhance its share of charge depletion leading in some cases to an extreme bonding situation, that is a weak $(\text{M-H}) \rightarrow \text{SiR}_3$ donor-acceptor interaction. In the latter, the silyl moiety interacts with both the hydrido ligand and the metal centre as a "silylium" Lewis acid; the M-H motif acting somewhat like a ditopic donor ligand. Scherer's concept of anomeric effect at silicon that describes the charge density transfer operated variably by the hydrido ligand^[83] is another formulation of our conclusion. It is believed that the unifying bonding concept proposed by Scherer et al.^[11f, 11h], which was tested on a limited number of cases to date, could constitute

solid grounds for understanding the structure-reactivity factors that influence bonding within the M-H-Si motif. From our viewpoint, understanding the factors that cause high silylicity or its collapse is of utmost importance at the prospect of designing new catalysts. This question will remain in our focus in the future.

Computational details

Starting geometries were either taken from the Cambridge Structural Database (CSD)^[91] or constructed from similar CSD structure or proposed catalytic intermediates^[33-34, 56, 71] and optimized as singlet ground states in the gas phase using the methods of the density functional theory (DFT). Geometry optimizations and energy decomposition analyses were performed with methods of the Density Functional Theory, i.e. the Perdew-Burke-Ernzerhof (PBE)^[92] GGA functional augmented with Grimme's D3(BJ) inclusion of mid-to-long range dispersion force with a Becke-Johnson (BJ) damping function^[37a, 39] implemented in the Amsterdam Density Functional package^[35a, 93] (ADF2016 version). The native hybrid PBE0^[29] functional was used for all analyses by the quantum theory of atoms in molecule (QTAIM) applied in single point calculations with geometries optimized with the PBE-D3(BJ) functional. Corminboeuf's PBE0-dDsC^[94] functional was used in the geometry optimization and QTAIM analysis of DVGGIN and CI-DVGGIN; the ETS-NOCV^[81] analysis for DVGGIN was carried out with the native PBE0 functional. All computations used the scalar relativistic *Zeroth Order Regular Approximation* (ZORA) and were carried out with *ad hoc* all-electron basis sets: single polarized triple- ζ (TZP) Slater type orbitals were used for all elements in this study^[30, 95]. Linearly independent basis sets with diffuse functions in fit were applied whenever PBE0 and PBE0-dDsC functionals were used. Geometry optimizations by energy gradient minimization were carried out in all cases with an integration grid accuracy comprised between 4 and 6.5, an energy gradient convergence criterion of 10^{-3} au and tight to very tight SCF convergence criterion (10^{-7} - 10^{-8} au). Counterpoise correction for basis set superposition error (BSSE) was estimated to represent about less than 3 % : corrected values of \mathcal{I} are listed in Table 1. BSSE energy values were computed using the fragmentation scheme used to investigate silylicity by applying the conventional method^[96] of "ghost atoms" with the all electron (ZORA) TZP basis set. Energy Decomposition analysis^[25] (EDA or "fragment analysis" in ADF) as well as calculations of vibrational modes (analytical second derivative frequencies) were performed using ADF2016 subroutines with optimized geometries at the ZORA-PBE-D3(BJ)/all electron TZP level. Vibrational modes were computed in all cases geometries at the ZORA-PBE-D3(BJ)/all electron TZP level to verify that the optimized geometries were related to an energy minimum. Natural atomic orbital (NAO) and natural bond orbital (NBO) analyses as well as Wiberg indice determination were performed with the GENNBO 6.0 module of ADF^[76, 97] with geometries relaxed at the ZORA-PBE-D3(BJ)/ all electron TZP level. QTAIM^[75] analyses and NCI region plots^[98] were achieved using the modules of ADF2016. Graphical representations of molecular structures, isosurfaces and contour plots were drawn using *ADFview* v13.

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Keywords: silicon • silanes • Si ligands • Coordination Chemistry: Ligand Classes • Transition metals

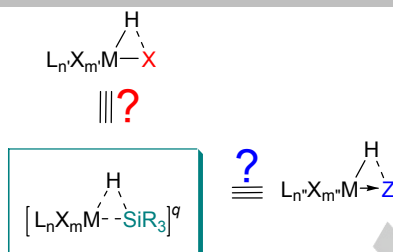
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FULL PAPER

The computation of metal-Si interaction energies reveals situations where the silyl group behaves as a Z-type ligand according to Green's covalent bond classification method.



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Is the R_3Si Moiety in Metal-Silyl Complexes a Z ligand ? An Answer from the Interaction Energy