DOCTORAL DISSERTATION

TRANSITION METAL–FREE HYDROELEMENTATION OF C=C AND C=O BONDS WITH P-BLOCK ELEMENTS – A QUANTUM CHEMICAL MECHANISTIC STUDY

IN THE FORM OF A THEMATICALLY COHERENT SERIES
OF SCIENTIFIC ARTICLES PUBLISHED IN SCIENTIFIC JOURNALS,
PREPARED IN THE FIELD OF SCIENCE,
IN THE DISCIPLINE OF CHEMICAL SCIENCES

MATEUSZ NOWICKI

PROMOTOR: PROF. DR HAB. MARCIN HOFFMANN

Poznań 2023

PODZIĘKOWANIA

Panu Profesorowi Marcinowi Hoffmannowi
za wszystkie lata opieki naukowej,
na przestrzeni których przekazał mi
mnóstwo wiedzy i umiejętności;
za to, że zawsze pomagał oglądać rzeczy
i zjawiska z niebanalnej perspektywy
i dostrzec ich ukryte aspekty;
za okazywaną na każdym kroku życzliwość.

Mojej Małżonce,
Rodzicom,
wszystkim krewnym,
przyjaciołom i dobroczyńcom,
bez których z pewnością
nie byłbym dziś tu, gdzie jestem.

Computations were carried out using the PL-Grid infrastructure.
The work was supported by Grant no. POWR.03.02.00-00-I020/17 co-financed by
the European Union through the European Social Fund.

sed omnia in mensura, et numero et pondere disposuisti

SCIENTIFIC RESUME

Education

2014-2017	Adam Mickiewicz University in Poznań, Forensic Chemistry – Bachelor 4.934 grade point average
2017-2019	Adam Mickiewicz University in Poznań, Forensic Chemistry – Master of Science *Maxima cum laude* 4.988 grade point average
2019-2023	Adam Mickiewicz University in Poznań, Faculty of Chemistry – Doctor of Philosophy (candidate) 4.971 grade point average

List of thematically related scientific articles published in JCR-listed journals constituting this dissertation

1. **Nowicki, M.**; Zaranek, M.; Pawluć, P.; Hoffmann, M. DFT Study of Trialkylborohydride-Catalysed Hydrosilylation of Alkenes – the Mechanism and Its Implications. *Catal. Sci. Technol.* **2020**, *10* (4), 1066–1072. https://doi.org/10.1039/C9CY02261A. (**Appendix A1**)
   IF = 6.177, MEiN = 140
2. **Nowicki, M**.; Zaranek, M.; Grzelak, M.; Pawluć, P.; Hoffmann, M. Mechanism of Silylation of Vinyl Arenes by Hydrodisiloxanes Driven by Stoichiometric Amounts of Sodium Triethylborohydride – a Combined DFT and Experimental Study. *Int. J. Mol. Sci.* **2023**, 24, 4924. https://doi.org/10.3390/ijms24054924. (**Appendix A2**)
   IF = 6.208, MEiN = 140
3. Zaranek, M.; **Nowicki, M.**; Andruszak, P.; Hoffmann, M.; Pawluć, P. Hydrogermylation Initiated by Trialkylborohydrides: A Living Anionic Mechanism. *Chem. Commun.* **2022**, *58* (100), 13979–13982. https://doi.org/10.1039/D2CC05567H. (**Appendix A3**)

IF = 6.065, MEiN = 200

4. **Nowicki, M.**; Kuciński, K.; Hreczycho, G.; Hoffmann, M. Catalytic and Non-Catalytic Hydroboration of Carbonyls: Quantum-Chemical Studies. *Org. Biomol. Chem.* **2021**, *19* (13), 3004–3015. https://doi.org/10.1039/D1OB00037C. (**Appendix A4**)
   IF = 3.890, MEiN = 100

List of other scientific articles published in JCR-listed journals

1. Pawłowska, A.; Volle, J.-N.; Virieux, D.; Pirat, J.-L.; Janiak, A.; **Nowicki, M.**; Hoffmann, M.; Pluskota-Karwatka, D. Perfluorophenyl Phosphonate Analogues of Aromatic Amino Acids: Synthesis, X-Ray and DFT Studies. *Tetrahedron* **2018**, *74* (9), 975–986. https://doi.org/10.1016/j.tet.2018.01.019.
   IF = 2.388, MEiN = 70

International conferences

1. Agata Pawłowska, Jean-Noël Volle, David Virieux, Jean-Luc Pirat, Agnieszka Janiak, **Mateusz Nowicki**, Marcin Hoffmann, Donata Pluskota-Karwatka *Perfluorophenyl phosphonate analogues of aromatic amino acids: synthesis, X-ray and DFT studies*, **II^e Assises franco polonaises de Chimie**, 14-15.03.2019, Paris, France.
2. **Mateusz Nowicki**, Maciej Zaranek, Piotr Pawluć, Marcin Hoffmann *Quantum-chemical study of the mechanisms of selected sodium triethylborohydride-catalysed styrene hydrosilylation reactions*, **French-Polish Chemistry Congress**, 4-6.07.2019, Paris, France.
3. **Mateusz Nowicki**, Marcin Hoffmann, Donata Pluskota-Karwatka, Agata Pawłowska, Jean-Noël Volle, David Virieux, Jean-Luc Pirat, Agnieszka Janiak *Perfluorophenyl phosphonate analogues of phenylglycine and homophenylalanine: synthesis and structural studies*, **4th International Conference on the Periodic Table: Mendeleev 150**, 26-28.07.2019, Petersburg, Russia.
4. **Mateusz Nowicki**, Maciej Zaranek, Piotr Pawluć, Marcin Hoffmann *The Mechanism of Trialkylborohydride-Catalyzed Hydrosilylation and Its Implications – a DFT Study*, **Scholars International Conference on Frontiers in Chemistry and Drug Discovery**, 2-3.12.2019, Madrid, Spain.

5. **Mateusz Nowicki**, Marcin Hoffmann *Trialkylborohydride-catalysed hydrosilylation of alkenes – a quantum chemical study of the mechanism and its consequences,* **Chemistry and Chemical Technology in XXI Century**, 21-24.09.2020, Tomsk, Russia. (online participation due to travel restrictions)
6. **Mateusz Nowicki**, Marcin Hoffmann, Piotr Andruszak, Maciej Zaranek, Piotr Pawluć Hydrogermylation of styrenes initiated by trialkylborohydrides – a quantum-chemical study of the mechanism, **Modeling and Design of Molecular Materials 2022**, 19-22.09.2022, Gdańsk, Poland.

Domestic conferences

1. **Mateusz Nowicki**, Marcin Hoffmann, *Ocena jakości paliw płynnych jako obiekt opinii biegłego sądowego,* **III Konferencja Młodych Chemików Sądowych**, 15-16.06.2018, Kraków.
2. **Mateusz Nowicki**, Marcin Hoffmann, Donata Pluskota-Karwatka, Tomasz Pędziński, *Quantum-chemical investigation of selected psychotropic drugs: quetiapine, olanzapine and trazodone*, **XVI Ogólnopolskim Seminarium Doktorantów „Na Pograniczu Chemii i Biologii”**, 17-20.06.2018, Karpacz.
3. Agata Pawłowska, Jean-Noël Volle, David Virieux, Jean-Luc Pirat, Agnieszka Janiak, **Mateusz Nowicki**, Marcin Hoffmann, Donata Pluskota-Karwatka, *Perfluorophenyl Phosphonate Analogues of Aromatic Amino Acids: Synthesis, X-Ray and DFT Studies,* **61. Zjazd Naukowy Polskiego Towarzystwa Chemicznego**, 17-21.09.2018, Kraków.
4. **Mateusz Nowicki**, Wojciech Jankowski, Marcin Hoffmann, *Zastosowanie narzędzi Google w monitorowaniu rynku nowych substancji psychoaktywnych*, **V Ogólnopolska Studencka Konferencja Kryminalistyczna „50 twarzy zbrodni”**, 7-9.12.2018, Poznań.
5. **Mateusz Nowicki**, Wojciech Jankowski, Marcin Hoffmann, *Zastosowanie narzędzi Google w monitorowaniu rynku nowych substancji psychoaktywnych*, **Zjazd Zimowy Sekcji Studenckiej Polskiego Towarzystwa Chemicznego,** 8.12.2018, Warszawa.
6. **Mateusz Nowicki**, Wojciech Jankowski, Marcin Hoffmann, *Zastosowanie narzędzi Google w monitorowaniu rynku nowych substancji psychoaktywnych*, **III Ogólnopolska Konferencja Naukowa „24h Kryminalistyki”**, 14-15.12.2018, Wrocław.

7. **Mateusz Nowicki**, Maciej Zaranek, Piotr Pawluć, Marcin Hoffmann, *Quantum-chemical study of the mechanisms of selected sodium triethylborohydride-catalysed styrene hydrosilylation reactions*, **Zjazd Wiosenny Sekcji Studenckiej Polskiego Towarzystwa Chemicznego**, 10-14.04.2019, Ustroń.
8. **Mateusz Nowicki**, Maciej Zaranek, Piotr Pawluć, Marcin Hoffmann, *Quantum-chemical study of the mechanisms of selected sodium triethylborohydride-catalysed styrene hydrosilylation reactions*, **XVII Ogólnopolskie Seminarium dla Doktorantów i Studentów „Na pograniczu chemii i biologii”,** 12-15.05.2019, Jastrzębia Góra.
9. **Mateusz Nowicki**, Marcin Hoffmann, *Stanisław Ulam – ojciec chrzestny obliczeń naukowych,* **Przełomowe osiągnięcia polskich nauk przyrodniczych i medycznych,** 3-4.06.2019, Poznań.
10. **Mateusz Nowicki**, Marcin Hoffmann, David Virieux, *Kwantowochemiczne badania wybranych związków fosforoorganicznych o symetrii* C_3 *jako potencjalnych śmigieł molekularnych,* **XIII Kopernikańskie Seminarium Doktoranckie,** 16-18.06.2019, Bachotek.
11. **Mateusz Nowicki**, Maciej Zaranek, Piotr Pawluć, Marcin Hoffmann, *Badania kwantowochemiczne mechanizmów wybranych reakcji hydrosililowania katalizowanych trietyloborowodorkiem sodu*, **XIII Kopernikańskie Seminarium Doktoranckie,** 16-18.06.2019, Bachotek.
12. **Mateusz Nowicki**, Maciej Zaranek, Piotr Pawluć, Marcin Hoffmann *Kwantowochemiczne badania mechanizmów wybranych reakcji hydrosililowania katalizowanych trietyloborowodorkiem sodu,* **62. Zjazd Naukowy Polskiego Towarzystwa Chemicznego**, 2-6.09.2019, Warszawa.
13. **Mateusz Nowicki**, Maciej Zaranek, Piotr Pawluć, Marcin Hoffmann *Metody obliczeniowe chemii kwantowej jako narzędzie do badania mechanizmów reakcji chemicznych – hydrosililowanie alkenów katalizowane trietyloborowodorkiem sodu,* **51. Ogólnopolska Szkoła Chemii „Władcy Chemii”**, 8-10.11.2019, Wrocław.
14. **Mateusz Nowicki**, Marcin Hoffmann, David Virieux, Jean-Luc Pirat *Badania termodynamiki i kinetyki interkonwersji atropoizomerów bisarylowych pochodnych metanofosfocyny,* **III Ogólnopolskie Sympozjum Chemii Bioorganicznej, Organicznej i Biomateriałów**, 7.12.2019, Poznań.

15. **Mateusz Nowicki**, Marcin Hoffmann, David Virieux, Jean-Luc Pirat *Badania termodynamiki i kinetyki interkonwersji atropoizomerów bisarylowych pochodnych metanofosfocyny metodami kwantowochemicznymi*, **Zjazd Zimowy Sekcji Studenckiej Polskiego Towarzystwa Chemicznego**, 14.12.2019, Poznań.

Scholarships and Awards

1. Scholarship of the Rector of Adam Mickiewicz University for the best students (2015/2016).
2. Scholarship of the Rector of Adam Mickiewicz University for the best students (2016/2017)..
3. Scholarship of the Rector of Adam Mickiewicz University for the best students (2018/2019)
4. Scientific scholarship of the Minister of Science and Higher Education of Poland (2018/2019).
5. Master of Science - *Maxima cum laude* diploma (2018/2019).
6. Medal for Graduates for outstanding scientific achievements awarded by Adam Mickiewicz University in Poznań (2019/2020).
7. Scientific scholarship of the Marshal of Greater Poland Voivodeship (2019/2020).
8. Scholarship of the Rector of Adam Mickiewicz University for the best doctoral candidates (2020/2021).
9. Increase in doctoral scholarship from the pro-quality grant candidates (2020/2021).
10. Scholarship of the Rector of Adam Mickiewicz University for the best doctoral candidates (2021/2022).
11. Increase in doctoral scholarship from the pro-quality grant candidates (2020/2021).

STRESZCZENIE

Niniejsza praca doktorska jest wynikiem badań nad mechanizmami wybranych reakcji hydrosililowania i hydrogermylowania alkenów oraz hydroborowania związków karbonylowych, katalizowanych lub inicjowanych przez proste związki chemiczne niezawierające metali przejściowych. Mechanizmy te badane były metodami obliczeniowymi chemii kwantowej, przede wszystkim – choć nie wyłącznie – metodami bazującymi na teorii funkcjonału gęstości (DFT), w szczególności hybrydowym funkcjonałem M06-2X. Składa się ona z czterech artykułów.

W pierwszym artykule przedstawiono wyniki badań DFT reakcji hydrosililowania wiązań C=C katalizowanych trietyloborowodorkami. Zaproponowano szczegółowy mechanizm i profil energetyczny dla reakcji styrenu z fenylosilanem oraz opisano struktury geometryczne i elektroniczne punktów stacjonarnych odpowiadających poszczególnym etapom reakcji. Zaproponowany model zaaplikowano również do szeregu innych alkenów i hydrosilanów. Wyniki obliczeń kwantowochemicznych nie tylko dostarczają spójnego wyjaśnienia wysokiej regioselektywności katalizowanej przez $NaHBEt_3$ reakcji hydrosililowania, ale także pozostają w zgodności z eksperymentalnie otrzymanymi wydajnościami w zależności od użytych substratów, co nie tylko dodatkowo wspiera przedstawiony mechanizm, ale także pozwala traktować zastosowaną metodologię jako narzędzie obliczeniowe do przewidywania reaktywności w tego typu układach.

W drugim artykule badane były reakcje winyloarenów z hydrodisiloksanami w obecności trietyloborowodorku sodu. Nie wykryto oczekiwanych produktów hydrosililowania, ponieważ trietyloborowodorku okazały się nie wykazywać aktywności katalitycznej obserwowanej w poprzednich badaniach; zidentyfikowano natomiast produkt formalnego sililowania dimetylosilanem, a trietyloborowodorku zużywane były w ilościach stechiometrycznych. W artykule szczegółowo opisano mechanizm reakcji z uwzględnieniem swobody konformacyjnej ważnych produktów pośrednich oraz krzywizny dwuwymiarowych przekrojów hiperpowierzchni energii potencjalnej. Zidentyfikowano prosty sposób przywrócenia katalitycznego charakteru przemiany i wyjaśniono go w odniesieniu do jej mechanizmu. Przedstawiona reakcja jest przykładem zastosowania prostego związku wolnego od metali przejściowych w

syntezie produktów sililowania, w której łatwopalne odczynniki gazowe zastąpiono wygodniejszym surogatem silanowym.

W trzecim artykule scharakteryzowano trialkiloborowodorki sodu jako inicjatory selektywnego hydrogermylowania aromatycznych alkenów. Stwierdzono, że addycja fenylogermananu i difenylogermananu w obecności 10 mol% NaHB(*sec*-Bu)$_3$ przebiega w sposób wysoce selektywny dając – w przeciwieństwie do analogicznego procesu hydrosililowania – produkty β-germylowania. Charakter tego procesu został wyjaśniony przy pomocy obliczeń DFT; zaproponowano, że mechanizm przebiega poprzez trójpodstawiony anion germankowy, którego atak na terminalny winylowy atom węgla jest przyczyną obserwowanej regioselektywności.

W ostatnim artykule przeanalizowano hydroborowanie związków karbonylowych zarówno bez katalizatora, jak i z udziałem KF. Wyniki obliczeń dla kilku potencjalnych ścieżek reakcji zostały zestawione z obliczeniami opartymi na danych eksperymentalnych, co pozwoliło ustalić wieloetapowe mechanizmy i profile energetyczne dla reakcji pinakoloboranu z benzaldehydem i acetofenonem (w obecności KF). Zastosowano pięć różnych poziomów teoretycznych w celu wybrania najbardziej odpowiedniego i opracowania protokołu obliczeniowego do dalszych badań. Po wybraniu najlepiej sprawdzających się metod można było przystąpić do badania układów złożonych z większej liczby atomów, co z kolei pozwoliło na odkrycie wielu ścieżek, tworzących kilka nakładających się na siebie cykli katalitycznych. Mechanizm hydroborowania bez katalizatora i rozpuszczalnika również został przeanalizowany przez pryzmat opracowanej metodologii, co doprowadziło do zupełnie nowego spojrzenia na ścieżki tej i podobnych reakcji, jako że wielocząsteczkowa kaskada transferów wodorku jest bardziej energetycznie preferowana niż czteroczłonowy stan przejściowy.

ABSTRACT

The present PhD thesis is the result of research into the mechanisms of selected hydrosilylation and hydrogermylation reactions of alkenes and hydroboration of carbonyl compounds, catalysed or initiated by simple transition metal– free chemical compounds. These mechanisms were investigated using quantum chemistry computational methods, primarily – but not exclusively – methods based on density functional theory (DFT), especially the hybrid M06-2X functional. It consists of four articles.

The first article presents the results of a DFT study of triethylborohydride-catalysed C=C bond hydrosilylation reactions. A detailed mechanism and energy profile for the reaction of styrene with phenylsilane is proposed and geometric and electronic structures of stationary points corresponding to each step are described. The model proposed is also applied to a number of other alkenes and hydrosilanes. The results of quantumchemical computations not only provide a consistent explanation of the high regioselectivity of $NaHBEt_3$-catalysed hydrosilylation, but are also in good agreement with the experimental yields depending on the substrates used, hence they not only further support the mechanism presented, but also make a computational toolkit for predicting reactivities.

In the second one, reactions of vinyl arenes with hydrodisiloxanes in the presence of sodium triethylborohydride are studied. The expected hydrosilylation products were not detected because triethylborohydrides did not exhibit catalytic activity observed in previous studies; instead, the product of formal silylation with dimethylsilane was identified, and triethylborohydride was consumed in stoichiometric amounts. In the article, the mechanism of the reaction is described in detail, with due consideration given to conformational freedom of important intermediates and two-dimensional curvature of the potential energy hypersurface cross sections. A simple way to reestablish the catalytic character of the transformation was identified and explained with reference to its mechanism. The reaction presented is an example of the application of a simple transition-metal-free species in the synthesis of silylation products with flammable gaseous reagents replaced by a more convenient silane surrogate.

The third article presents sodium trialkylborohydrides as initiators of selective hydrogermylation of aromatic alkenes. Addition of phenylgermane and diphenylgermane in the presence of 10 mol% of $NaHB(\textit{sec}\text{-}Bu)_3$ is found to proceed in a highly selective manner to give – in contrast to the analogous hydrosilylation process – β-germylated products. The nature of this process was explained with the aid of DFT calculations and it was proposed that the mechanism proceeds via a trisubstituted germanide anion whose attack on the terminal vinyl carbon is the source of selectivity.

The last article examines both catalyst-free and KF-mediated hydroboration of carbonyl compounds. The results of computations for several potential reaction pathways are juxtaposed with experiment-based calculations, which leads to stepwise mechanisms and energy profiles for the reactions of pinacolborane with benzaldehyde and acetophenone (in the presence of KF). Five different levels of theory are employed to select the most applicable theoretical approach and develop a computational protocol for further research. Upon selection of the best-performing methods, larger molecular systems are studied, which brings up multi-pathway, overlapping catalytic cycles. The mechanism of solvent-free, catalyst-free hydroboration of aldehydes is also revisited through the prism of the elaborated methodology, which leads to a whole new perspective on the pathways of this and similar reactions, with a multimolecular cascade of hydride transfers being more energetically favoured than a four-membered transition state.

I. STATE OF THE ART

I.1. COMPUTATIONAL CHEMISTRY

Although the first calculations in the field of theoretical chemistry can be traced back to 1926,[1–4] computational chemistry in the strict sense, i.e. a branch of chemistry that exploits the capabilities of computers to study a wide variety of chemical questions, did not develop until the 1950s, following the advent and widespread use of modern electronic computers. The systematic increase in computing power that has continued since then has contributed to a steady improvement in the accuracy with which a given system can be studied and in the size of the system that can be studied at a given level of accuracy.[5] Some of the many methods available to researchers today are briefly discussed below.

I.1.1. Newtonian mechanics–based methods

Molecular dynamics allows the evolution of a system over time to be described by integrating the equations of motion of individual atoms (or groups of atoms, or even molecules as a whole) with a given kinetic energy, often taking into account not only collisions but also other (e.g. electrostatic) interactions between them. It allows the study of the largest systems, consisting of up to hundreds of thousands of atoms. Monte Carlo simulations have a similar range of applications, although on a different (mainly statistical) basis.[5,6]

Molecular mechanics is based on the application of a force field. It consists of a relatively simple (compared to e.g. ab initio methods) algebraic expression for the potential energy of the system and a set of parameters characterizing each atom (e.g. atomic mass, atomic radius, partial charge depending on bonded atoms, polarizability), pair (equilibrium bond length), triple (equilibrium valence angle) and quadruple (equilibrium torsion angle). Based on these parameters, the actual position of the atoms in the system, and a number of approximations (including the harmonic oscillator, the Morse oscillator, and the Lennard Jones potential), the force field determines the energy of the system, essentially assigning an energy 'penalty' for any deviation from the equilibrium positions. An appropriate choice of force field allows, for example, the modelling of biological macromolecules such as proteins and nucleic acids.[5,6]

I.1.2. Quantum mechanics–based methods

Quantum mechanics was developed in the 1920s as a theory to explain phenomena that Newtonian mechanics could not.[5] It postulates the existence of a wave function that completely describes the state of a system at any given time; the solution of the Schrödinger equation makes it possible to calculate the exact energy of a system described by a given wave function.[7] At the present state of science, the analytical solution of the Schrödinger equation is only possible for simple systems (e.g. an isolated hydrogen atom); for the vast majority of scientific problems, the use of simplifications is necessary to make calculations feasible.[6]

I.1.2.1. Ab initio methods

Ab initio (Latin for 'from the beginning') methods do not use empirical data, but only universal physical constants. The most common of these is the Hartree–Fock–Roothaan method, also known as the SCF LCAO MO method.[8] It works by approximating the wave function of a system as a Slater determinant[9] of the one-electron functions (molecular spin orbitals — MOs),[10] which describe the motion of individual electrons in the averaged field generated by other electrons (mean-field approximation) and at fixed positions of the nuclei (Born–Oppenheimer approximation).[11] Each of these MOs is a Linear Combination of Atomic Orbitals (LCAO), which is usually a contraction of several Gaussian-type functions centered on individual atoms; each atomic orbital is assigned a coefficient corresponding to its contribution to the molecular orbital. The minimum energy of the system is found by iteratively solving the Fock equations until successive iterations lead to a negligibly small change in energy (Self Consistent Field (SCF) method). This method is based on the variational principle, which states that the calculated energy is greater than or equal to the actual energy of the system. In practice, the calculated energy is always higher due to numerous approximations.[5] The SCF LCAO MO method neglects the dynamic correlation of the electrons; many methods have been developed to take this into account, such as the Configuration Interaction (CI) method,[12] the Multi-Configurational Self-Consistent Field (MC SCF) method,[13] the Coupled Cluster (CC) method,[14] and the Møller-Plesset Perturbation Theory (MP).[15] The price of their higher accuracy is a significant computational cost — depending on the level of theory, these methods can be reasonably applied to systems of a few to a few hundred electrons.

I.1.2.2. Semiempirical methods

As an alternative, semi-empirical methods are based on similar theoretical principles as *ab initio* methods, the main difference being the significant simplification of part of the calculation (e.g. neglecting core electrons or two-electron integrals) and the compensation of the resulting error with parameters based on experimental data or more accurate calculations. These methods can be successfully applied to the study of extended organic molecules, but care must be taken to ensure that the parameterization range matches the calculated quantities and that the system is as similar as possible to those used to develop the parameters.

I.1.2.3. DFT methods

A different approach is based on density functional theory (DFT) methods, which are based on two Hohenberg–Kohn theorems.[16] The first theorem states that there is a certain functional which, when applied to the electron density, allows one to obtain complete information about the state of the system (without using the wave function); the second theorem states that the energy of the system for a given electron density, calculated by means of an exact but as yet unknown functional, is always higher than or equal to the exact energy. The practical implementation of the method involves solving the Kohn–Sham equations,[17] the most sensitive point of which is the consideration of the exchange–correlation potential (XC). Improvements in DFT methods focus on the development of increasingly accurate approximations to the XC functionals, the explicit form of which is not known[5]. Within these, hybrid functionals can be distinguished, which to some extent take into account the exchange potential calculated by the Hartree–Fock method (the expression for the exchange energy in the HF method is known exactly).[18] Computational experience shows that comparable and often more accurate results can be obtained with DFT methods at a computational cost comparable to ab initio methods, also for organic molecules;[19–22] however, the quality of the results strongly depends on the choice of the specific functional for the problem in question.[23–26]

I.1.3. Basis sets

Most quantum chemistry calculations approximate the electron wave function in terms of a molecular orbital, which is a linear combination of atomic orbitals that form the basis set.[5] These orbitals are usually of two basic types: Slater-Type Orbitals (STO),[27] or Gaussian-Type Orbitals (GTO).[28] Slater-Type Orbitals are based on the solution of the Schrödinger equation for a hydrogen-like atom and thus describe the behavior of electrons near and far from the nucleus quite correctly. However, they are computationally very expensive due to the need to solve the two-electron integrals numerically and are therefore generally rarely used.[5] Results of similar quality can be obtained by using basis functions which are linear combinations of several Gaussian orbitals (primitive functions – Figure 1).[29] The coefficients on the individual primitive functions are defined by the author of the basis set and are not subject to optimization in the course of the calculations.[30]

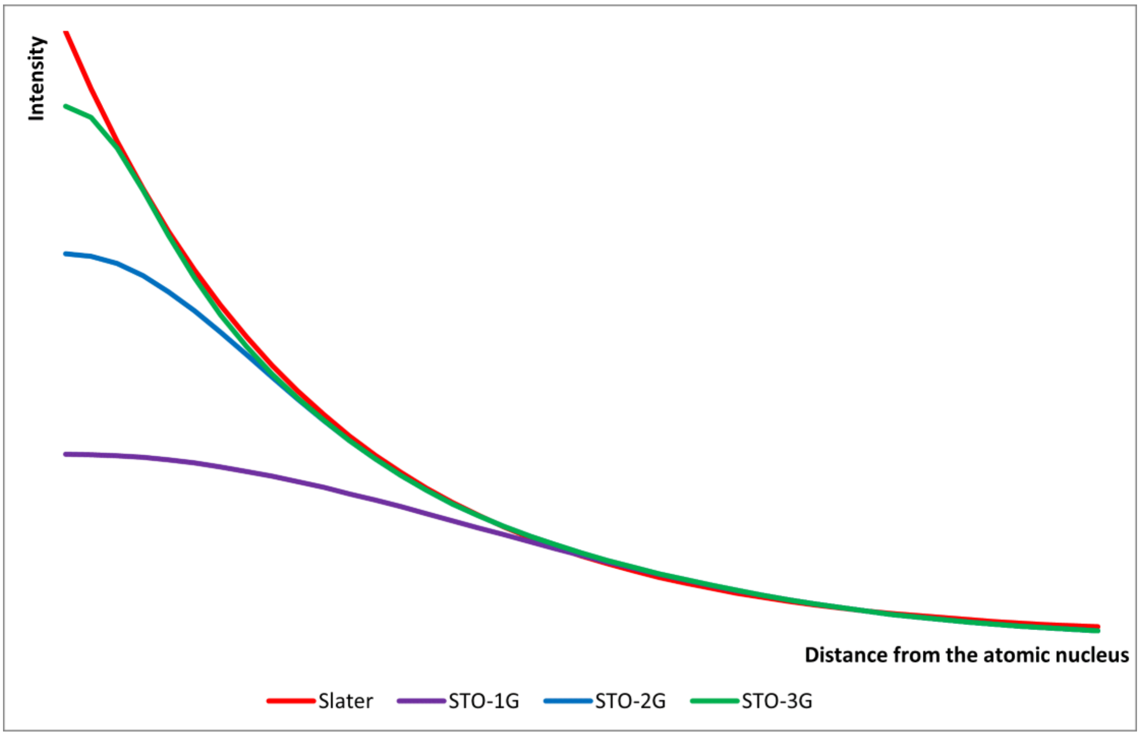


Figure 1 A single Gaussian orbital (STO-1G) is a very poor approximation of the Staterian orbital near the atomic nucleus. By constructing a linear combination of an increasing number of Gaussian orbitals (STO-2G, STO-3G), an increasingly better approximation of the Slater orbital is obtained.

Basis sets with one function (contraction) per occupied atomic orbital, called minimal bases, give poor-quality results and are generally not used.[30] N-zeta basis sets use a larger number of functions: double-zeta with two base functions per occupied orbital, triple-zeta with three, and so on. This gives greater flexibility to the atomic orbitals and allows them to be described more accurately according to their molecular environment. However, since valence orbitals play a key role in the interactions between atoms, in practice split valence bases are often used, providing additional basis functions only for the highest shell orbitals.[31] This is the optimal solution in terms of the accuracy of results and computational time.

For a more accurate description of the bond, it is often necessary to further extend the basis set with polarization functions.[32] These correspond to higher (unoccupied) shells and allow a greater asymmetry of the molecular orbitals around the nuclei and thus a better characterization of the electron density shifts during bond formation and bond breaking within and between molecules. A correct description of interactions at longer distances (and thus mainly intermolecular), especially when considering anions, often requires the additional consideration of diffusion functions,[33] which better characterize the wave function at a large distance from the nucleus. Both polarization and diffusion functions can be added to all atoms or only to some, especially heavy atoms (all except hydrogen), depending on the system under consideration.[6,30]

Since each basis function allows only an approximate representation of the molecular orbital to be obtained (the actual form of the molecular orbital is a linear combination of an infinite number of basis functions), the number of basis functions used and their quality, together with the method chosen for the calculation, are a key factor in determining the quality of the results obtained (Figure 2). Although a larger number of available basis functions generally leads to more accurate calculations, the choice of basis set should always be made in conjunction with the method used; for relatively simple methods, extending the basis set beyond a certain level leads to a marginal improvement in the results with a significant increase in the time required for the calculations. The same relationship is observed when using complex methods in small basis sets.[6,30,34] It should also be borne in mind that functional basis sets are often optimized for a particular group of calculation methods, such as correlation-consistent basis sets[35] for electron correlation calculations, and polarization-consistent basis sets[36] for HF and DFT calculations.

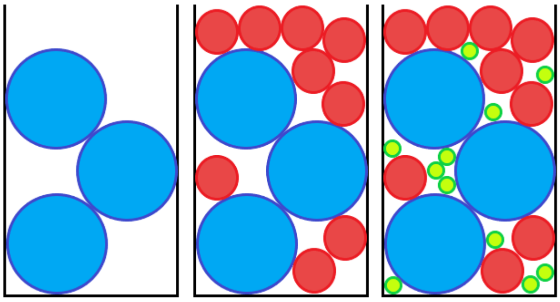


Figure 2 A symbolic representation of the impact of an increase in the size and quality of the functional base on the accuracy of the results obtained, but also on the time-consumption of the calculations.

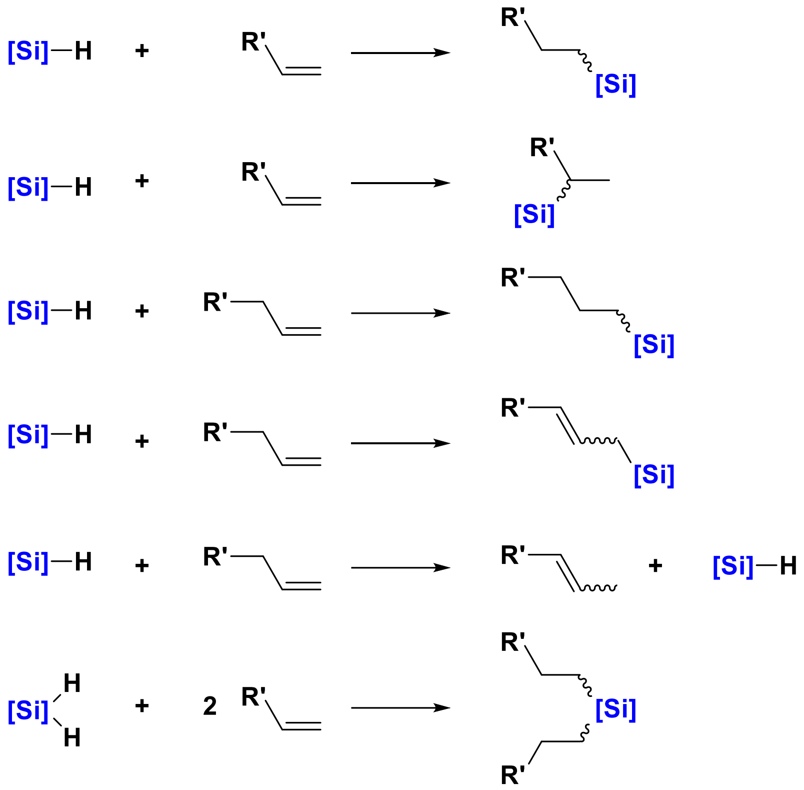
I.1.4. Challenges and perspectives

Despite the numerous approximations, simplifications, and omissions implemented by the computational methods of quantum chemistry, the main problem remains the rapid increase in the required computational time with increasing system size. Most commonly used methods scale nominally in the range of N^3 (most implementations of DFT methods) to N^7 (MP4 and CCSD(T) methods), which means that each doubling of the number of bodies in the system increases the number of computations required from 8 to 128 times.[5] There are ways to improve the scaling of the method (i.e. to reduce its complexity), such as the choice of the optimal representation[37] or the pre-selection of the integrals,[38–40] which consists of a cursory estimation of their values and the rejection of those whose value is close to zero. There are great advantages in using the fast multipole moment method, which allows the calculation of Coulomb interactions between distant elements of the system based on the representation of the field generated by them in the form of a multipole expansion.[41] In recent years, there have been increasing number of reports in the literature of the development of algorithms that allow linear scaling of computational methods with relatively small error, offering the prospect of further reductions in the time required for accurate calculations of very complex structures such as proteins, nucleic acids or synthetic polymers.[42–51] Much hope is also being placed in the development of quantum computers, which promise a level of computational power unattainable by even the most powerful classical (bit-based) computers.[52–55]

I.2. HYDROELEMENTATION

Every year, new examples of reactions with great potential for use in chemical synthesis are being discovered by scientists in universities and research institutes around the world. This catalogue is highly diverse, encompassing catalytic and non-catalytic, solvent and solvent-free, equilibrium and nonequilibrium reactions, varying in substrate tolerance and chemo-, regio- and enantioselectivity. Within this rich assortment, a valuable tool in the hands of the synthetic chemist is the hydroelementation reaction — the addition of an H–X bond to a multiple bond, most commonly C=C, C≡C, C=O, C=N and C≡N. While some of these reactions, such as hydrohalogenation[56] or hydration,[57] were known and well described in the 19th century and are now part of the core high school curricula, others, such as hydrostibination,[58] are still in their infancy, and some, such as hydrobismuthation,[59] are still awaiting the first fruitful attempts. Looking at the literature reports, both in terms of their total number in the databases and their growth in recent years, it is clear that hydrosilylation and hydroboration reactions — in this order — are of greatest interest to researchers.

In principle, the addition of an H–X bond to a multiple bond can clearly exhibit one of two basic regioselectivities, a fact already described by Markovnikov in his notable research.[56] In practice, the range of possible reaction products between two compounds is wider and includes, for example, products of dehydrogenative elementation (cross-dehydrogenative coupling),[60–62] polyhydroelementation[63–65] or even simple isomerisation[66–68] of an unsaturated compound (Scheme 1). The possibility of chiral product formation, either as a racemate or with some enantiomeric excess, or in the case of addition to alkynes, geometric isomers, should also be considered.[69,70] The final outcome of the reaction is influenced by various factors such as the substrates used and their stoichiometric ratio, the presence and type of catalyst, co-catalyst, initiator or solvent used, temperature, pressure, reaction time, and many others, but virtually all of these factors can be explained in terms of the reaction mechanism on the ground of collision theory.[71,72] Determining the mechanism by experimental methods, especially for multi-step and newly described reactions, can sometimes involve various technical, temporal, and financial difficulties.[73,74] As will be shown in this dissertation, computational chemistry can be an invaluable aid to this task.



Scheme 1 Possible products of the reaction between a hydrosilane and an alkene.

I.2.1. Hydrosilylation

Hydrosilylation of alkenes is one of the most extensively used processes employing homogeneous catalysis.[75] Owing to its ultimate atom economy and versatility, this reaction is now successfully used in the high-volume synthesis of various industrially applicable chemicals: adhesives, coatings, surfactants, lubricants, etc.[76] It can also be a step in more sophisticated synthetic processes in organic chemistry.[77,78] In terms of regioselectivity, two basic possible hydrosilylation products can be distinguished, with the vast majority of scientific reports dealing with 1,2-addition products, i.e. inconsistent with the Markovnikov rule. This is no surprise if one considers the usefulness of the products of such a reaction in the manufacture of formulations mentioned, but also the mechanism of action of most conventional catalysts.[79] Much fewer 2,1-addition catalysts, and consequently products, have been identified to date; however, the number was quite dynamically increasing in recent decades.[80] Reactions involving the formal substitution of a hydrogen atom by a silyl group, with or without a change in the position of the double bond,[81–84] or even alkene isomerization alone,[85] should also be mentioned. Other unsaturated compounds of interest for hydrosilylation include alkynes,[86–90] imines,[91–96] nitriles,[93,97–99] aldehydes, and ketones.[100–105] Of particular interest is the use of hydrosilylation as an intermediate in multi-step organic syntheses where, in combination with subsequent hydrolysis, it can yield a product of selective multiple bond reduction, often with the desired stereoselectivity.[106–108,77,109,110]

Although the reaction itself has already been described in 1946,[111–113] the two milestones in the development of hydrosilylation were the discovery of a platinum(IV) catalyst, known as Speier catalyst[114] and the discovery of Karstedt catalyst, based on a platinum(0) complex.[115] The use of the latter allowed a significant reduction in catalyst loading, down to a few tens of parts per million, making it suitable for use in industrial synthesis. Although very active, platinum-based catalysts still represent a significant fraction of the price of the final product, mainly due to the limited supply and hence the very high price of this precious metal and its non-recoverability.[79] This fact, combined with the inexorable tendency to try and replace any platinum group metal, is driving research towards non-precious metal[116,117] and even non-metallic[118,119] catalysts. The first group includes first-row d-block metals, primarily iron,[120–122] cobalt[120,121,123] and nickel,[120,121,124] as well as rare earth elements such as scandium, yttrium, lanthanum, cerium, samarium, holmium, and lutetium.[125–129] Several studies also describe hydrosilylation driven by s-block metals[130–132] and aluminum.[133–136] Non-metallic catalysis was reported as early as the early 1960s,[137] but only gained momentum in the 21st century and is associated with the use of Lewis-acidic and/or Lewis-basic organic compounds containing phosphorus, nitrogen, or boron.[138–142] Only in recent years have there been reports of hydrosilylation reactions catalyzed by simple trialkylborohydrides, including the reactions of hydrosilanes and hydrodisiloxanes in the presence of sodium trialkylborohydride which partly inspired the present work.[143–145] There are also increasing indications that some compounds of group 14 elements may, in the context of hydroelementation, exhibit catalytic properties reminiscent of those exhibited by transition metals.[146,147]

I.2.2. Hydrogermylation

The position of germanium in the periodic table — just below silicon (and above tin) is reflected in the reactivity of organogermanium compounds, which is characterized by numerous analogies to the behavior of organosilicon and organotin compounds. As is the case with classical hydrosilylation catalysts, hydrogermylation is mostly based on the activation of the Ge–H bond by a platinum group metal complex, such as rhodium and platinum.[148] First-row d-block catalysts,[149–154] radical-initiated reactions[155,156] and, in recent years, catalysts containing only main group elements[146,157] have also been described; interestingly, triethylborane (but not metal triethylborohydrides) was already used in hydrogermylation at the turn of the century.[158–160] It should be noted, however, that first reports of hydrogermylation are almost a decade later than hydrosilylation;[161] the former has been incomparably less explored so far, and it appears that the potential of this process is much broader than what has been described, and documented to date. As an aside, it is worth mentioning another use of organogermanium compounds, which is cross-coupling reactions. The properties exhibited by organogermanes allow their use in regio- and chemoselective carbon–carbon bond formation to obtain larger organic compounds.[162–165]

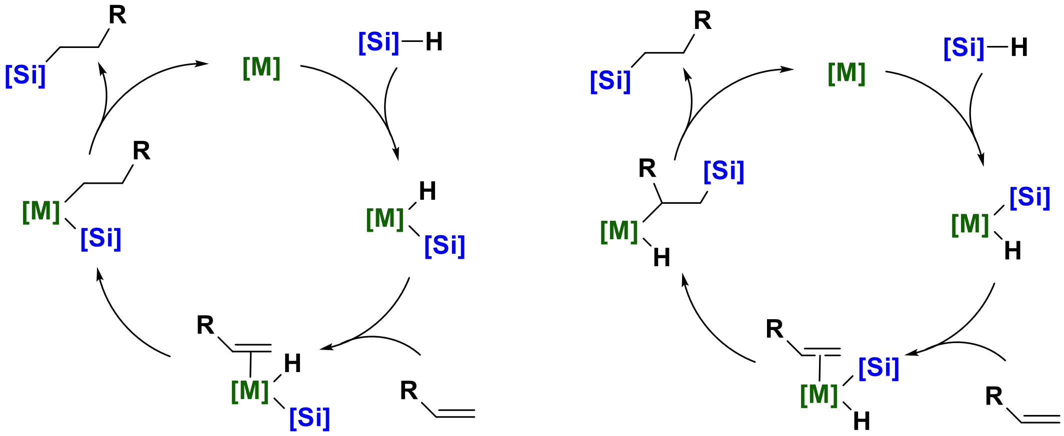
I.2.3. Hydroboration

As far as hydroboration reactions are concerned, it is not surprising that platinum group metal-based catalysts are also of exceptional performance and industrial utility.[166–169] However, it must be made clear that boron, as a group 13 element with a valence configuration $2s^2 2p^1$, will exhibit a reactivity that is not present in the two hydroelementation reactions previously discussed. We are mainly talking about reactions that take place without the presence of a catalyst or initiator, or even without the use of a solvent.[170–175] As far as reactions catalyzed by main group elements or first-row transition metals are concerned, these are relatively frequently observed and appear in literature reports almost as early as hydroboration itself.[176–180] On the other hand, the process has not yet found wider industrial application on a mass scale and is mainly used to produce specific fine chemicals and as an intermediate in complex syntheses.[117]

I.3. MECHANISMS OF HYDROELEMENTATION

I.3.1. Hydrosilylation of alkenes

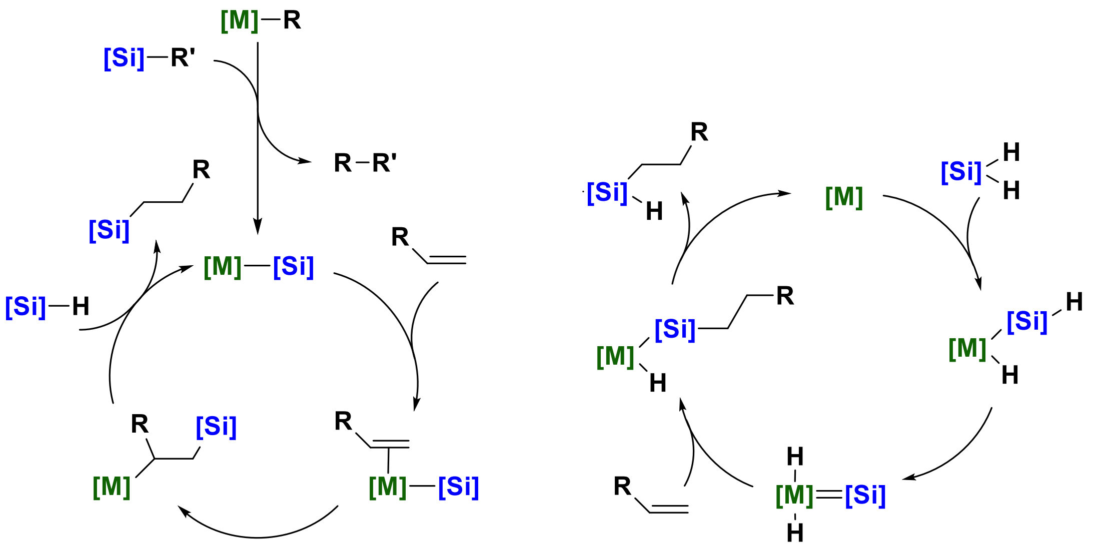
Despite the large catalogue of hydrosilylation catalysts described so far and the correspondingly large number of substrates, in the vast majority of cases, they can be classified, with some simplification, according to one of several basic mechanisms. Since 1965, the Chalk–Harrod mechanism,[181] originally proposed for alkene hydrosilylation reactions catalyzed by platinum complexes, has remained the fundamental one (Scheme 2). In the idealized form of this mechanism, one can distinguish 1) oxidative addition of the hydrosilane to the metal complex, which proceeds through the formation of a σ-complex between the Si–H bond and the metal atom/cation, 2) formation of a π-complex between the alkene double bond and the metal, 3) insertion of the alkene into the metal–hydrogen bond, 4) cleavage of the metal–carbon and metal–silicon bonds and formation of the carbon–silicon bond, i.e. reductive elimination of the resulting compound from the metal complex.



Scheme 2 A schematic representation of the Chalk–Harrod mechanism (left) and the modified Chalk Harrod mechanism (right).

In its alternative version, called the modified Chalk–Harrod mechanism,[182–185] the alkene is inserted into the metal–silicon bond, while the carbon–hydrogen bond is formed in the final step of the reaction (Scheme 2).

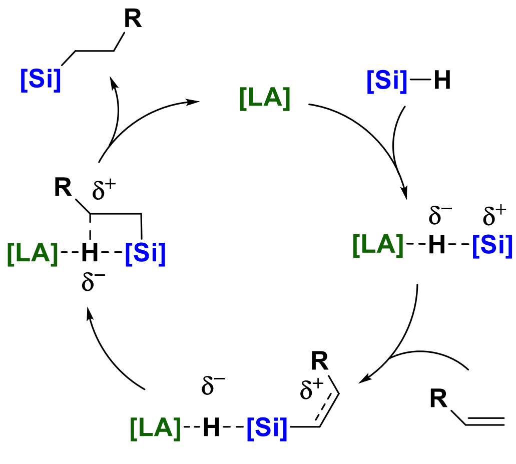
Sometimes the first reaction step is to produce the metal–silicon species through σ-bond metathesis, releasing a molecule with a newly created H–H, C–H or C–C bond (depending on the ligand abstracted from the metal complex – Scheme 3).[186,187]



Scheme 3 A schematic representation of the mechanism of metal silyl complex-catalyzed hydrosilylation (left) and Glaser–Tilley mechanism (right).

Another notable mechanism has been described by Glaser and Tilley and involves the metal–silylene complex; the migration of hydrides from the silicon atom to the metal atom increases the electrophilicity of the former, facilitating the further course of the reaction (Scheme 3).[188–191]

The Si–H bond can also be activated by the use of Lewis acid, for example in the form of aluminum or boron compounds. This makes it possible to create an electrophilic silicon species (either in the form of a cation or as a positively polarized moiety in a larger complex), which is later reproduced in the catalytic cycle (Scheme 4).[135,138,139,192]



Scheme 4 A schematic representation of the mechanism of Lewis acid-catalyzed hydrosilylation (starting with Si–H bond activation).

Special mention should certainly be made of systems called frustrated Lewis pairs (Figure 3). These are pairs of compounds between which the donor–acceptor bond, which would be desirable from the point of view of orbital energies, cannot be formed due to steric constraints, and the interaction is limited to the formation of a weak van der Waals complex. Such an interaction promotes the cleavage not only of such weak and polar bonds as Si–H, but also, for example, of the bond in molecular hydrogen, opening up catalytic possibilities far beyond hydrosilylation.[193]

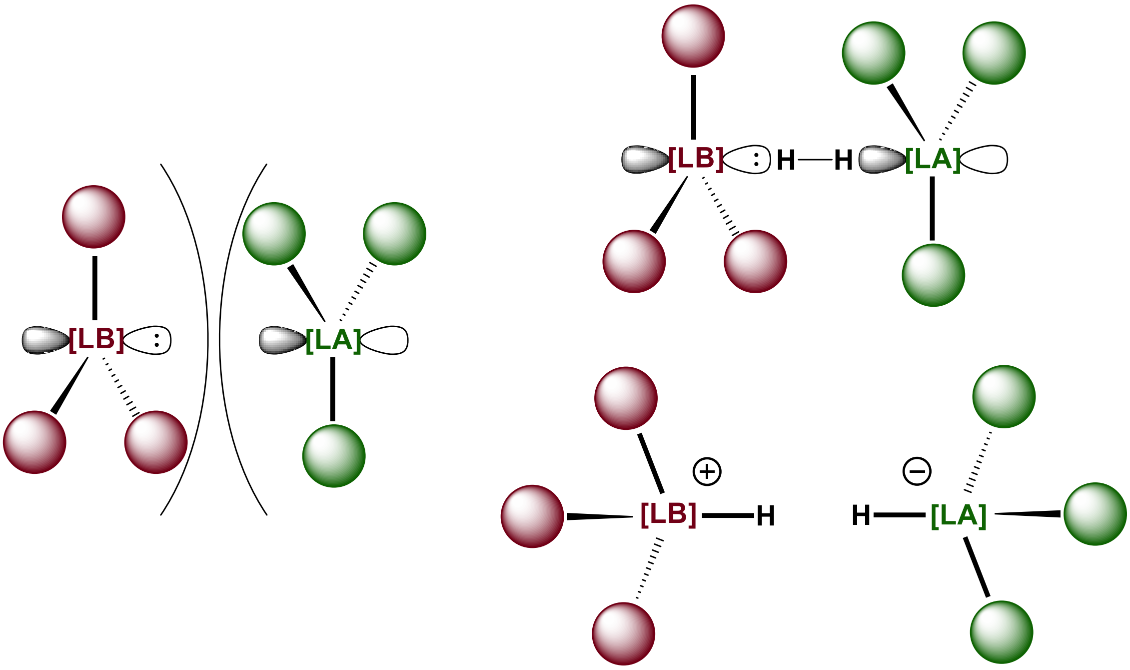
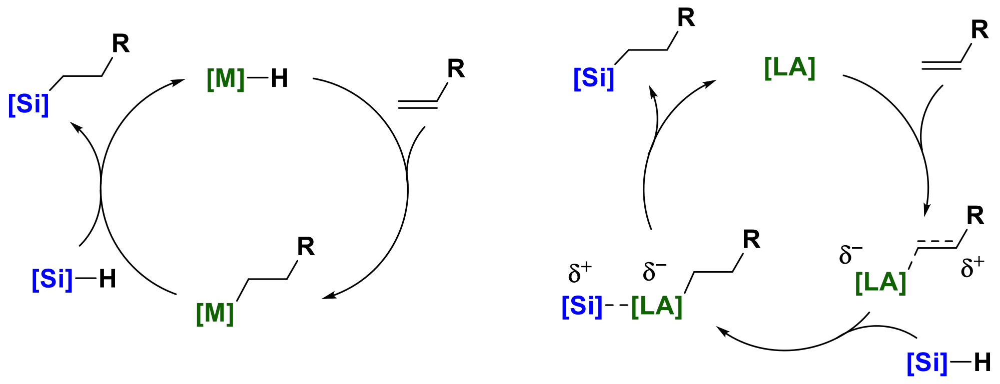


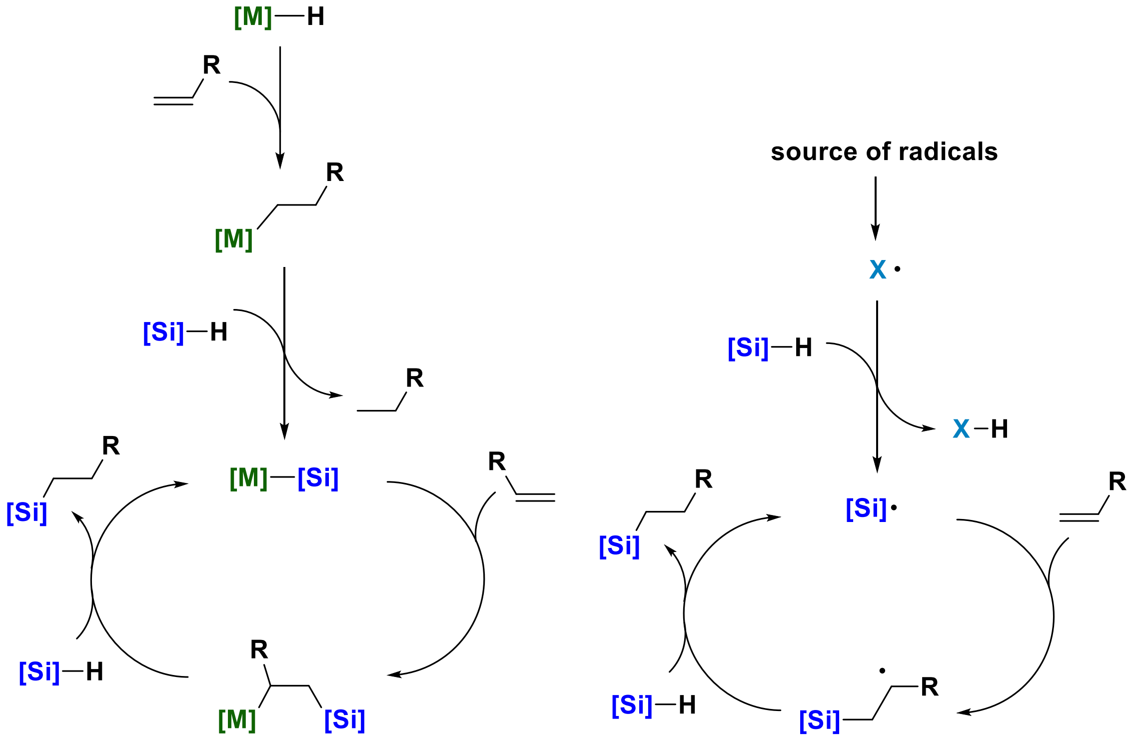
Figure 3 Frustrated Lewis pairs are unable to combine into a complex (left) but are able to cooperatively induce bond cleavage in another molecule (right).

The catalytic cycle does not need to be opened by activating the Si–H bond; there is no shortage of such proposed mechanisms in which the first step is to activate a multiple bond in the olefin. In the case of metal hydrides (but also, for example, borohydrides), this can be done by inserting the unsaturated compound into the M–H bond,[133,194] while in the case of Lewis acids, their role may be to form a complex that facilitates the insertion of the olefin into the Si–H bond (similar to the Chalk–Harrod mechanism, but without the formation of the M–Si bond – Scheme 5).[134]



Scheme 5 A schematic representation of the mechanism of metal hydride–catalyzed (left) and Lewis acid–catalyzed (right) hydrosilylation (starting with C=C activation).

It is also not uncommon to see reactions in which the hydride anion is transferred from the initiator to the multiple bond, the resulting anion removes hydrogen from the hydrosilane to form a hydrogenated by-product, and only the silicon species thus formed enters the catalytic cycle (Scheme 6).[195]

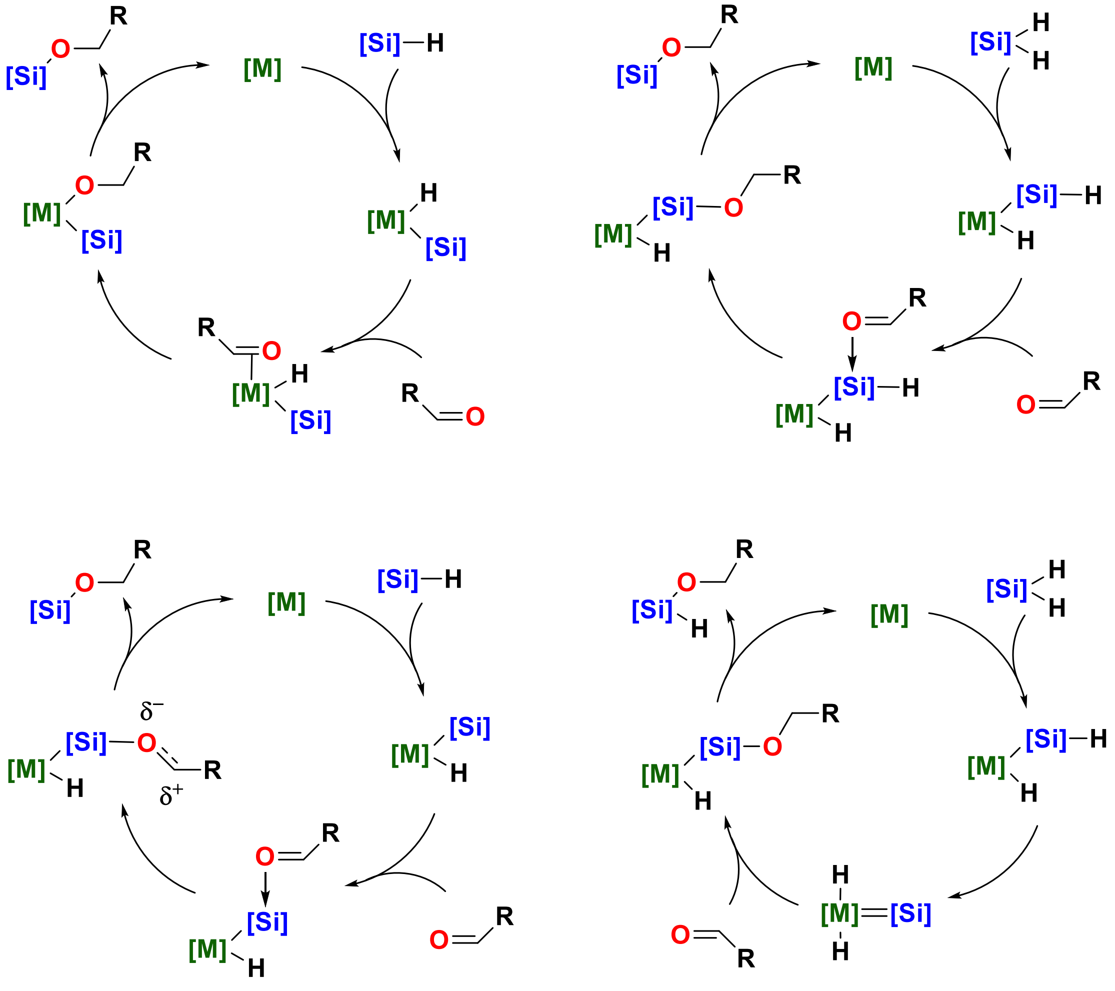


Scheme 6 A schematic representation of the mechanism of metal hydride-initiated, metal silyl complex–catalyzed (left) and radical-initiated (right) hydrosilylation.

A separate group consists of reactions that proceed by a radical mechanism, where the initiator usually removes hydrogen from the hydrosilane, forming a radical on the silicon atom (Scheme 6).[111]

I.3.2. Hydrosilylation of carbonyls

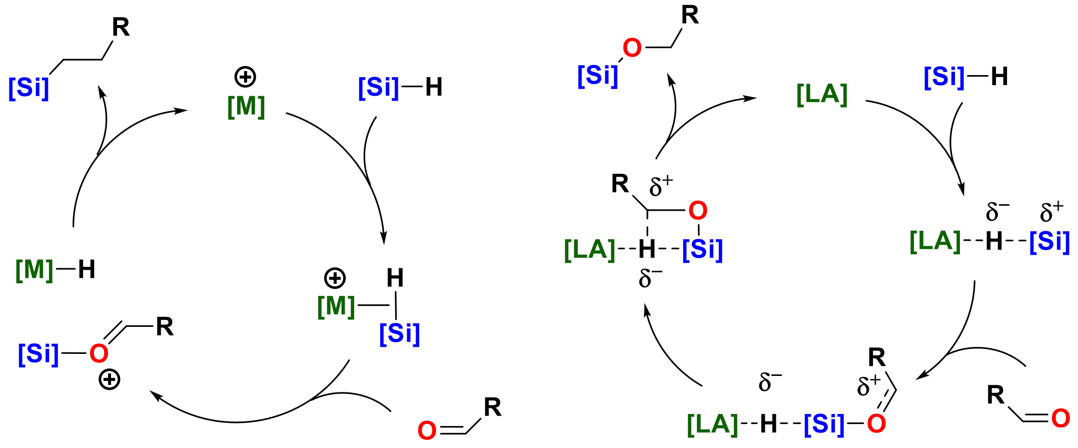
Mutatis mutandis, the known mechanisms for the hydrosilylation of carbonyl compounds are not very different from those for the hydrosilylation of olefins. The classical counterpart to the Chalk–Harrod mechanism, derived from reactions catalyzed by transition metal complexes, is the Ojima mechanism (Scheme 7).[196] The important difference, of course, is the significant polarization of the C=O bond, so that it is the negatively polarized, lone pair–possessing oxygen atom that forms a bond with the metal catalyst and then, after insertion into the M–Si bond, with the silicon atom.



Scheme 7 A schematic representation of the Ojima mechanism (top-left) and its modifications: with insertion of carbonyl into Si–H bond (top-right) and with hydrogen transfer from metal to carbonyl carbon: via Si–O complex (bottom-left) and via metal silylene (bottom-right).

In modified variants, the carbonyl oxygen may attack the silicon atom directly, either with subsequent insertion of the carbonyl into the Si–H bond[197] (only in di- and trihydrosilanes) or with hydrogen transfer to the carbonyl carbon[198] (in the latter case, the oxygen attack on the silicon may be preceded by the formation of silylene)[199,200]; in either case, the cycle ends with reductive elimination (Scheme 7).

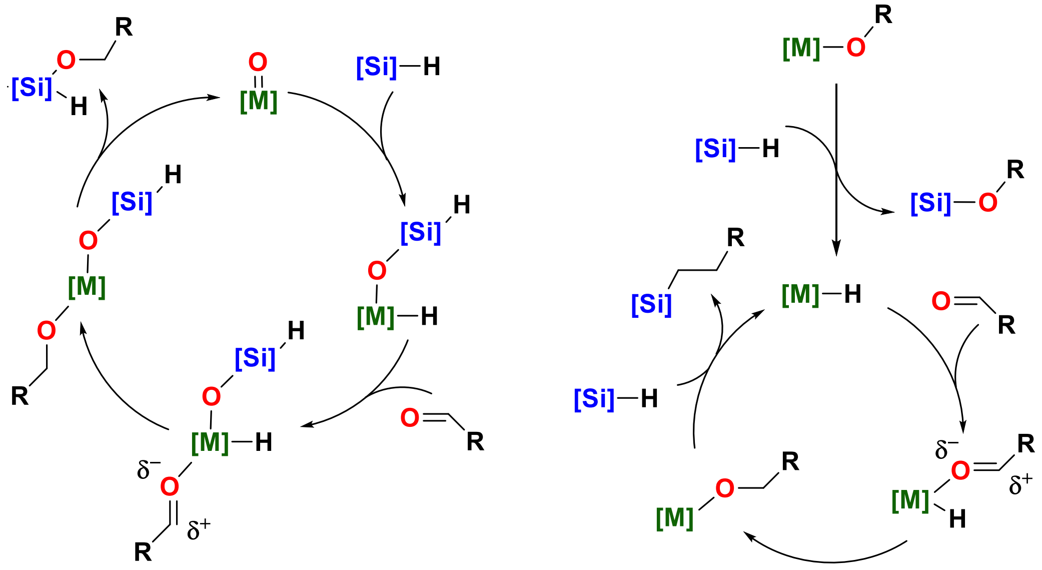
Reactions are also known in which there is no oxidative addition of the hydrosilane to the central metal atom, but only the formation of a σ-complex, which allows the activation of the Si–H bond and its addition to the carbonyl compound (Scheme 8).[201–203]



Scheme 8 A schematic representation of the mechanism of carbonyl hydrosilylation starting with Si–H bond weakening via σ-complex (left) and via axial polarization (right).

Another possibility is the already described weakening of the Si–H bond by its polarization,[204,205] especially by borane species,[206–208] which increases the electrophilicity of silicon and facilitates the attack of carbonyl oxygen on it (Scheme 8).

For some catalysts, hydrosilane can attach to the complex without the formation of an M–Si bond, but with the bonding of silicon to the heteroatom containing the free electron pair. This is possible, for example, with oxo ligands (Scheme 9).[209,210]



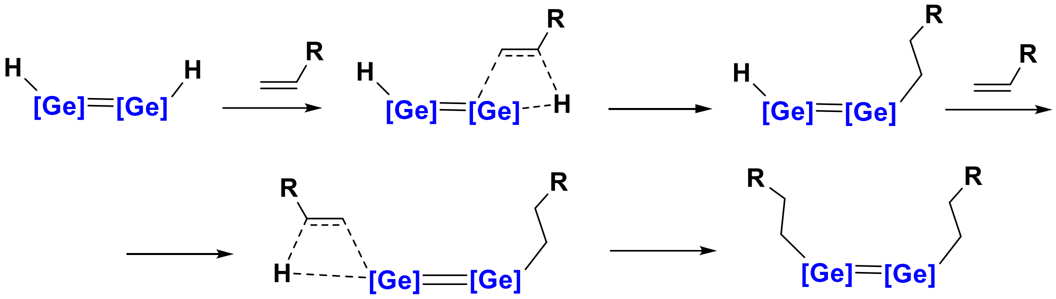
Scheme 9 A schematic representation of the mechanism of carbonyl hydrosilylation via Si–H addition across M=O bond (left) and via carbonyl insertion into M–H bond (right).

Again, we will find reactions where the unsaturated compound reacts first with the catalyst and only such a complex breaks the Si–H bond of the hydrosilane. This will be seen particularly in the case of metal hydrides, where the carbonyl group will insert itself into the M–H bond; still, the hydride itself can be generated from a precursor via σ-bond metathesis with a hydrosilane (Scheme 9).[211–215]

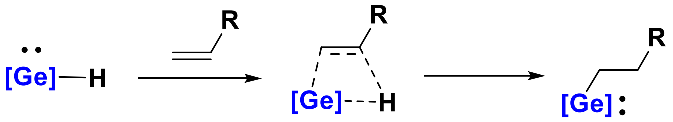
I.3.3. Hydrogermylation

Much less research has been undertaken on the mechanisms of hydrogermylation reactions. Not surprisingly, it is often carried out as an extension of analogous studies on organosilicon compounds, which are more attractive from an industrial point of view, more available, and cheaper. As this is not a detailed review, but only a context for the studies carried out, we could limit ourselves to saying that the hydrogermylation reactions generally fall within the mechanisms discussed above;[154,216–220] however, some nuances are worth noting.

Organic compounds of germanium, which is below silicon in the periodic table and therefore larger and with a higher nuclear charge, react relatively easily, under mild conditions, via radical mechanism, while offering better possibilities for reaction control than organotin compounds.[221–223] In addition, reactions catalyzed by Lewis acids generally have a wider substrate tolerance than is the case with hydrosilylation.[224] Non-catalytic reactions involving digermenes (Scheme 10) or germanium(II) hydrides (Scheme 11) are also abundant (relative to the overall science of hydrogermylation).[225–228]



Scheme 10 A simplified representation of alkene hydrogermylation with digermenes.

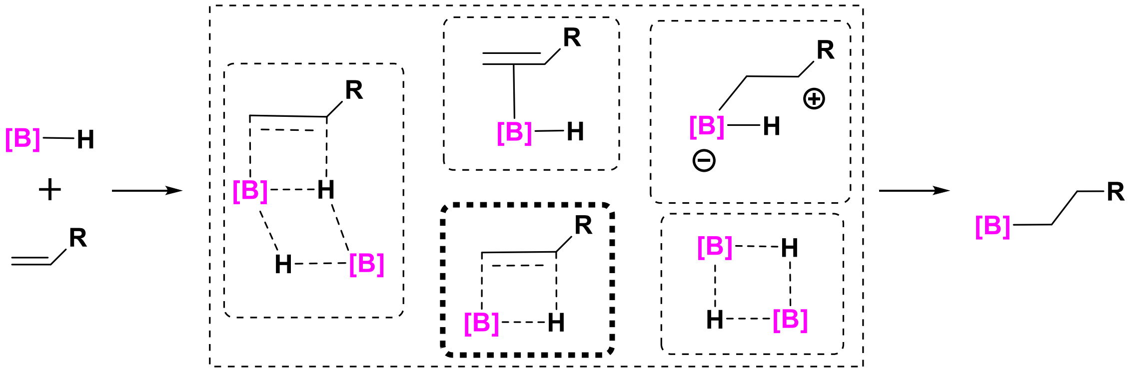


Scheme 11 A simplified representation of alkene hydrogermylation with germanium(II) hydrides.

I.3.4. Hydroboration

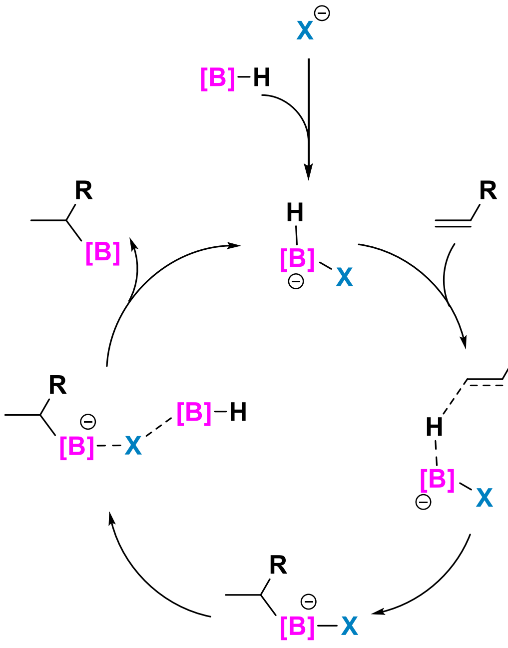
As indicated a few pages before, the hydroboration reactions differ significantly from the others due to the presence of a vacant p orbital in many of the available and used boron compounds. These differences will inevitably be reflected in the mechanisms of these reactions, the discussion of which should be given some space. First, however, it should be noted that reactions following the classical mechanisms already discussed are not at all uncommon, and many transition metal–based catalysts can also be used for hydroboration.[195,229–239] Instead, we will concentrate on discussing the differences.

The first ever literature report of an alkene hydroboration reaction shows what is still unthinkable for hydrosilylation today: two simple compounds (a few-carbon alkene and a diborane) react in ether with great efficiency within minutes at room temperature without the addition of any catalyst.[240] While the following decades saw the rapid development of hydroboration and a Nobel Prize for Herbert C. Brown, the mechanism of these reactions aroused lively debate in the scientific community. It was debated whether the hydroborane dimer (or the hydroborane complex with a Lewis base, such as a solvent) reacts directly with the unsaturated compound or undergoes a prior dissociation; whether a π-complex is formed and, if so, whether it transforms into a σ-complex; which step determines the rate of the reaction; and, finally, whether the transition state is three- or four-membered.[241–245] As further studies have shown, the actual mechanism depends on the substrates, but also, for instance, on the solvent;[246,247] nevertheless, for most non-catalytic reactions of hydroboranes with unsaturated compounds, a four-membered transition state with borane monomer is assumed (Scheme 12).[248,249]

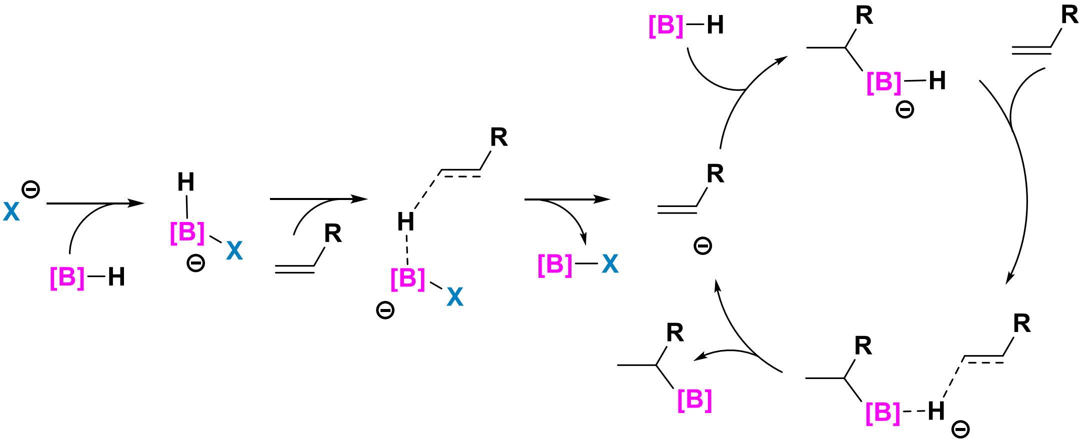


Scheme 12 Some of the proposed intermediates and transition states in the reaction of borane with simple alkenes (the predominant transition state shown in bold box).

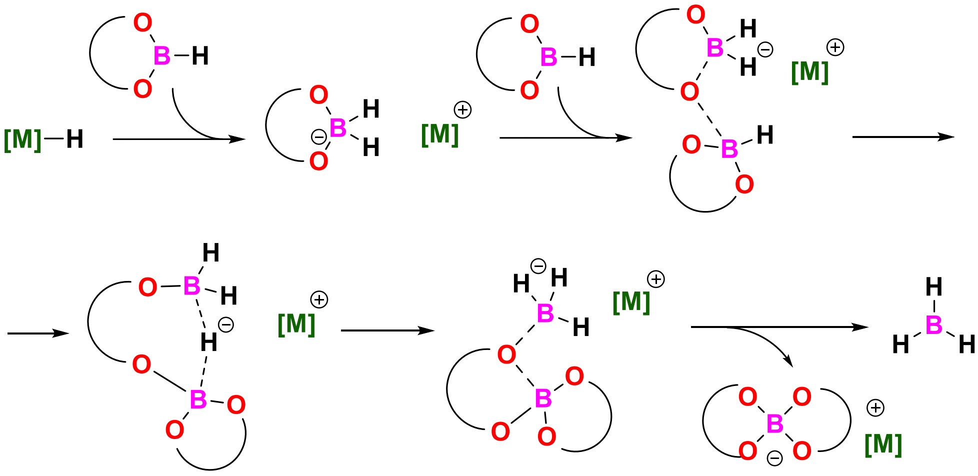
For compounds with low hydride donor capacity, such as pinacolborane or even more so catecholborane, it is necessary to increase the hydridic character of the hydrogen atom so that it can reduce the unsaturated bond.[250] This can be done by attaching a simple nucleophile, such as an alkoxy group or even a halide, to the boron atom,[251,252] or by heterolytic cleavage of the dimer;[253] of course, such an entity will not form a cyclic quaternary transition state, but will be able to reduce, for example, a carbonyl carbon. Compounds providing these ligands may act as catalysts *sensu stricto* (Scheme 13),[254,255] but they often prove to barely mediate the reaction, either by initiating a „living” process, for example, through an alkoxide species (Scheme 14),[251] or by reducing borane to an active form like BH_3 (Scheme 15);[256–258] care must be taken to perform the necessary control experiments to determine the actual role of the species used.



Scheme 13 A simplified representation of nucleophile-catalyzed hydroboration of alkenes.

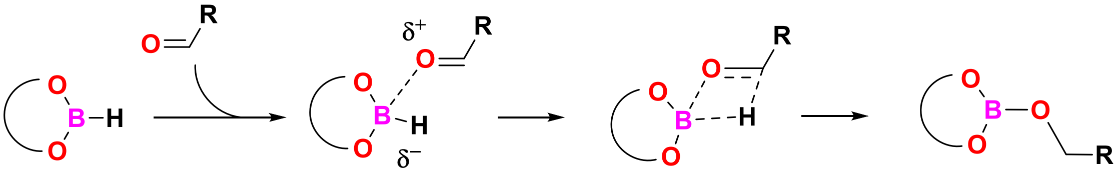


Scheme 14 A simplified representation of nucleophile-initiated „living” hydroboration of alkenes.



Scheme 15 Mechanism of BH_3 generation from 1,3,2-dioxaborolanes and metal hydrides.

In recent years there have also been reports of reactions of such poorly hydridic hydroboranes with unsaturated compounds without a catalyst, for which a four-membered transition state is postulated, preceded — in case of carbonyl groups — by the formation of a B–O complex to increase the hydride donor ability of the substrate. A similar mechanism was proposed for catalyst- and solvent-free reactions (Scheme 16).[170,171]



Scheme 16 Suggested mechanism of catalyst-free hydroboration of carbonyl compounds with 1,3,2-dioxaborolanes.

I.3.5. General

In recent decades, a number of mechanisms have been proposed that represent some modification of those described above, the full enumeration and characterisation of which is far beyond the scope of this introduction. The interested reader will find much more extensive reviews on the subject in the available literature.[75,76,179,259–266]

While the first mentions of the mechanism of hydrosilylation reaction were merely intuitive attempts to explain a posteriori the observed chemo- and regioselectivity of the reaction, over time there have been more and more detailed studies of the exact course of the catalytic cycles by computational methods (often in combination with instrumental methods), either as work that accompanies experiments or even precedes and guides them.[267,268] It turns out that these pathways often intertwine, turn around, branch off and lead either by different routes to a single point or to completely different reactions, such as dehydrogenative silylation or cis–trans isomerisation.[210,229,262,269–271] Even an accurate determination of the energy profiles of individual pathways at a high level of theory may not be sufficient to categorically identify one pathway and exclude others, but on the other hand, they can indicate ways to control reaction outcome.[267,268]

II. OBJECTIVE OF THIS WORK

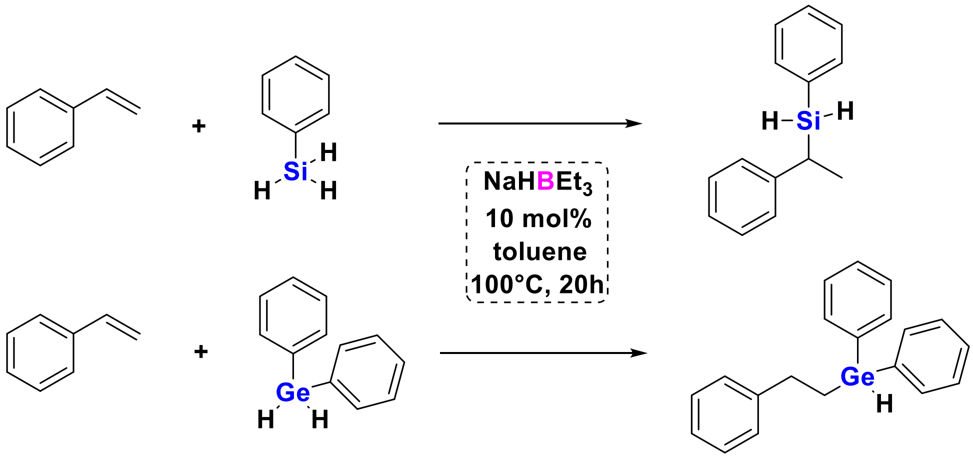
The main objective of the present work was to thoroughly investigate the mechanisms of selected hydrosilylation, hydrogermylation, and hydroboration reactions catalyzed by simple transition metal–free inorganic compounds. In the case of hydrosilylation and hydrogermylation, it was sodium triethylborohydride $NaHBEt_3$, and in the case of hydroboration, it was potassium fluoride KF. To achieve this goal, quantum chemistry methods based on density functional theory were used, in particular the M06–2X functional. With such an approach, it was possible to determine the geometric and electronic structure of the stationary points on the potential energy hypersurface corresponding to substrates, products, intermediates and transition states, and to calculate the relative energies of these chemical entities, so that, as a result, it was possible to determine the energy profiles and propose the mechanisms of these reactions and explain the experimentally observed significant differences in the reactivity of substrates and regioselectivity of seemingly analogous reactions.

This dissertation is a collection of published and thematically related scientific articles:

1. Nowicki, M.; Zaranek, M.; Pawluć, P.; Hoffmann, M. DFT Study of Trialkylborohydride-Catalysed Hydrosilylation of Alkenes – the Mechanism and Its Implications. *Catal. Sci. Technol.* **2020**, *10* (4), 1066–1072. https://doi.org/10.1039/C9CY02261A. (**Appendix A1**)
2. Nowicki, M.; Zaranek, M.; Grzelak, M.; Pawluć, P.; Hoffmann, M. Mechanism of Silylation of Vinyl Arenes by Hydrodisiloxanes Driven by Stoichiometric Amounts of Sodium Triethylborohydride – a Combined DFT and Experimental Study. *Int. J. Mol. Sci.* **2023**, 24, 4924. https://doi.org/10.3390/10.3390/ijms24054924. (**Appendix A2**)
3. Zaranek, M.; Nowicki, M.; Andruszak, P.; Hoffmann, M.; Pawluć, P. Hydrogermylation Initiated by Trialkylborohydrides: A Living Anionic Mechanism. *Chem. Commun.* **2022**, *58* (100), 13979–13982. https://doi.org/10.1039/D2CC05567H. (**Appendix A3**)
4. Nowicki, M.; Kuciński, K.; Hreczycho, G.; Hoffmann, M. Catalytic and Non-Catalytic Hydroboration of Carbonyls: Quantum-Chemical Studies. *Org.*

Biomol. Chem. **2021**, *19* (13), 3004–3015. https://doi.org/10.1039/D1OB00037C. (**Appendix A4**)

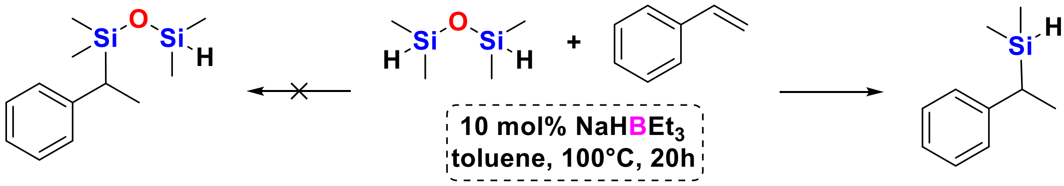
The aim of the **A1** and **A3** papers was to determine the mechanisms of the hydrosilylation (**A1**) and hydrogermylation (**A3**) reactions of selected alkenes with hydrosilanes in the presence of sodium trialkylborohydrides in order to explain the opposite regioselectivity of these reactions (Scheme 17).



Scheme 17 Hydrosilylation and hydrogermylation of styrene in the presence of sodium triethylborohydride.

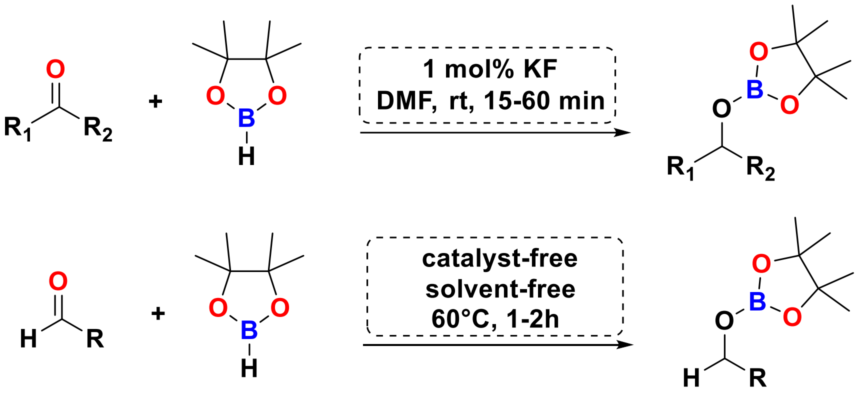
In the case of paper **A1**, an attempt was also made to clarify the reactivity of the substrates depending on the substituents at the C=C bond and on the silicon atom.

In the **A2** publication, the determination of the mechanism of the reaction of certain vinylarenes with hydrodisiloxanes in the presence of sodium triethylborohydride served to explain the observed result of this reaction, where instead of the expected hydrosilylation product (a more substituted disiloxane), a product of formal hydrosilylation with a dihydrosilane was observed in the reaction mixture (Scheme 18).



Scheme 18 Expected (left) vs. observed (right) product of the reaction of styrene with 1,1,3,3-tetramethyldisiloxane.

Finally, the aim of the study described in **A4** was to thoroughly investigate possible reaction pathways for the hydroboration of acetophenone and benzaldehyde with pinacolborane in the presence of potassium fluoride, as well as, based on experimental observations and conclusions from these reactions, to compare the performance of different theoretical methods and to present a contribution to the study of the mechanism of a solvent-free reaction of aldehyde with pinacolborane (Scheme 19).

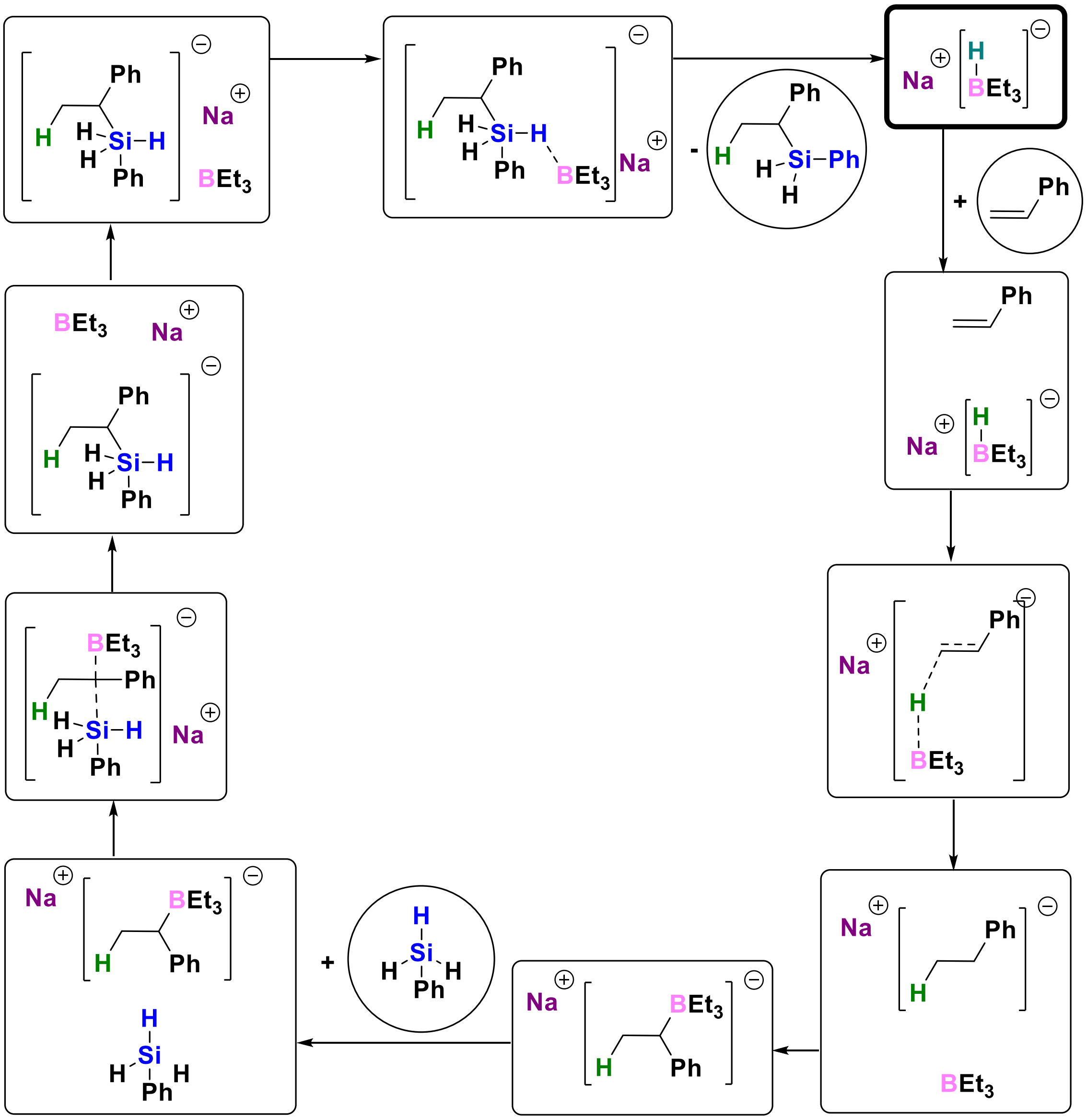


Scheme 19 Hydroboration of carbonyl compounds with pinacolborane in the presence of sodium fluoride (top) and catalyst-free (bottom).

III. RESULTS AND DISCUSSION

III.1. HYDROSILYLATION CATALYZED BY $NaHBEt_3$

The catalytic action of the trialkylborohydride was found to follow a stepwise mechanism at M06–2X/6–31++G(d,p)//M06–2X/6–31+G(d) level of theory (Scheme 20). The first step identified is the activation of the substrates by the transfer of a hydride anion from $HBMe_3^-$ to the styrene double bond. This step yields a carbanion, which is in a very shallow van der Waals potential minimum and is rapidly stabilized by the coordination of a BMe_3 molecule released in the previous step. This leads to a deep energy minimum, about −28 kcal/mol lower than the substrates, without any additional energy input. The next step involved B–C electron migration towards the silicon atom and Si–C bond formation; this can be considered as the rate- and turnover-determining step of the reaction. The pentacoordinate silicon anion formed is much less stable than the tetraalkylborane, as the latter allows a much more effective charge delocalization; the interactions between the silicon species and BMe_3, oriented to prevent further reaction, are responsible for the apparent stability of this structure. However, with a suitable geometric arrangement, a hydride anion can be abstracted by the trialkylborane molecule, leading to catalyst regeneration and the final product, with an overall Gibbs free energy gain of −29 kcal/mol. Closer inspection revealed a transient complex which was formed after Si–H bond cleavage, but both Si–H bond cleavage and dissociation of the resulting B–H–Si complex proceeded without energy barrier. An attempt to optimize a direct addition of the B–H bond through a cyclic transition state was also made, as well as a six-membered transition state (one-step mechanism), both unsuccessful because the calculations were not convergent, but indicated the presence of a much higher activation barrier of at least 40 kcal/mol. In the case of the anti-Markovnikov hydrosilylation according to the determined mechanism, all minima and transition states are significantly higher in energy, which was not surprising given the experimental regioselectivity of the reaction. This was mainly attributed to the fact that the anti-Markovnikov carbanion cannot be stabilized by resonance and is therefore not favored, nor is the transition state leading to its formation.



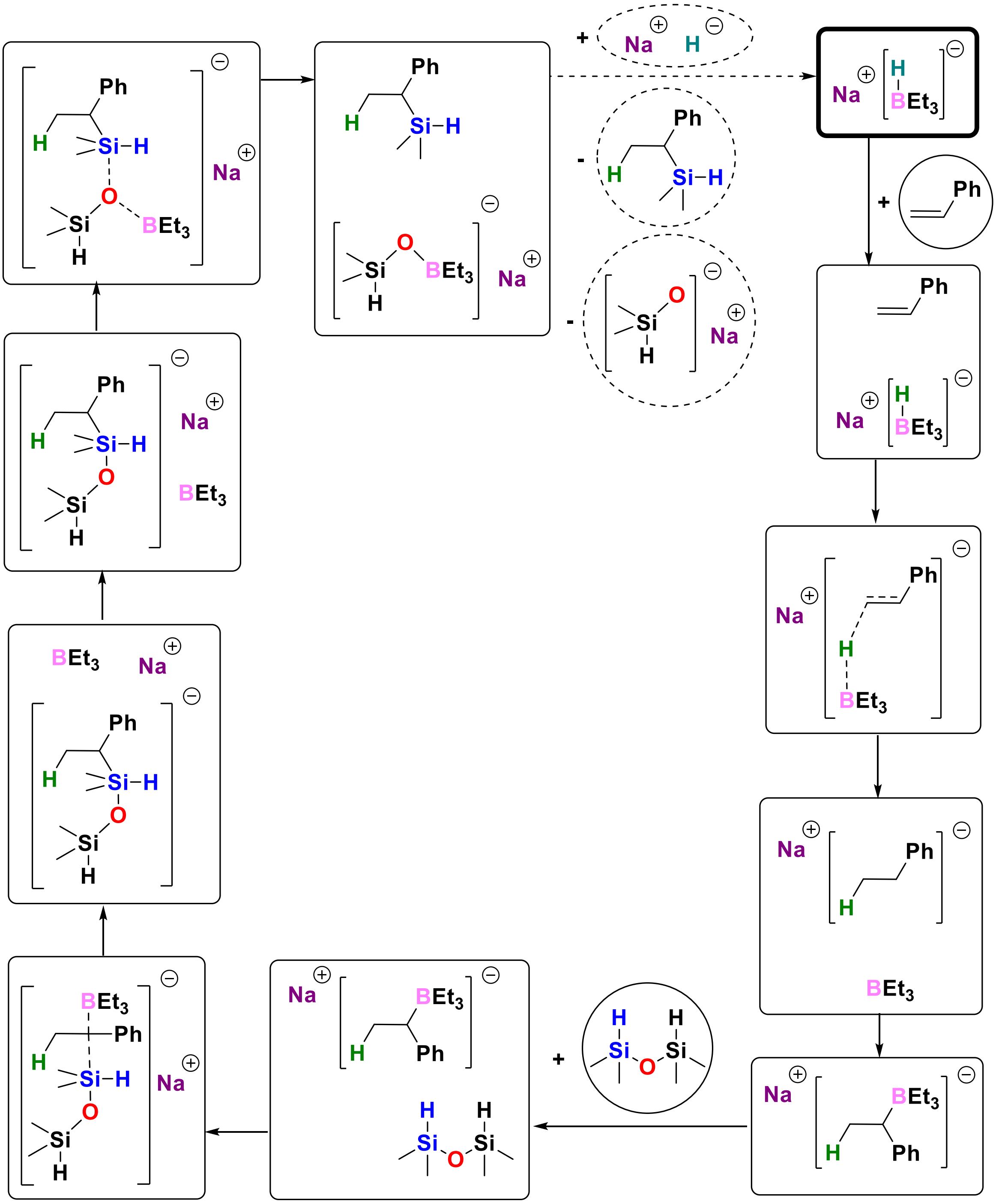
Scheme 20 Proposed mechanism of sodium triethylborohydride–catalyzed hydrosilylation of styrene with phenylsilane.

Energy profiles for Markovnikov reactions of several other alkenes and hydrosilanes were calculated to verify the relevance of the mechanism determined. In the case of the hydrosilylation of 1,1-diphenylethene with phenylsilane, the relative energy barriers were even slightly lower than for styrene, due to the additional resonance stabilization by another aromatic ring; on the other hand, the flat, shallow minimum corresponding to the pentacoordinate silicon species (which decays back easily) and the final product, which has a slightly higher Gibbs free energy than I2, deteriorate the yield of the reaction. For propene, potential energy surface scans revealed a cyclic geometry of the C=C bond activation transition state, with an activation energy of almost 60 kcal/mol, which is unlikely to proceed even at elevated temperatures. Both results are in agreement with experimental observations, with 1,1-diphenylethene giving a lower yield (78%) and hex-1-ene being completely unreactive.

For the reactions of dimethylphenylsilane and trimethylsilane with styrene, the reactions appeared to be stuck at the tetraalkylborane stage. In fact, detailed scans of Si–C distances did not show any extremes that could correspond to pentacoordinate silicon species. Nevertheless, it is noteworthy that a favorable collision energy and geometry would result in the abstracted BMe_3 molecule orbiting the silicon anion and reaching a favorable position for abstraction of a hydride anion; equilibrium dissociation of the tetraalkylborane to leave a bare carbanion and BMe_3 should also not be excluded (although strongly disfavored). This is particularly plausible for dimethylphenylsilane, for which an almost flat shoulder is observed on the cross section of the potential energy hypersurface as silicon displaces boron. These observations are also in remarkable agreement with the yields of the hydrosilylation products reported in the experimental research, namely 0 % for Me_3SiH and 30 % GC yield for Me_2PhSiH.

III.1.1. Hydrosilylation with a hydrosilane surrogate catalyzed by $NaHBEt_3$

The initial steps of this reaction, including the formation of the pentacoordinate silicanion, were found to be identical to those described above (Scheme 21). Again, the further course of the reaction depended on the repositioning of the trialkylborane in such a way that it could detach a negatively charged fragment to form a neutral molecule. The attack can come from either the hydrogen atom (with Si–H cleavage leading to a more substituted disiloxane) or the oxygen atom (with Si–O cleavage leading to a disiloxane). Indeed, for the reaction of styrene with TMDSO, abstraction of the $–OSiMe_2H$ moiety leads to a product that is approximately 14 kcal/mol lower in Gibbs free energy than the substrates, but slightly higher than the product formed after Si–H bond cleavage. However, the reaction leads to dimethyl(1-phenylethyl)silane due to lower transition states and intermediates.



Scheme 21 Proposed mechanism of the reaction of styrene with 1,1,3,3-tetramethyldisiloxane in the presence of sodium triethylborohydride. The dashed arrow indicates catalytic character of this transformation in the presence of sodium hydride.

The silicanion can exist as three stable rotamers generated by rotation around the C–Si bond, with corresponding three different structures of subsequent transition states, intermediates and final products. Although the Gibbs free energy differences between them do not exceed 6 kcal/mol, they prove to be of great importance. All three rotamers can undergo Si–O bond cleavage without a free energy barrier, as was the case for Si–H cleavage in phenylsilane. On the other hand, only the least favored rotamer (with the highest energy) can remove a hydride anion without an additional transition state. For the lowest energy conformer, this additional free energy barrier is almost 7 kcal/mol, which is not without significance for already high energy pentacoordinate silicon intermediates. Similar relationships are evident for PMDSO when it binds to the carbanion with a less substituted silicon atom. However, when it binds to a more substituted atom, or when HMDSO is used, the corresponding structures have energies 4–14 kcal/mol higher than those for TMDSO. Again, this agrees well with experimental results where PMDSO gave almost identical results to TMDSO but HMDSO was unreactive.

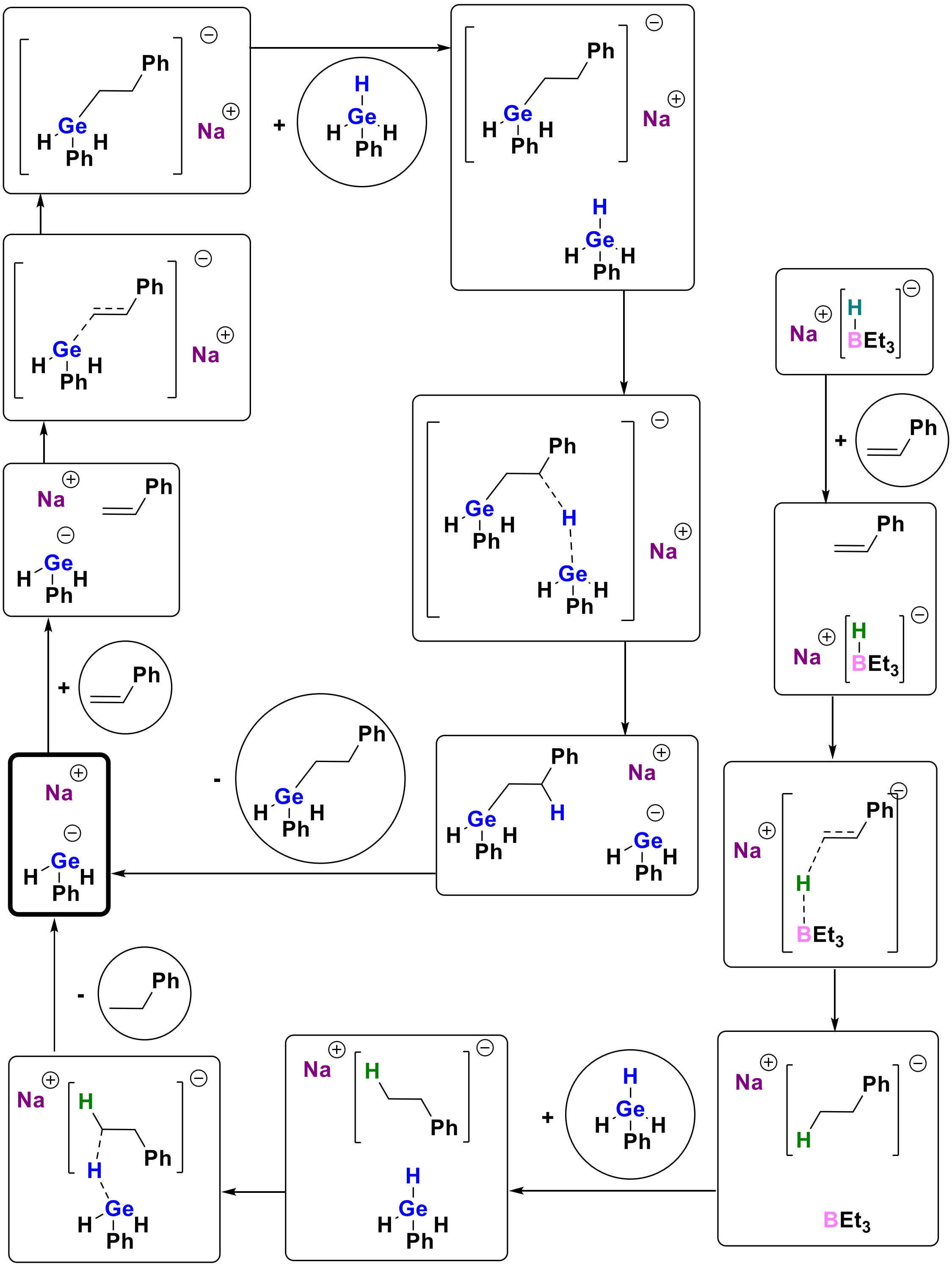
Given the spatial proximity of the key O and H atoms, to confirm our findings we performed a potential energy hypersurface scan, controlling both B–O and B–H interatomic distances simultaneously, to obtain a more illustrative three-dimensional graph for the conformer that most readily leads to both products. Even a brief analysis of the resulting graph shows well why the system evolves more easily from the upper right corner towards hydrosilane (lower left purple part) rather than disiloxane (right purple part) — the smooth, wide path is preferred to a steep, narrow one.

The established mechanism explained well the stoichiometric consumption of NaHBEt3 during the reaction, but it remained to be clarified how the addition of superstoichiometric amounts of sodium hydride allows the reaction to proceed with good efficiency (albeit slowly) in the presence of catalytic amounts of $NaHBEt_3$ (or, more precisely, BEt_3 — $NaHBEt_3$ is generated in situ). We looked more closely at the interaction of the latter with the borasiloxyl salt produced in the main reaction. Our results suggest that the reaction proceeds according to the S_N2 mechanism, regenerating sodium trialkylborohydride and producing sodium dimethylsilanolate as the final product, with a Gibbs free energy barrier of 28.6 kcal/mol and a total change of −11.2 kcal/mol.

III.2. HYDROGERMYLATION INITIATED BY $NaHB(s\text{-}Bu)_3$

While a slight modification of the original mechanism was sufficient to explain the course of the reaction with disiloxanes, the result of an analogous reaction with hydrogermanes, in which the main product showed opposite regioselectivity, seemed at first sight to contradict previous findings, especially after initial calculations confirmed that the reaction was again initiated by a nucleophilic attack of a borohydride anion on the terminal carbon atom of styrene. Further studies led to a pathway similar to hydrosilylation; however, despite its coherence, this mechanism could not be applied to hydrogermylation because it would lead to the formation of Markovnikov products.

Instead, the likely reaction pathway we have devised proceeds with the formation of a dihydro(phenyl)germanide, a species described in the literature in a different context, as the product of hydrogermane deprotonation with e.g. benzylpotassium (Scheme 22). Next, the germanide attacks a styrene molecule at its terminal carbon, forming a carbanion. This is a resonance-stabilized benzylic one, but this time the germanium atom is in the beta position. After the carbanion abstracts a hydrogen cation from phenylgermane, leading to the regeneration of sodium dihydro(phenyl)germanide and the start of a new cycle, the final anti-Markovnikov product is released. Importantly, the formation of $NaPhGeH_2$ was calculated to proceed with a low barrier of 13.6 kcal/mol, with a reverse reaction being essentially irreversible (31 kcal/mol barrier). The cycle itself contains two transition states: a relative 16.7 kcal/mol one of styrene activation and a 12.7 kcal/mol one of $NaPhGeH_2$ regeneration; both are significantly lower than the activation of styrene by $NaHBMe_3$. The Gibbs free energy profiles show similar features for diphenylgermane. It is important to note that similar calculations were carried out for phenylsilane, but in this case all the transition states — both for the initial silanide formation and for the catalytic cycle — were found to be 6 to 13 kcal/mol higher than for phenylgermane, as were almost all the intermediates. This is extremely important because it shows that the new mechanism does not falsify previous findings in any way.

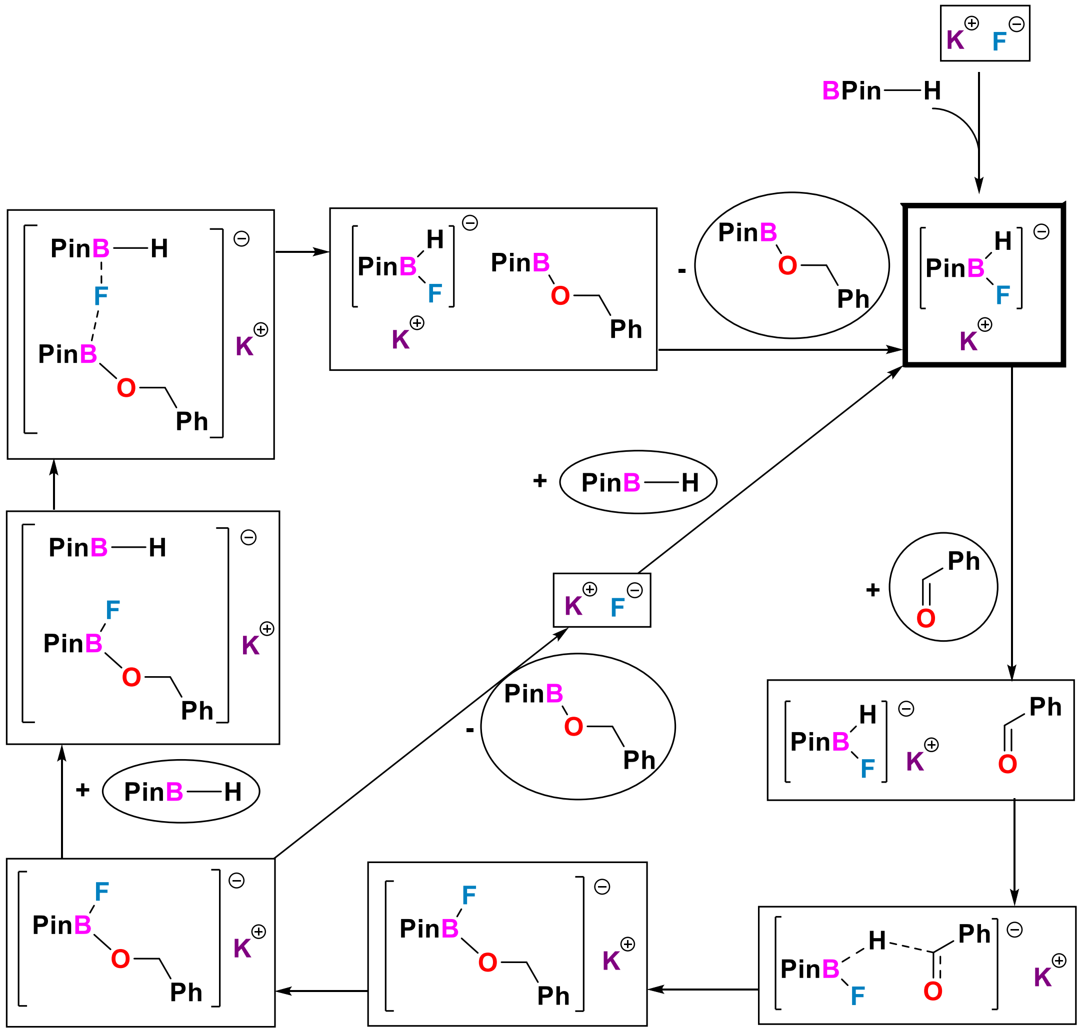


Scheme 22 Proposed mechanism of sodium triethylborohydride–initiated hydrosilylation of styrene with phenylsilane.

To our delight, an experiment confirmed the unexpected germanide intermediate, as benzylsodium was indeed able to initiate hydrogermylation. The mode of initial germanide formation was further supported by an experiment showing that increasing the amount of trialkylborohydride resulted in a proportional increase in the amount of alkene hydration product. The position of the deuterium in this product when deuterogermanes were used finally supported the computationally derived mechanism.

III.3. HYDROBORATION MEDIATED BY KF

Investigation of the role of KF led to two complete and coherent pathways, one of which (which required fluoride to attack the carbonyl carbon atom) was widely disfavored and quickly discarded. The accepted mechanism (Scheme 23) involved the formation of a weak complex between the oxygen in pinacolborane and potassium, followed by coordination of the fluorine atom to the hypovalent boron atom. This increases the hydridic character of the boron-bonded hydrogen, which is reflected in geometric and electronic parameters. Next, this species forms a weakly interacting complex with a carbonyl compound and subsequently hydride transfer is observed, resulting in a transient alkoxide anion. This structure is not stable and the lone electron pair on the oxygen immediately attacks the boron atom, forming a thermodynamically stable intermediate; removal of potassium fluoride from this structure yields the boronate ester, completing the catalytic cycle.



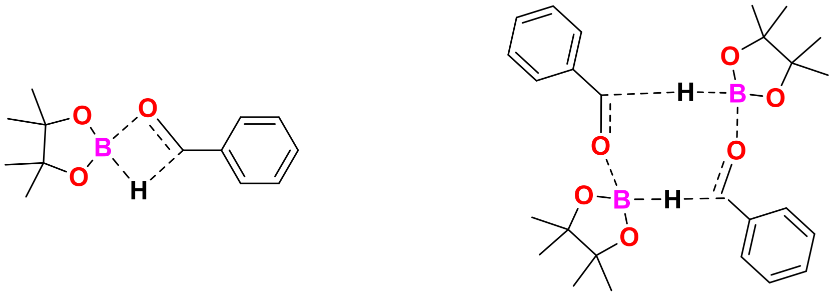
Scheme 23 Proposed mechanism of potassium fluoride–mediated hydroboration of benzaldehyde with pinacolborane (see Appendix A4 for other possible reaction pathways).

With these results in hand, but also with a basic knowledge of reaction kinetics under experimental conditions, we were able to see to what extent the energy differences calculated using different theoretical approaches could be reconciled with laboratory observations. The method was essentially very simple: the activation energy was calculated from the time taken for the reaction to complete, assuming that it occurred in a single step. A number of additional simplifications were chosen so that the calculated energy (21 kcal/mol) was certainly not an underestimate, and most likely a significant overestimate. Thus, all theoretical protocols leading to a rate-determining step barrier in the previously determined mechanism significantly higher than this value could be rejected. Thus, it was found that the M06–2X and *ω*B97X–D functionals with 6–311++G(2d,p) basis sets best reproduced the actual reaction energy profiles among the methods tested.

Having proposed the most appropriate level of theory for the reaction studied, we used it to investigate other mechanistic concepts and possible catalytic cycles, based on the previous literature, in particular the reports of various meanderings and pitfalls in the study of the mechanisms of hydroboration reactions involving pinacolborane and catecholborane.[257,258] Several offshoots of the original catalytic cycle and even a separate autocatalytic cycle have been identified. The first of these is the release of the product not by dissociation of the KF unit, but by a direct transfer of the fluoride to the next pinacolborane molecule. Another possibility, this time significantly different from the original cycle, is the attack of the reactive alkoxy anion not on the boron atom that was the hydride donor, but on the next pinacolborane molecule. The intermediate thus formed can also be a hydride donor; if the molecule attacked is fluoropinacolborane, the original catalyst is restored, but if it is a carbonyl compound, we have a 'living' process in which fluoride no longer plays a role. Interestingly, although the full picture of possible pathways rather points to a fluoride-catalyzed mechanism, the energy profiles of the individual cycles do not allow the unambiguous identification of the only correct reaction path. This is especially true when one considers that the actual course of the reaction is determined not only by energy differences between the individual stationary states, but also by dynamic and even purely statistical considerations (there are more substrate molecules in the mixture than catalyst molecules). The only possibility that was considered, and which was in fact completely ruled out, was the opening of the 1,3,2-dioxaborolane ring, leading to the release of BH_3.

III.4. CATALYST- AND SOLVENT-FREE HYDROBORATION

The last part of the study, which was to look at the reaction occurring without a catalyst and without a solvent, required the adoption of a number of sharp simplifications, resulting, for example, from the inability to adequately account for the effects exerted by neighboring molecules on those that happen to be reacting with each other (this environment constantly changes dramatically as the reaction progresses). With all awareness of the limitations of the calculations carried out, results have been obtained that justify the view that the mechanism of such a reaction is much more complex than the single step postulated so far proceeding through a four-molecule cyclic transition state (Scheme 24).[170,171] Already in a four-molecule system (two aldehyde molecules and two pinacolborane molecules), the calculated activation barrier (taking into account, of course, the error of base superposition) was lower by about 20%, leading through an eight-molecule transition state (although this is not a concerted reaction, but rather a cascade). If one takes into account the fact that there are not four, but many substrate molecules in close proximity in the reaction mixture, then even with the awareness of the constantly changing physicochemical properties of the mixture, it seems completely reasonable that the reaction mechanism is much more complex than independent addition of individual B–H bonds to individual carbonyl moieties, possibly involving multiple cascades of hydride transfers.



Scheme 24 Literature-based four-membered (left) vs. more favorable eight-membered (right) transition state in catalyst- and solvent-free reaction between benzaldehyde and pinacolborane.

IV. CONCLUSIONS

Using quantum chemistry methods based on density functional theory, it has been possible to determine the mechanisms of a number of C=C and C=O bond hydrosilylation, hydrogermylation, and hydroboration reactions.

Article A1 established a detailed mechanism for the reaction of phenylsilane with styrene, explaining the uncommon Markovnikov regioselectivity, which was then successfully applied to several other hydrosilanes and alkenes, each time achieving decent agreement of the results with experimental work. The key factors determining the efficiency of the reaction turned out to be the influence of groups close to the C=C bond (the absence of aromatic groups, stabilizing the negative charge on the benzylic carbon atom by resonance, prevented the activation of styrene and the reaction from taking place) and substituents on the silicon atom (the presence of electron-donating groups hinders the formation of the C–Si bond, and steric reasons may hinder the reconstitution of the B–H bond).

Article A2 elucidates why, although the hydrosilylation reaction would lead to thermodynamically more stable products, the actual reaction produces a borasiloxyl salt and a hydrosilane. The energy differences between different rotamers of key intermediates, and transition states correspond to the steric hindrance of the hydridic hydrogen atom; even an apparent exposure of hydrogen in a rotamer gives way to the proximity of the oxygen atom, with two lone electron pairs and a much higher electron density, which prevents the formation of the B–H bond. This observation should be widely taken into account by scientists studying reaction mechanisms computationally — seemingly insignificant energy discrepancies between individual conformers can have a decisive effect on chemo-, regio- and enantioselectivity, in line with the Curtin–Hammett principle. It is also noteworthy that, although much more time-consuming and resource-intensive than a one-dimensional scan, two-variable hypersurface PE scan provides a much more complete picture of the interactions and mechanism, especially when the reaction path splits smoothly into two, each leading to completely different products, on a very flat part of the PES.

In **Article 3**, an entirely new mechanism was proposed to find an explanation for the regioselectivity of the hydrogermylation of styrene in the presence of trialkyl borohydride, opposite to that of hydrosilylation. The compound that initially appeared to be the catalyst was found to be only the activator of this reaction, while the germanide anion was identified as the active agent that maintains the "living" hydrogermylation. It is worth noting that in this work it was the computational modelling that acted as the main driving force, guiding the experimentalists towards appropriate control experiments that could help verify the identified mechanism.

In **Article 4**, a number of plausible reaction pathways were identified, leading to a comprehensive, well-founded, multi-pathway mechanism for fluorine-mediated hydroboration of aldehydes and ketones. It was shown how the reductive power of the boron-bonded hydrogen atom is enhanced by a fluoride bond to boron, and why the catalytic cycle involving this tetracoordinate boron species is favored. An autocatalytic cycle, although not supported by our results, was also identified and discussed in the light of previous research. With significant but sensible simplifications, it was possible to use relatively simple mathematics to juxtapose experimental data on reaction kinetics with computational results to indicate the most appropriate level of theory for the system under investigation. An important result of the research carried out was to challenge the two-molecule, one-step reaction mechanism for the catalyst- and solvent-free hydroboration of carbonyl compounds, although it must be stressed that the results obtained are certainly not conclusive and that the mechanism of this type of reaction still requires numerous studies, both computational and experimental.

V. LITERATURE

(1) Schrödinger, E. Quantisierung als Eigenwertproblem. *Ann. Phys.* **1926**, *384* (4), 361–376. https://doi.org/10.1002/andp.19263840404.

(2) Heitler, W.; London, F. Wechselwirkung neutraler Atome und homöopolare Bindung nach der Quantenmechanik. *Z. Für Phys.* **1927**, *44* (6–7), 455–472. https://doi.org/10.1007/BF01397394.

(3) Hartree, D. R. The Wave Mechanics of an Atom with a Non-Coulomb Central Field. Part I. Theory and Methods. *Math. Proc. Camb. Philos. Soc.* **1928**, *24* (1), 89–110. https://doi.org/10.1017/S0305004100011919.

(4) Fock, V. Näherungsmethode zur Lösung des quantenmechanischen Mehrkörperproblems. *Z. Für Phys.* **1930**, *61* (1–2), 126–148. https://doi.org/10.1007/BF01340294.

(5) Piela, L. *Idee chemii kwantowej*, Wyd. 1, dodr 2.; Wydawnictwo Naukowe PWN: Warszawa, 2006.

(6) Young, D. C. *Computational Chemistry: A Practical Guide for Applying Techniques to Real World Problems*; Wiley: New York, 2001.

(7) Schrödinger, E. An Undulatory Theory of the Mechanics of Atoms and Molecules. *Phys. Rev.* **1926**, *28* (6), 1049–1070. https://doi.org/10.1103/PhysRev.28.1049.

(8) Roothaan, C. C. J. New Developments in Molecular Orbital Theory. *Rev. Mod. Phys.* **1951**, *23* (2), 69–89. https://doi.org/10.1103/RevModPhys.23.69.

(9) Slater, J. C. The Theory of Complex Spectra. *Phys. Rev.* **1929**, *34* (10), 1293–1322. https://doi.org/10.1103/PhysRev.34.1293.

(10) Lennard-Jones, J. E. The Electronic Structure of Some Diatomic Molecules. *Trans. Faraday Soc.* **1929**, *25*, 668. https://doi.org/10.1039/tf9292500668.

(11) Born, M.; Oppenheimer, R. Zur Quantentheorie der Molekeln. *Ann. Phys.* **1927**, *389* (20), 457–484. https://doi.org/10.1002/andp.19273892002.

(12) Hylleraas, E. A. Neue Berechnung der Energie des Heliums im Grundzustande, sowie des tiefsten Terms von Ortho-Helium. *Z. Für Phys.* **1929**, *54* (5–6), 347–366. https://doi.org/10.1007/BF01375457.

(13) McWeeny, R.; Coulson, C. A. On the Basis of Orbital Theories. *Proc. R. Soc. Lond. Ser. Math. Phys. Sci.* **1955**, *232* (1188), 114–135. https://doi.org/10.1098/rspa.1955.0205.

(14) Coester, F. Bound States of a Many-Particle System. *Nucl. Phys.* **1958**, *7*, 421–424. https://doi.org/10.1016/0029-5582(58)90280-3.

(15) Møller, Chr.; Plesset, M. S. Note on an Approximation Treatment for Many-Electron Systems. *Phys. Rev.* **1934**, *46* (7), 618–622. https://doi.org/10.1103/PhysRev.46.618.

(16) Hohenberg, P.; Kohn, W. Inhomogeneous Electron Gas. *Phys. Rev.* **1964**, *136* (3B), B864–B871. https://doi.org/10.1103/PhysRev.136.B864.

(17) Kohn, W.; Sham, L. J. Self-Consistent Equations Including Exchange and Correlation Effects. *Phys. Rev.* **1965**, *140* (4A), A1133–A1138. https://doi.org/10.1103/PhysRev.140.A1133.

(18) Becke, A. D. A New Mixing of Hartree–Fock and Local Density-functional Theories. *J. Chem. Phys.* **1993**, *98* (2), 1372–1377. https://doi.org/10.1063/1.464304.

(19) Baker, J.; Muir, M.; Andzelm, J. A Study of Some Organic Reactions Using Density Functional Theory. *J. Chem. Phys.* **1995**, *102* (5), 2063–2079. https://doi.org/10.1063/1.468728.

(20) Swart, M.; van Duijnen, P. Th.; Snijders, J. G. Mean Polarizabilities of Organic Molecules. A Comparison of Restricted Hartree Fock, Density Functional Theory and Direct Reaction Field Results. *J. Mol. Struct. THEOCHEM* **1998**, *458* (1–2), 11–17. https://doi.org/10.1016/S0166-1280(98)00350-9.

(21) Stephens, P. J.; Devlin, F. J.; Cheeseman, J. R.; Frisch, M. J. Ab Initio Prediction of Optical Rotation: Comparison of Density Functional Theory and Hartree-Fock Methods for Three 2,7,8-Trioxabicyclo[3.2.1]Octanes. *Chirality* **2002**, *14* (4), 288–296. https://doi.org/10.1002/chir.10039.

(22) Streitwieser, A.; Leong, Y. H. A Comparison of Density-Functional Theory and *Hartree–Fock* Modeling of Organolithium Equilibria. *Helv. Chim. Acta* **2012**, *95* (10), 1976–1984. https://doi.org/10.1002/hlca.201200424.

(23) Andzelm, J.; Wimmer, E. Density Functional Gaussian-type-orbital Approach to Molecular Geometries, Vibrations, and Reaction Energies. *J. Chem. Phys.* **1992**, *96* (2), 1280–1303. https://doi.org/10.1063/1.462165.

(24) Davidson, E. R. How Robust Is Present-Day DFT? *Int. J. Quantum Chem.* **1998**, *69* (3), 241–245. https://doi.org/10.1002/(SICI)1097-461X(1998)69:3<241::AID-QUA3>3.0.CO;2-V.

(25) Scheiner, A. C.; Baker, J.; Andzelm, J. W. Molecular Energies and Properties from Density Functional Theory: Exploring Basis Set Dependence of Kohn?Sham Equation Using Several Density Functionals. *J. Comput. Chem.* **1997**, *18* (6), 775–795. https://doi.org/10.1002/(SICI)1096-987X(19970430)18:6<775::AID-JCC4>3.0.CO;2-P.

(26) McKechnie, S.; Booth, G. H.; Cohen, A. J.; Cole, J. M. On the Accuracy of Density Functional Theory and Wave Function Methods for Calculating Vertical Ionization Energies. *J. Chem. Phys.* **2015**, *142* (19), 194114. https://doi.org/10.1063/1.4921037.

(27) Slater, J. C. Atomic Shielding Constants. *Phys. Rev.* **1930**, *36* (1), 57–64. https://doi.org/10.1103/PhysRev.36.57.

(28) Boys, S. F.; Egerton, A. C. Electronic Wave Functions - I. A General Method of Calculation for the Stationary States of Any Molecular System. *Proc. R. Soc. Lond. Ser. Math. Phys. Sci.* **1950**, *200* (1063), 542–554. https://doi.org/10.1098/rspa.1950.0036.

(29) Hehre, W. J.; Stewart, R. F.; Pople, J. A. Self-Consistent Molecular-Orbital Methods. I. Use of Gaussian Expansions of Slater-Type Atomic Orbitals. *J. Chem. Phys.* **1969**, *51* (6), 2657–2664. https://doi.org/10.1063/1.1672392.

(30) Kaczmarek-Kędziera, A.; Ziegler-Borowska, M.; Kędziera, D. *Chemia obliczeniowa w laboratorium organicznym*; Wydawnictwo Naukowe Uniwersytetu Mikołaja Kopernika: Toruń, 2014.

(31) Ditchfield, R.; Hehre, W. J.; Pople, J. A. Self-Consistent Molecular-Orbital Methods. IX. An Extended Gaussian-Type Basis for Molecular-Orbital Studies of Organic Molecules. *J. Chem. Phys.* **1971**, *54* (2), 724–728. https://doi.org/10.1063/1.1674902.

(32) Hariharan, P. C.; Pople, J. A. The Influence of Polarization Functions on Molecular Orbital Hydrogenation Energies. *Theor. Chim. Acta* **1973**, *28* (3), 213–222. https://doi.org/10.1007/BF00533485.

(33) Clark, T.; Chandrasekhar, J.; Spitznagel, G. W.; Schleyer, P. V. R. Efficient Diffuse Function-Augmented Basis Sets for Anion Calculations. III. The 3-21+G Basis Set for First-Row Elements, Li-F. *J. Comput. Chem.* **1983**, *4* (3), 294–301. https://doi.org/10.1002/jcc.540040303.

(34) Foresman, J. B.; Frisch, Ae. *Exploring Chemistry with Electronic Structure Methods*, Third edition.; Gaussian, Inc: Wallingford, CT, 2015.

(35) Dunning, T. H. Gaussian Basis Sets for Use in Correlated Molecular Calculations. I. The Atoms Boron through Neon and Hydrogen. *J. Chem. Phys.* **1989**, *90* (2), 1007–1023. https://doi.org/10.1063/1.456153.

(36) Jensen, F. Polarization Consistent Basis Sets: Principles. *J. Chem. Phys.* **2001**, *115* (20), 9113–9125. https://doi.org/10.1063/1.1413524.

(37) Mardirossian, N.; McClain, J. D.; Chan, G. K.-L. Lowering of the Complexity of Quantum Chemistry Methods by Choice of Representation. *J. Chem. Phys.* **2018**, *148* (4), 044106. https://doi.org/10.1063/1.5007779.

(38) Lambrecht, D. S.; Ochsenfeld, C. Multipole-Based Integral Estimates for the Rigorous Description of Distance Dependence in Two-Electron Integrals. *J. Chem. Phys.* **2005**, *123* (18), 184101. https://doi.org/10.1063/1.2079967.

(39) Kussmann, J.; Ochsenfeld, C. Pre-Selective Screening for Matrix Elements in Linear-Scaling Exact Exchange Calculations. *J. Chem. Phys.* **2013**, *138* (13), 134114. https://doi.org/10.1063/1.4796441.

(40) Maurer, S. A.; Lambrecht, D. S.; Kussmann, J.; Ochsenfeld, C. Efficient Distance-Including Integral Screening in Linear-Scaling Møller-Plesset Perturbation Theory. *J. Chem. Phys.* **2013**, *138* (1), 014101. https://doi.org/10.1063/1.4770502.

(41) Greengard, L.; Rokhlin, V. A Fast Algorithm for Particle Simulations. *J. Comput. Phys.* **1997**, *135* (2), 280–292. https://doi.org/10.1006/jcph.1997.5706.

(42) Strain, M. C.; Scuseria, G. E.; Frisch, M. J. Achieving Linear Scaling for the Electronic Quantum Coulomb Problem. *Science* **1996**, *271* (5245), 51–53. https://doi.org/10.1126/science.271.5245.51.

(43) Izmaylov, A. F.; Brothers, E. N.; Scuseria, G. E. Linear-Scaling Calculation of Static and Dynamic Polarizabilities in Hartree-Fock and Density Functional Theory for Periodic Systems. *J. Chem. Phys.* **2006**, *125* (22), 224105. https://doi.org/10.1063/1.2404667.

(44) Ziółkowski, M.; Jansík, B.; Kjærgaard, T.; Jørgensen, P. Linear Scaling Coupled Cluster Method with Correlation Energy Based Error Control. *J. Chem. Phys.* **2010**, *133* (1), 014107. https://doi.org/10.1063/1.3456535.

(45) Dziedzic, J.; Hill, Q.; Skylaris, C.-K. Linear-Scaling Calculation of Hartree-Fock Exchange Energy with Non-Orthogonal Generalised Wannier Functions. *J. Chem. Phys.* **2013**, *139* (21), 214103. https://doi.org/10.1063/1.4832338.

(46) Mohr, S.; Ratcliff, L. E.; Genovese, L.; Caliste, D.; Boulanger, P.; Goedecker, S.; Deutsch, T. Accurate and Efficient Linear Scaling DFT Calculations with Universal Applicability. *Phys. Chem. Chem. Phys.* **2015**, *17* (47), 31360–31370. https://doi.org/10.1039/C5CP00437C.

(47) Saitow, M.; Becker, U.; Riplinger, C.; Valeev, E. F.; Neese, F. A New Near-Linear Scaling, Efficient and Accurate, Open-Shell Domain-Based Local Pair Natural Orbital Coupled Cluster Singles and Doubles Theory. *J. Chem. Phys.* **2017**, *146* (16), 164105. https://doi.org/10.1063/1.4981521.

(48) Mohr, S.; Eixarch, M.; Amsler, M.; Mantsinen, M. J.; Genovese, L. Linear Scaling DFT Calculations for Large Tungsten Systems Using an Optimized

Local Basis. *Nucl. Mater. Energy* **2018**, *15*, 64–70. https://doi.org/10.1016/j.nme.2018.01.002.

(49) Prentice, J. C. A.; Aarons, J.; Womack, J. C.; Allen, A. E. A.; Andrinopoulos, L.; Anton, L.; Bell, R. A.; Bhandari, A.; Bramley, G. A.; Charlton, R. J.; Clements, R. J.; Cole, D. J.; Constantinescu, G.; Corsetti, F.; Dubois, S. M.-M.; Duff, K. K. B.; Escartín, J. M.; Greco, A.; Hill, Q.; Lee, L. P.; Linscott, E.; O'Regan, D. D.; Phipps, M. J. S.; Ratcliff, L. E.; Serrano, Á. R.; Tait, E. W.; Teobaldi, G.; Vitale, V.; Yeung, N.; Zuehlsdorff, T. J.; Dziedzic, J.; Haynes, P. D.; Hine, N. D. M.; Mostofi, A. A.; Payne, M. C.; Skylaris, C.-K. The ONETEP Linear-Scaling Density Functional Theory Program. *J. Chem. Phys.* **2020**, *152* (17), 174111. https://doi.org/10.1063/5.0004445.

(50) Guo, Y.; Riplinger, C.; Becker, U.; Liakos, D. G.; Minenkov, Y.; Cavallo, L.; Neese, F. Communication: An Improved Linear Scaling Perturbative Triples Correction for the Domain Based Local Pair-Natural Orbital Based Singles and Doubles Coupled Cluster Method [DLPNO-CCSD(T)]. *J. Chem. Phys.* **2018**, *148* (1), 011101. https://doi.org/10.1063/1.5011798.

(51) Riplinger, C.; Pinski, P.; Becker, U.; Valeev, E. F.; Neese, F. Sparse Maps—A Systematic Infrastructure for Reduced-Scaling Electronic Structure Methods. II. Linear Scaling Domain Based Pair Natural Orbital Coupled Cluster Theory. *J. Chem. Phys.* **2016**, *144* (2), 024109. https://doi.org/10.1063/1.4939030.

(52) Lanyon, B. P.; Whitfield, J. D.; Gillett, G. G.; Goggin, M. E.; Almeida, M. P.; Kassal, I.; Biamonte, J. D.; Mohseni, M.; Powell, B. J.; Barbieri, M.; Aspuru-Guzik, A.; White, A. G. Towards Quantum Chemistry on a Quantum Computer. *Nat. Chem.* **2010**, *2* (2), 106–111. https://doi.org/10.1038/nchem.483.

(53) Moll, N.; Fuhrer, A.; Staar, P.; Tavernelli, I. Optimizing Qubit Resources for Quantum Chemistry Simulations in Second Quantization on a Quantum Computer. *J. Phys. Math. Theor.* **2016**, *49* (29), 295301. https://doi.org/10.1088/1751-8113/49/29/295301.

(54) Veis, L.; Višňák, J.; Nishizawa, H.; Nakai, H.; Pittner, J. Quantum Chemistry beyond Born-Oppenheimer Approximation on a Quantum Computer: A Simulated Phase Estimation Study. *Int. J. Quantum Chem.* **2016**, *116* (18), 1328–1336. https://doi.org/10.1002/qua.25176.

(55) Ryabinkin, I. G.; Yen, T.-C.; Genin, S. N.; Izmaylov, A. F. Qubit Coupled Cluster Method: A Systematic Approach to Quantum Chemistry on a Quantum Computer. *J. Chem. Theory Comput.* **2018**, *14* (12), 6317–6326. https://doi.org/10.1021/acs.jctc.8b00932.

(56) Markownikoff, W. I. Ueber die Abhängigkeit der verschiedenen Vertretbarkeit des Radicalwasserstoffs in den isomeren Buttersäuren. *Ann. Chem. Pharm.* **1870**, *153* (2), 228–259. https://doi.org/10.1002/jlac.18701530204.

(57) Wischnegradsky, A. Ueber verschiedene Amylene und Amylalkohole. *Justus Liebigs Ann. Chem.* **1878**, *190* (3), 328–366. https://doi.org/10.1002/jlac.18781900307.

(58) Marczenko, K. M.; Zurakowski, J. A.; Bamford, K. L.; MacMillan, J. W. M.; Chitnis, S. S. Hydrostibination. *Angew. Chem. Int. Ed.* **2019**, *58* (50), 18096–18101. https://doi.org/10.1002/anie.201911842.

(59) Lau, S.; Hood, T. M.; Webster, R. L. Broken Promises? On the Continued Challenges Faced in Catalytic Hydrophosphination. *ACS Catal.* **2022**, *12* (17), 10939–10949. https://doi.org/10.1021/acscatal.2c03144.

(60) Li, C.-J.; Li, Z. Green Chemistry: The Development of Cross-Dehydrogenative Coupling (CDC) for Chemical Synthesis. *Pure Appl. Chem.* **2006**, *78* (5), 935–945. https://doi.org/10.1351/pac200678050935.

(61) Scheuermann, C. J. Beyond Traditional Cross Couplings: The Scope of the Cross Dehydrogenative Coupling Reaction. *Chem. - Asian J.* **2010**, *5* (3), 436–451. https://doi.org/10.1002/asia.200900487.

(62) Peng, K.; Dong, Z. Recent Advances in Cross-Dehydrogenative Couplings (CDC) of C−H Bond in Aqueous Media. *Adv. Synth. Catal.* **2021**, *363* (5), 1185–1201. https://doi.org/10.1002/adsc.202001358.

(63) Jim, C. K. W.; Qin, A.; Lam, J. W. Y.; Mahtab, F.; Yu, Y.; Tang, B. Z. Metal-Free Alkyne Polyhydrothiolation: Synthesis of Functional Poly(Vinylenesulfide)s with High Stereoregularity by Regioselective Thioclick Polymerization. *Adv. Funct. Mater.* **2010**, *20* (8), 1319–1328. https://doi.org/10.1002/adfm.200901943.

(64) Lu, P.; Lam, J. W. Y.; Liu, J.; Jim, C. K. W.; Yuan, W.; Chan, C. Y. K.; Xie, N.; Hu, Q.; Cheuk, K. K. L.; Tang, B. Z. Regioselective Alkyne Polyhydrosilylation: Synthesis and Photonic Properties of Poly(Silylenevinylene)s. *Macromolecules* **2011**, *44* (15), 5977–5986. https://doi.org/10.1021/ma201203w.

(65) He, B.; Wu, Y.; Qin, A.; Tang, B. Z. Copper-Catalyzed Electrophilic Polyhydroamination of Internal Alkynes. *Macromolecules* **2017**, *50* (15), 5719–5728. https://doi.org/10.1021/acs.macromol.7b00992.

(66) Doyle, M. P.; Devora, G. A.; Nefedov, A. O.; High, K. G. Addition/Elimination in the Rhodium(II) Perfluorobutyrate Catalyzed Hydrosilylation of 1-Alkenes. Rhodium Hydride Promoted Isomerization and Hydrogenation. *Organometallics* **1992**, *11* (2), 549–555. https://doi.org/10.1021/om00038a008.

(67) Morrill, T. C.; D'Souza, C. A. Efficient Hydride-Assisted Isomerization of Alkenes via Rhodium Catalysis. *Organometallics* **2003**, *22* (8), 1626–1629. https://doi.org/10.1021/om0207358.

(68) Molloy, J. J.; Schäfer, M.; Wienhold, M.; Morack, T.; Daniliuc, C. G.; Gilmour, R. Boron-Enabled Geometric Isomerization of Alkenes via Selective Energy-Transfer Catalysis. *Science* **2020**, *369* (6501), 302–306. https://doi.org/10.1126/science.abb7235.

(69) Miyaura, Norio.; Suzuki, Akira. Palladium-Catalyzed Cross-Coupling Reactions of Organoboron Compounds. *Chem. Rev.* **1995**, *95* (7), 2457–2483. https://doi.org/10.1021/cr00039a007.

(70) Breit, B.; Seiche, W. Recent Advances on Chemo-, Regio- and Stereoselective Hydroformylation. *Synthesis* **2001**, *2001* (01), 0001–0036. https://doi.org/10.1055/s-2001-9739.

(71) Trautz, M. Das Gesetz Der Reaktionsgeschwindigkeit Und Der Gleichgewichte in Gasen. Bestätigung Der Additivität von C_v-3/2R. Neue Bestimmung Der Integrationskonstanten Und Der Moleküldurchmesser. *Z. Für Anorg. Allg. Chem.* **1916**, *96* (1), 1–28. https://doi.org/10.1002/zaac.19160960102.

(72) Lewis, W. C. M. XLI.—Studies in Catalysis. Part IX. The Calculation in Absolute Measure of Velocity Constants and Equilibrium Constants in Gaseous Systems. *J Chem Soc Trans* **1918**, *113* (0), 471–492. https://doi.org/10.1039/CT9181300471.

(73) Meek, S. J.; Pitman, C. L.; Miller, A. J. M. Deducing Reaction Mechanism: A Guide for Students, Researchers, and Instructors. *J. Chem. Educ.* **2016**, *93* (2), 275–286. https://doi.org/10.1021/acs.jchemed.5b00160.

(74) Study and Description of Organic Reaction Mechanisms. In *Advanced Organic Chemistry*; Advanced Organic Chemistry; Kluwer Academic Publishers: Boston, 2002; pp 187–261. https://doi.org/10.1007/0-306-46856-5_4.

(75) Nakajima, Y.; Shimada, S. Hydrosilylation Reaction of Olefins: Recent Advances and Perspectives. *RSC Adv.* **2015**, *5* (26), 20603–20616. https://doi.org/10.1039/C4RA17281G.

(76) Troegel, D.; Stohrer, J. Recent Advances and Actual Challenges in Late Transition Metal Catalyzed Hydrosilylation of Olefins from an Industrial Point of View. *Coord. Chem. Rev.* **2011**, *255* (13–14), 1440–1459. https://doi.org/10.1016/j.ccr.2010.12.025.

(77) Addis, D.; Das, S.; Junge, K.; Beller, M. Selective Reduction of Carboxylic Acid Derivatives by Catalytic Hydrosilylation. *Angew. Chem. Int. Ed.* **2011**, *50* (27), 6004–6011. https://doi.org/10.1002/anie.201100145.

(78) Guo, P.; Liu, H.; Zhao, J. Transforming Bulk Alkenes and Alkynes into Fine Chemicals Enabled by Single-Atom Site Catalysis. *Nano Res.* **2022**, *15* (9), 7840–7860. https://doi.org/10.1007/s12274-022-4495-z.

(79) Hofmann, R.; Vlatković, M.; Wiesbrock, F. Fifty Years of Hydrosilylation in Polymer Science: A Review of Current Trends of Low-Cost Transition-Metal and Metal-Free Catalysts, Non-Thermally Triggered Hydrosilylation Reactions, and Industrial Applications. *Polymers* **2017**, *9* (12), 534. https://doi.org/10.3390/polym9100534.

(80) Zaranek, M.; Pawluc, P. Markovnikov Hydrosilylation of Alkenes: How an Oddity Becomes the Goal. *ACS Catal.* **2018**, *8* (10), 9865–9876. https://doi.org/10.1021/acscatal.8b03104.

(81) Hartwig, J. F. Borylation and Silylation of C–H Bonds: A Platform for Diverse C–H Bond Functionalizations. *Acc. Chem. Res.* **2012**, *45* (6), 864–873. https://doi.org/10.1021/ar200206a.

(82) Richter, S. C.; Oestreich, M. Emerging Strategies for C–H Silylation. *Trends Chem.* **2020**, *2* (1), 13–27. https://doi.org/10.1016/j.trechm.2019.07.003.

(83) Jiang, Y.; Blacque, O.; Fox, T.; Frech, C. M.; Berke, H. Highly Selective Dehydrogenative Silylation of Alkenes Catalyzed by Rhenium Complexes. *Chem. - Eur. J.* **2009**, *15* (9), 2121–2128. https://doi.org/10.1002/chem.200802019.

(84) Atienza, C. C. H.; Diao, T.; Weller, K. J.; Nye, S. A.; Lewis, K. M.; Delis, J. G. P.; Boyer, J. L.; Roy, A. K.; Chirik, P. J. Bis(Imino)Pyridine Cobalt-Catalyzed Dehydrogenative Silylation of Alkenes: Scope, Mechanism, and Origins of Selective Allylsilane Formation. *J. Am. Chem. Soc.* **2014**, *136* (34), 12108–12118. https://doi.org/10.1021/ja5060884.

(85) Bai, X.-F.; Song, T.; Deng, W.-H.; Wei, Y.-L.; Li, L.; Xia, C.-G.; Xu, L.-W. $(EtO)_3SiH$-Promoted Palladium-Catalyzed Isomerization of Olefins: Convenient Synthesis of Internal Alkenes from Terminal Alkenes. *Synlett* **2013**, *25* (03), 417–422. https://doi.org/10.1055/s-0033-1340290.

(86) He, P.; Hu, M.-Y.; Zhang, X.-Y.; Zhu, S.-F. Transition-Metal-Catalyzed Stereo- and Regioselective Hydrosilylation of Unsymmetrical Alkynes. *Synthesis* **2022**, *54* (01), 49–66. https://doi.org/10.1055/a-1605-9572.

(87) Guo, J.; Lu, Z. Highly Chemo-, Regio-, and Stereoselective Cobalt-Catalyzed Markovnikov Hydrosilylation of Alkynes. *Angew. Chem. Int. Ed.* **2016**, *55* (36), 10835–10838. https://doi.org/10.1002/anie.201605501.

(88) Hu, M.-Y.; He, P.; Qiao, T.-Z.; Sun, W.; Li, W.-T.; Lian, J.; Li, J.-H.; Zhu, S.-F. Iron-Catalyzed Regiodivergent Alkyne Hydrosilylation. *J. Am. Chem. Soc.* **2020**, *142* (39), 16894–16902. https://doi.org/10.1021/jacs.0c09083.

(89) Wu, C.; Teo, W. J.; Ge, S. Cobalt-Catalyzed (*E*)-Selective *Anti* -Markovnikov Hydrosilylation of Terminal Alkynes. *ACS Catal.* **2018**, *8* (7), 5896–5900. https://doi.org/10.1021/acscatal.8b01410.

(90) Wu, G.; Chakraborty, U.; Jacobi von Wangelin, A. Regiocontrol in the Cobalt-Catalyzed Hydrosilylation of Alkynes. *Chem. Commun.* **2018**, *54* (87), 12322–12325. https://doi.org/10.1039/C8CC07267A.

(91) Riant, O.; Mostefaï, N.; Courmarcel, J. Recent Advances in the Asymmetric Hydrosilylation of Ketones, Imines and Electrophilic Double Bonds. *Synthesis* **2004**, No. 18, 2943–2958. https://doi.org/10.1055/s-2004-834932.

(92) Castro, L. C. M.; Sortais, J.-B.; Darcel, C. NHC-Carbene Cyclopentadienyl Iron Based Catalyst for a General and Efficient Hydrosilylation of Imines. *Chem Commun* **2012**, *48* (1), 151–153. https://doi.org/10.1039/C1CC14403K.

(93) Pérez, M.; Qu, Z.-W.; Caputo, C. B.; Podgorny, V.; Hounjet, L. J.; Hansen, A.; Dobrovetsky, R.; Grimme, S.; Stephan, D. W. Hydrosilylation of Ketones, Imines and Nitriles Catalysed by Electrophilic Phosphonium Cations: Functional Group Selectivity and Mechanistic Considerations. *Chem. - Eur. J.* **2015**, *21* (17), 6491–6500. https://doi.org/10.1002/chem.201406356.

(94) Corre, Y.; Iali, W.; Hamdaoui, M.; Trivelli, X.; Djukic, J.-P.; Agbossou-Niedercorn, F.; Michon, C. Efficient Hydrosilylation of Imines Using Catalysts Based on Iridium(III) Metallacycles. *Catal. Sci. Technol.* **2015**, *5* (3), 1452–1458. https://doi.org/10.1039/C4CY01233J.

(95) Bezłada, A.; Szewczyk, M.; Mlynarski, J. Enantioselective Hydrosilylation of Imines Catalyzed by Chiral Zinc Acetate Complexes. *J. Org. Chem.* **2016**, *81* (1), 336–342. https://doi.org/10.1021/acs.joc.5b02613.

(96) Elsen, H.; Fischer, C.; Knüpfer, C.; Escalona, A.; Harder, S. Early Main Group Metal Catalysts for Imine Hydrosilylation. *Chem. – Eur. J.* **2019**, *25* (70), 16141–16147. https://doi.org/10.1002/chem.201904148.

(97) Gutsulyak, D. V.; Nikonov, G. I. Chemoselective Catalytic Hydrosilylation of Nitriles. *Angew. Chem. Int. Ed.* **2010**, *49* (41), 7553–7556. https://doi.org/10.1002/anie.201003069.

(98) Boone, C.; Korobkov, I.; Nikonov, G. I. Unexpected Role of Zinc Hydride in Catalytic Hydrosilylation of Ketones and Nitriles. *ACS Catal.* **2013**, *3* (10), 2336–2340. https://doi.org/10.1021/cs400581w.

(99) Ito, M.; Itazaki, M.; Nakazawa, H. Selective Double Hydrosilylation of Nitriles Catalyzed by an Iron Complex Containing Indium Trihalide. *ChemCatChem* **2016**, *8* (21), 3323–3325. https://doi.org/10.1002/cctc.201600940.

(100) Zuo, Z.; Sun, H.; Wang, L.; Li, X. Hydrosilylation of Aldehydes and Ketones Catalyzed by Hydrido Iron Complexes Bearing Imine Ligands. *Dalton Trans.* **2014**, *43* (30), 11716. https://doi.org/10.1039/C4DT00944D.

(101) Lipshutz, B. H.; Chrisman, W.; Noson, K. Hydrosilylation of Aldehydes and Ketones Catalyzed by $[Ph_3P(CuH)]_6$. *J. Organomet. Chem.* **2001**, *624* (1–2), 367–371. https://doi.org/10.1016/S0022-328X(00)00903-7.

(102) Fernandes, A. C.; Fernandes, R.; Romão, C. C.; Royo, B. [MoO_2Cl_2] as Catalyst for Hydrosilylation of Aldehydes and Ketones. *Chem Commun* **2005**, No. 2, 213–214. https://doi.org/10.1039/B414145H.

(103) Tondreau, A. M.; Lobkovsky, E.; Chirik, P. J. Bis(Imino)Pyridine Iron Complexes for Aldehyde and Ketone Hydrosilylation. *Org. Lett.* **2008**, *10* (13), 2789–2792. https://doi.org/10.1021/ol800906b.

(104) Chakraborty, S.; Krause, J. A.; Guan, H. Hydrosilylation of Aldehydes and Ketones Catalyzed by Nickel PCP-Pincer Hydride Complexes. *Organometallics* **2009**, *28* (2), 582–586. https://doi.org/10.1021/om800948f.

(105) Raya-Barón, Á.; Oña-Burgos, P.; Fernández, I. Iron-Catalyzed Homogeneous Hydrosilylation of Ketones and Aldehydes: Advances and Mechanistic Perspective. *ACS Catal.* **2019**, *9* (6), 5400–5417. https://doi.org/10.1021/acscatal.9b00201.

(106) Nishiyama, H.; Kondo, M.; Nakamura, T.; Itoh, K. Highly Enantioselective Hydrosilylation of Ketones with Chiral and C_2-Symmetrical Bis(Oxazolinyl)Pyridine-Rhodium Catalysts. *Organometallics* **1991**, *10* (2), 500–508. https://doi.org/10.1021/om00048a029.

(107) Fürstner, A.; Radkowski, K. A Chemo- and Stereoselective Reduction of Cycloalkynes to (E)-Cycloalkenes. *Chem Commun* **2002**, No. 18, 2182–2183. https://doi.org/10.1039/B207169J.

(108) Junge, K.; Wendt, B.; Shaikh, N.; Beller, M. Iron-Catalyzed Selective Reduction of Nitroarenes to Anilines Using Organosilanes. *Chem. Commun.* **2010**, *46* (10), 1769. https://doi.org/10.1039/b924228g.

(109) Ogiwara, Y.; Uchiyama, T.; Sakai, N. Reductive Amination/Cyclization of Keto Acids Using a Hydrosilane for Selective Production of Lactams versus Cyclic Amines by Switching of the Indium Catalyst. *Angew. Chem. Int. Ed.* **2016**, *55* (5), 1864–1867. https://doi.org/10.1002/anie.201509465.

(110) Fang, C.; Lu, C.; Liu, M.; Zhu, Y.; Fu, Y.; Lin, B.-L. Selective Formylation and Methylation of Amines Using Carbon Dioxide and Hydrosilane Catalyzed by Alkali-Metal Carbonates. *ACS Catal.* **2016**, *6* (11), 7876–7881. https://doi.org/10.1021/acscatal.6b01856.

(111) Sommer, L. H.; Pietrusza, E. W.; Whitmore, F. C. Peroxide-Catalyzed Addition of Trichlorosilane to 1-Octene. *J. Am. Chem. Soc.* **1947**, *69* (1), 188–188. https://doi.org/10.1021/ja01193a508.

(112) Mackenzie, C.; Spialter, L.; Schoffman, M. Organosilicon Compounds. French Patent 961,878, May 24, 1950.

(113) Wagner, G. H.; Strother, C. O. Process of Producing Organosilicon Compounds. Swiss Patent 279,280, March 1, 1952.

(114) Speier, J. L.; Webster, J. A.; Barnes, G. H. The Addition of Silicon Hydrides to Olefinic Double Bonds. Part II. The Use of Group VIII Metal Catalysts. *J. Am. Chem. Soc.* **1957**, *79* (4), 974–979. https://doi.org/10.1021/ja01561a054.

(115) Karstedt, B. D. Platinum Complexes of Unsaturated Siloxanes and Platinum Containing Organopolysiloxanes. US Patent 3775452, November 27, 1973.

(116) Chen, J.; Guo, J.; Lu, Z. Recent Advances in Hydrometallation of Alkenes and Alkynes via the First Row Transition Metal Catalysis: Recent Advances in Hydrometallation of Alkenes and Alkynes via the First Row Transition Metal Catalysis. *Chin. J. Chem.* **2018**, *36* (11), 1075–1109. https://doi.org/10.1002/cjoc.201800314.

(117) Obligacion, J. V.; Chirik, P. J. Earth-Abundant Transition Metal Catalysts for Alkene Hydrosilylation and Hydroboration. *Nat. Rev. Chem.* **2018**, *2* (5), 15–34. https://doi.org/10.1038/s41570-018-0001-2.

(118) Stephan, D. W.; Erker, G. Frustrated Lewis Pair Chemistry: Development and Perspectives. *Angew. Chem. Int. Ed.* **2015**, *54* (22), 6400–6441. https://doi.org/10.1002/anie.201409800.

(119) Oestreich, M.; Hermeke, J.; Mohr, J. A Unified Survey of Si–H and H–H Bond Activation Catalysed by Electron-Deficient Boranes. *Chem. Soc. Rev.* **2015**, *44* (8), 2202–2220. https://doi.org/10.1039/C4CS00451E.

(120) Du, X.; Huang, Z. Advances in Base-Metal-Catalyzed Alkene Hydrosilylation. *ACS Catal.* **2017**, *7* (2), 1227–1243. https://doi.org/10.1021/acscatal.6b02990.

(121) Wang, L.; Sun, W.; Liu, C. Homodinuclear Ferrous Group Metal Complexes and Their Application in Homogeneous Catalysis. *Acta Phys.-Chim. Sin.* **2019**, *35* (7), 697–708. https://doi.org/10.3866/PKU.WHXB201807071.

(122) Zhang, M.; Zhang, A. Iron-Catalyzed Hydrosilylation Reactions. *Appl. Organomet. Chem.* **2010**, *24* (11), 751–757. https://doi.org/10.1002/aoc.1701.

(123) Sun, J.; Deng, L. Cobalt Complex-Catalyzed Hydrosilylation of Alkenes and Alkynes. *ACS Catal.* **2016**, *6* (1), 290–300. https://doi.org/10.1021/acscatal.5b02308.

(124) Arora, V.; Narjinari, H.; Nandi, P. G.; Kumar, A. Recent Advances in Pincer–Nickel Catalyzed Reactions. *Dalton Trans.* **2021**, *50* (10), 3394–3428. https://doi.org/10.1039/D0DT03593A.

(125) Fu, P.-F.; Brard, L.; Li, Y.; Marks, T. J. Regioselection and Enantioselection in Organolanthanide-Catalyzed Olefin Hydrosilylation. A Kinetic and Mechanistic Study. *J. Am. Chem. Soc.* **1995**, *117* (27), 7157–7168. https://doi.org/10.1021/ja00132a015.

(126) Rastätter, M.; Zulys, A.; Roesky, P. W. Bis(Phosphinimino)Methanide Rare Earth Amides: Synthesis, Structure, and Catalysis of Hydroamination/Cyclization, Hydrosilylation, and Sequential Hydroamination/Hydrosilylation. *Chem. - Eur. J.* **2007**, *13* (13), 3606–3616. https://doi.org/10.1002/chem.200601510.

(127) Abinet, E.; Spaniol, T. P.; Okuda, J. Olefin Hydrosilylation Catalysts Based on Allyl Bis(Phenolato) Complexes of the Early Lanthanides. *Chem. - Asian J.* **2011**, *6* (2), 389–391. https://doi.org/10.1002/asia.201000598.

(128) Konkol, M.; Kondracka, M.; Voth, P.; Spaniol, T. P.; Okuda, J. Rare-Earth Metal Alkyl and Hydrido Complexes Containing a Thioether-Functionalized Bis(Phenolato) Ligand: Efficient Catalysts for Olefin Hydrosilylation. *Organometallics* **2008**, *27* (15), 3774–3784. https://doi.org/10.1021/om800161u.

(129) Zhan, G.; Teng, H.-L.; Luo, Y.; Lou, S.-J.; Nishiura, M.; Hou, Z. Enantioselective Construction of Silicon-Stereogenic Silanes by Scandium-Catalyzed Intermolecular Alkene Hydrosilylation. *Angew. Chem. Int. Ed.* **2018**, *57* (38), 12342–12346. https://doi.org/10.1002/anie.201807493.

(130) Buch, F.; Brettar, J.; Harder, S. Hydrosilylation of Alkenes with Early Main-Group Metal Catalysts. *Angew. Chem. Int. Ed.* **2006**, *45* (17), 2741–2745. https://doi.org/10.1002/anie.200504164.

(131) Harder, S. Early Main Group Metal-Catalyzed Hydrosilylation of Unsaturated Bonds. In *Early Main Group Metal Catalysis*; Harder, S., Ed.; Wiley, 2020; pp 151–173. https://doi.org/10.1002/9783527818020.ch6.

(132) Schuhknecht, D.; Spaniol, T. P.; Maron, L.; Okuda, J. Regioselective Hydrosilylation of Olefins Catalyzed by a Molecular Calcium Hydride Cation. *Angew. Chem. Int. Ed.* **2020**, *59* (1), 310–314. https://doi.org/10.1002/anie.201909585.

(133) Oertle, K.; Wetter, H. Hydrosilylation of Tetrasubstituted Olefins. *Tetrahedron Lett.* **1985**, *26* (45), 5511–5514. https://doi.org/10.1016/S0040-4039(01)80873-X.

(134) Asao, N.; Sudo, T.; Yamamoto, Y. Lewis Acid-Catalyzed *Trans* -Hydrosilylation of Alkynes. *J. Org. Chem.* **1996**, *61* (22), 7654–7655. https://doi.org/10.1021/jo961508g.

(135) Song, Y.-S.; Yoo, B. R.; Lee, G.-H.; Jung, I. N. Lewis Acid-Catalyzed Regio- and Stereoselective Hydrosilylation of Alkenes with Trialkylsilanes. *Organometallics* **1999**, *18* (16), 3109–3115. https://doi.org/10.1021/om990220p.

(136) Jakobsson, K.; Chu, T.; Nikonov, G. I. Hydrosilylation of Olefins Catalyzed by Well-Defined Cationic Aluminum Complexes: Lewis Acid versus Insertion Mechanisms. *ACS Catal.* **2016**, *6* (11), 7350–7356. https://doi.org/10.1021/acscatal.6b01694.

(137) Pike, R. A. Base-Catalyzed Additions of Trichlorosilane to Hydrocarbon Olefins. *J. Org. Chem.* **1962**, *27* (6), 2186–2190. https://doi.org/10.1021/jo01053a071.

(138) Holthausen, M. H.; Mehta, M.; Stephan, D. W. The Highly Lewis Acidic Dicationic Phosphonium Salt: $[(SIMes)PFPh_2][B(C_6F_5)_4]_2$. *Angew. Chem. Int. Ed.* **2014**, *53* (25), 6538–6541. https://doi.org/10.1002/anie.201403693.

(139) Pérez, M.; Hounjet, L. J.; Caputo, C. B.; Dobrovetsky, R.; Stephan, D. W. Olefin Isomerization and Hydrosilylation Catalysis by Lewis Acidic Organofluorophosphonium Salts. *J. Am. Chem. Soc.* **2013**, *135* (49), 18308–18310. https://doi.org/10.1021/ja410379x.

(140) Kim, D. W.; Joung, S.; Kim, J. G.; Chang, S. Metal-Free Hydrosilylation Polymerization by Borane Catalyst. *Angew. Chem.* **2015**, *127* (49), 15018–15022. https://doi.org/10.1002/ange.201507863.

(141) Wilkins, L. C.; Howard, J. L.; Burger, S.; Frentzel-Beyme, L.; Browne, D. L.; Melen, R. L. Exploring Multistep Continuous-Flow Hydrosilylation Reactions Catalyzed by Tris(Pentafluorophenyl)Borane. *Adv. Synth. Catal.* **2017**, *359* (15), 2580–2584. https://doi.org/10.1002/adsc.201700349.

(142) Shi, Q.; Chen, Z.; Hu, J. Recent Advances in Organocatalyzed Asymmetric Hydrosilylations. *Curr. Org. Chem.* **2018**, *22* (6), 557–580. https://doi.org/10.2174/1385272822666171227145613.

(143) Zaranek, M.; Witomska, S.; Patroniak, V.; Pawluć, P. Unexpected Catalytic Activity of Simple Triethylborohydrides in the Hydrosilylation of Alkenes. *Chem. Commun.* **2017**, *53* (39), 5404–5407. https://doi.org/10.1039/C7CC01531C.

(144) Skrodzki, M.; Zaranek, M.; Witomska, S.; Pawluc, P. Direct Dehydrogenative Coupling of Alcohols with Hydrosilanes Promoted by Sodium Tri(Sec-Butyl)Borohydride. *Catalysts* **2018**, *8* (12), 618. https://doi.org/10.3390/catal8120618.

(145) Skrodzki, M.; Witomska, S.; Pawluć, P. Sodium Triethylborohydride as a Catalyst for the Dehydrogenative Silylation of Terminal Alkynes with Hydrosilanes. *Dalton Trans.* **2018**, *47* (17), 5948–5951. https://doi.org/10.1039/C8DT00684A.

(146) Hadlington, T. J.; Hermann, M.; Frenking, G.; Jones, C. Two-Coordinate Group 14 Element(II) Hydrides as Reagents for the Facile, and Sometimes Reversible, Hydrogermylation/Hydrostannylation of Unactivated Alkenes and Alkynes. *Chem. Sci.* **2015**, *6* (12), 7249–7257. https://doi.org/10.1039/C5SC03376D.

(147) Hadlington, T. J.; Driess, M.; Jones, C. Low-Valent Group 14 Element Hydride Chemistry: Towards Catalysis. *Chem. Soc. Rev.* **2018**, *47* (11), 4176–4197. https://doi.org/10.1039/C7CS00649G.

(148) Corriu, R. J. P.; Moreau, J. J. E. Stereospecific Route to Asymmetric Vinylgermanes: Hydrogermylation of Phenylacetylene Catalysed by Rhodium and Platinum Complexes. *J. Chem. Soc. Chem. Commun.* **1971**, No. 15, 812. https://doi.org/10.1039/c29710000812.

(149) Salimgareeva, I. M.; Bogatova, N. G.; Panasenko, A. A.; Khalilov, L. M.; Purlei, I. I.; Mavrodiev, V. K.; Yur'ev, V. P. Hydrogermylation of 1,3-Dienes Using Nickel Catalyst Systems. *Bull. Acad. Sci. USSR Div. Chem. Sci.* **1983**, *32* (7), 1456–1461. https://doi.org/10.1007/BF00954357.

(150) Itazaki, M.; Kamitani, M.; Nakazawa, H. Trans-Selective Hydrogermylation of Alkynes Promoted by Methyliron and Bis(Germyl)Hydridoiron Complexes as a Catalyst Precursor. *Chem. Commun.* **2011**, *47* (27), 7854. https://doi.org/10.1039/c1cc12530c.

(151) Liang, H.; Ji, Y.-X.; Wang, R.-H.; Zhang, Z.-H.; Zhang, B. Visible-Light-Initiated Manganese-Catalyzed *E*-Selective Hydrosilylation and Hydrogermylation of Alkynes. *Org. Lett.* **2019**, *21* (8), 2750–2754. https://doi.org/10.1021/acs.orglett.9b00701.

(152) Radzhabov, M. R.; Mankad, N. P. Cobalt-Catalyzed (*E*)-β-Selective Hydrogermylation of Terminal Alkynes. *Org. Lett.* **2021**, *23* (8), 3221–3226. https://doi.org/10.1021/acs.orglett.1c00928.

(153) Zhang, J.; Lu, B.; Meng, L.; Li, X. Charge-Regulated Regioselective Mechanism of Bicobalt-Catalyzed Hydrogermylation of Alkynes: DFT Investigation. *Mol. Catal.* **2022**, *526*, 112379. https://doi.org/10.1016/j.mcat.2022.112379.

(154) Lin, W.; You, L.; Yuan, W.; He, C. Cu-Catalyzed Enantioselective Hydrogermylation: Asymmetric Synthesis of Unnatural β-Germyl α-Amino Acids. *ACS Catal.* **2022**, *12* (23), 14592–14600. https://doi.org/10.1021/acscatal.2c04571.

(155) David-Quillot, F.; Thiéry, V.; Abarbri, M.; Thibonnet, J.; Besson, T.; Duchéne, A. Regio- and Stereoselective Synthesis of (Z)-Vinylgermanes by Hydrogermylation of Alkynes. *Main Group Met. Chem.* **2007**, *30* (5). https://doi.org/10.1515/MGMC.2007.30.5.235.

(156) Miura, K.; Ootsuka, K.; Hosomi, A. Homolytic Hydrogermylation of Alkenes with Dibutylchlorogermane. *J. Organomet. Chem.* **2007**, *692* (1–3), 514–519. https://doi.org/10.1016/j.jorganchem.2006.04.043.

(157) Keess, S.; Oestreich, M. Access to Fully Alkylated Germanes by $B(C_6F_5)_3$-Catalyzed Transfer Hydrogermylation of Alkenes. *Org. Lett.* **2017**, *19* (7), 1898–1901. https://doi.org/10.1021/acs.orglett.7b00672.

(158) Tanaka, S.; Nakamura, T.; Yorimitsu, H.; Shinokubo, H.; Oshima, K. Et_3B-Induced Hydrogermylation of Alkenes and Silyl Enol Ethers. *Org. Lett.* **2000**, *2* (13), 1911–1914. https://doi.org/10.1021/ol005977n.

(159) Nakamura, T.; Tanaka, S.; Yorimitsu, H.; Shinokubo, H.; Oshima, K. Triethylborane-Induced Hydrogermylation of Alkenes with Tri-2-

Furylgermane. *Comptes Rendus Académie Sci. - Ser. IIC - Chem.* **2001**, *4* (6), 461–470. https://doi.org/10.1016/S1387-1609(01)01248-8.

(160) Schwier, T.; Gevorgyan, V. *Trans*- and *Cis*- Selective Lewis Acid Catalyzed Hydrogermylation of Alkynes. *Org. Lett.* **2005**, *7* (23), 5191–5194. https://doi.org/10.1021/ol0521026.

(161) Fischer, A. K.; West, R. C.; Rochow, E. G. The Addition Reaction between Trichlorogermane and an Olefin. *J. Am. Chem. Soc.* **1954**, *76* (22), 5878–5878. https://doi.org/10.1021/ja01651a102.

(162) Spivey, A. C.; Gripton, C. J. G.; Hannah, J. P.; Tseng, C.-C.; de Fraine, P.; Parr, N. J.; Scicinski, J. J. The Development of a ‘Safety-Catch’ Arylgermane for Biaryl Synthesis by Palladium-Catalysed Germyl-Stille Cross-Coupling. *Appl. Organomet. Chem.* **2007**, *21* (7), 572–589. https://doi.org/10.1002/aoc.1270.

(163) Pitteloud, J.-P.; Zhang, Z.-T.; Liang, Y.; Cabrera, L.; Wnuk, S. F. Fluoride-Promoted Cross-Coupling of Chloro(Mono-, Di-, or Triphenyl)Germanes with Aryl Halides in “Moist” Toluene. Multiple Transfer of the Phenyl Group from Organogermane Substrates and Comparison of the Coupling Efficiencies of Chloro(Phenyl)Germanes with Their Corresponding Stannane and Silane Counterparts. *J. Org. Chem.* **2010**, *75* (23), 8199–8212. https://doi.org/10.1021/jo101848f.

(164) Fricke, C.; Schoenebeck, F. Organogermanes as Orthogonal Coupling Partners in Synthesis and Catalysis. *Acc. Chem. Res.* **2020**, *53* (11), 2715–2725. https://doi.org/10.1021/acs.accounts.0c00527.

(165) Dahiya, A.; Fricke, C.; Schoenebeck, F. Gold-Catalyzed Chemoselective Couplings of Polyfluoroarenes with Aryl Germanes and Downstream Diversification. *J. Am. Chem. Soc.* **2020**, *142* (17), 7754–7759. https://doi.org/10.1021/jacs.0c02860.

(166) Evans, D. A.; Fu, G. C.; Hoveyda, A. H. Rhodium(I)- and Iridium(I)-Catalyzed Hydroboration Reactions: Scope and Synthetic Applications. *J. Am. Chem. Soc.* **1992**, *114* (17), 6671–6679. https://doi.org/10.1021/ja00043a009.

(167) Yamamoto, Y.; Fujikawa, R.; Yamada, A.; Miyaura, N. A Regio- and Stereoselective Platinum(0)-Catalyzed Hydroboration of Allenes Controlled by Phosphine Ligands. *Chem. Lett.* **1999**, *28* (10), 1069–1070. https://doi.org/10.1246/cl.1999.1069.

(168) Ohmura, T.; Yamamoto, Y.; Miyaura, N. Rhodium- or Iridium-Catalyzed *Trans* -Hydroboration of Terminal Alkynes, Giving (*Z*)-1-Alkenylboron Compounds. *J. Am. Chem. Soc.* **2000**, *122* (20), 4990–4991. https://doi.org/10.1021/ja0002823.

(169) Gunanathan, C.; Hölscher, M.; Pan, F.; Leitner, W. Ruthenium Catalyzed Hydroboration of Terminal Alkynes to *Z* -Vinylboronates. *J. Am. Chem. Soc.* **2012**, *134* (35), 14349–14352. https://doi.org/10.1021/ja307233p.

(170) Stachowiak, H.; Kaźmierczak, J.; Kuciński, K.; Hreczycho, G. Catalyst-Free and Solvent-Free Hydroboration of Aldehydes. *Green Chem.* **2018**, *20* (8), 1738–1742. https://doi.org/10.1039/C8GC00042E.

(171) Wang, W.; Luo, M.; Yao, W.; Ma, M.; Pullarkat, S. A.; Xu, L.; Leung, P.-H. Catalyst-Free and Solvent-Free Hydroboration of Ketones. *New J. Chem.* **2019**, *43* (27), 10744–10749. https://doi.org/10.1039/C9NJ02722J.

(172) Harinath, A.; Bhattacharjee, J.; Panda, T. K. Facile Reduction of Carboxylic Acids to Primary Alcohols under Catalyst-Free and Solvent-Free Conditions.

Chem. Commun. **2019**, *55* (10), 1386–1389. https://doi.org/10.1039/C8CC08841A.

(173) Pandey, V. K.; Donthireddy, S. N. R.; Rit, A. Catalyst-Free and Solvent-Free Facile Hydroboration of Imines. *Chem. – Asian J.* **2019**, *14* (19), 3255–3258. https://doi.org/10.1002/asia.201901016.

(174) Xu, X.; Yan, D.; Zhu, Z.; Kang, Z.; Yao, Y.; Shen, Q.; Xue, M. Catalyst-Free Approach for Hydroboration of Carboxylic Acids under Mild Conditions. *ACS Omega* **2019**, *4* (4), 6775–6783. https://doi.org/10.1021/acsomega.9b00406.

(175) Jaladi, A. K.; Choi, H. S.; An, D. K. Catalyst-Free and Solvent-Free Hydroboration of Alkynes. *New J. Chem.* **2020**, *44* (32), 13626–13632. https://doi.org/10.1039/D0NJ02612C.

(176) Brown, H. C.; Rao, B. C. S. A New Technique for the Conversion of Olefins into Organoboranes and Related Alcohols. *J. Am. Chem. Soc.* **1956**, *78* (21), 5694–5695. https://doi.org/10.1021/ja01602a063.

(177) Chakraborty, S.; Bhattacharya, P.; Dai, H.; Guan, H. Nickel and Iron Pincer Complexes as Catalysts for the Reduction of Carbonyl Compounds. *Acc. Chem. Res.* **2015**, *48* (7), 1995–2003. https://doi.org/10.1021/acs.accounts.5b00055.

(178) Kuciński, K.; Hreczycho, G. Hydrosilylation and Hydroboration in a Sustainable Manner: From Earth-Abundant Catalysts to Catalyst-Free Solutions. *Green Chem.* **2020**, *22* (16), 5210–5224. https://doi.org/10.1039/D0GC01430C.

(179) Magre, M.; Szewczyk, M.; Rueping, M. S-Block Metal Catalysts for the Hydroboration of Unsaturated Bonds. *Chem. Rev.* **2022**, *122* (9), 8261–8312. https://doi.org/10.1021/acs.chemrev.1c00641.

(180) Das, A.; Panda, T. K. Metal-Free Catalytic Hydroboration of Unsaturated Compounds: A Greener Strategy for the Synthesis of Organoboranes. *ChemCatChem* **2023**, *15* (2). https://doi.org/10.1002/cctc.202201011.

(181) Chalk, A. J.; Harrod, J. F. Homogeneous Catalysis. II. The Mechanism of the Hydrosilation of Olefins Catalyzed by Group VIII Metal Complexes. *J. Am. Chem. Soc.* **1965**, *87* (1), 16–21. https://doi.org/10.1021/ja01079a004.

(182) Reichel, C. L.; Wrighton, M. S. Photochemistry of Cobalt Carbonyl Complexes Having a Cobalt-Silicon Bond and Its Importance in Activation of Catalysis. *Inorg. Chem.* **1980**, *19* (12), 3858–3860. https://doi.org/10.1021/ic50214a058.

(183) Randolph, C. L.; Wrighton, M. S. Photochemical Reactions of (η^5-Pentamethylcyclopentadienyl)Dicarbonyliron Alkyl and Silyl Complexes: Reversible Ethylene Insertion into an Iron-Silicon Bond and Implications for the Mechanism of Transition-Metal-Catalyzed Hydrosilation of Alkenes. *J. Am. Chem. Soc.* **1986**, *108* (12), 3366–3374. https://doi.org/10.1021/ja00272a035.

(184) Seitz, F.; Wrighton, M. S. Photochemical Reaction of $[(CO)_4Co(SiEt_3)]$ with Ethylene: Implications for Cobaltcarbonyl-Catalyzed Hydrosilation of Alkenes. *Angew. Chem. Int. Ed. Engl.* **1988**, *27* (2), 289–291. https://doi.org/10.1002/anie.198802891.

(185) Brookhart, M.; Grant, B. E. Mechanism of a Cobalt(III)-Catalyzed Olefin Hydrosilation Reaction: Direct Evidence for a Silyl Migration Pathway. *J. Am. Chem. Soc.* **1993**, *115* (6), 2151–2156. https://doi.org/10.1021/ja00059a008.

(186) Perrin, L.; Maron, L.; Eisenstein, O. A DFT Study of SiH_4 Activation by Cp_2LnH. *Inorg. Chem.* **2002**, *41* (17), 4355–4362. https://doi.org/10.1021/ic011275y.

(187) Perrin, L.; Maron, L.; Eisenstein, O.; Tilley, T. D. Bond Activations of $PhSiH_3$by Cp_2SmH: A Mechanistic Investigation by the DFT Method. *Organometallics* **2009**, *28* (13), 3767–3775. https://doi.org/10.1021/om900106n.

(188) Glaser, P. B.; Tilley, T. D. Catalytic Hydrosilylation of Alkenes by a Ruthenium Silylene Complex. Evidence for a New Hydrosilylation Mechanism. *J. Am. Chem. Soc.* **2003**, *125* (45), 13640–13641. https://doi.org/10.1021/ja037620v.

(189) Brunner, H. A New Hydrosilylation Mechanism—New Preparative Opportunities. *Angew. Chem. Int. Ed.* **2004**, *43* (21), 2749–2750. https://doi.org/10.1002/anie.200301742.

(190) Beddie, C.; Hall, M. B. A Theoretical Investigation of Ruthenium-Catalyzed Alkene Hydrosilation: Evidence To Support an Exciting New Mechanistic Proposal. *J. Am. Chem. Soc.* **2004**, *126* (42), 13564–13565. https://doi.org/10.1021/ja046525z.

(191) Fasulo, M. E.; Lipke, M. C.; Tilley, T. D. Structural and Mechanistic Investigation of a Cationic Hydrogen-Substituted Ruthenium Silylene Catalyst for Alkene Hydrosilation. *Chem. Sci.* **2013**, *4* (10), 3882. https://doi.org/10.1039/c3sc51585k.

(192) Rubin, M.; Schwier, T.; Gevorgyan, V. Highly Efficient $B(C_6F_5)_3$-Catalyzed Hydrosilylation of Olefins. *J. Org. Chem.* **2002**, *67* (6), 1936–1940. https://doi.org/10.1021/jo016279z.

(193) Stephan, D. W. The Broadening Reach of Frustrated Lewis Pair Chemistry. *Science* **2016**, *354* (6317), aaf7229. https://doi.org/10.1126/science.aaf7229.

(194) Gribble, M. W.; Pirnot, M. T.; Bandar, J. S.; Liu, R. Y.; Buchwald, S. L. Asymmetric Copper Hydride-Catalyzed Markovnikov Hydrosilylation of Vinylarenes and Vinyl Heterocycles. *J. Am. Chem. Soc.* **2017**, *139* (6), 2192–2195. https://doi.org/10.1021/jacs.6b13029.

(195) Barros, N.; Eisenstein, O.; Maron, L. Catalytic Hydrosilylation of Olefins with Organolanthanides: A DFT Study. Part I: Hydrosilylation of Propene by SiH_4. *Dalton Trans.* **2010**, *39* (44), 10749. https://doi.org/10.1039/c0dt00329h.

(196) Ojima, I.; Nihonyanagi, M.; Kogure, T.; Kumagai, M.; Horiuchi, S.; Nakatsugawa, K.; Nagai, Y. Reduction of Carbonyl Compounds via Hydrosilylation. *J. Organomet. Chem.* **1975**, *94* (3), 449–461. https://doi.org/10.1016/S0022-328X(00)86954-5.

(197) Zheng, G. Z.; Chan, T. H. Regiocontrolled Hydrosilation of α,β-Unsaturated Carbonyl Compounds Catalyzed by Hydridotetrakis(Triphenylphosphine)Rhodium(I). *Organometallics* **1995**, *14* (1), 70–79. https://doi.org/10.1021/om00001a015.

(198) Dioumaev, V. K.; Bullock, R. M. A Recyclable Catalyst That Precipitates at the End of the Reaction. *Nature* **2003**, *424* (6948), 530–532. https://doi.org/10.1038/nature01856.

(199) Gade, L. H.; César, V.; Bellemin-Laponnaz, S. A Modular Assembly of Chiral Oxazolinylcarbene–Rhodium Complexes: Efficient Phosphane-Free Catalysts for the Asymmetric Hydrosilylation of Dialkyl Ketones. *Angew. Chem. Int. Ed.* **2004**, *43* (8), 1014–1017. https://doi.org/10.1002/anie.200353133.

(200) Schneider, N.; Finger, M.; Haferkemper, C.; Bellemin-Laponnaz, S.; Hofmann, P.; Gade, L. H. Metal Silylenes Generated by Double Silicon-Hydrogen Activation: Key Intermediates in the Rhodium-Catalyzed Hydrosilylation of Ketones. *Angew. Chem. Int. Ed.* **2009**, *48* (9), 1609–1613. https://doi.org/10.1002/anie.200804993.

(201) Gutsulyak, D. V.; Vyboishchikov, S. F.; Nikonov, G. I. Cationic Silane σ-Complexes of Ruthenium with Relevance to Catalysis. *J. Am. Chem. Soc.* **2010**, *132* (17), 5950–5951. https://doi.org/10.1021/ja101583m.

(202) Fuchs, J.; Klare, H. F. T.; Oestreich, M. Two-Silicon Cycle for Carbonyl Hydrosilylation with Nikonov's Cationic Ruthenium(II) Catalyst. *ACS Catal.* **2017**, *7* (12), 8338–8342. https://doi.org/10.1021/acscatal.7b03336.

(203) Ning, X.; Wang, J.; Wei, H. New Insights into Mechanism of Molybdenum(VI)–Dioxo Complex Catalyzed Hydrosilylation of Carbonyls: An Alternative Model for Activating Si–H Bond. *J. Phys. Chem. A* **2016**, *120* (24), 4167–4178. https://doi.org/10.1021/acs.jpca.6b01978.

(204) Park, S.; Brookhart, M. Hydrosilylation of Carbonyl-Containing Substrates Catalyzed by an Electrophilic η^1-Silane Iridium(III) Complex. *Organometallics* **2010**, *29* (22), 6057–6064. https://doi.org/10.1021/om100818y.

(205) Wang, J.; Huang, L.; Yang, X.; Wei, H. Mechanistic Investigation Into Catalytic Hydrosilylation with a High-Valent Ruthenium(VI)–Nitrido Complex: A DFT Study. *Organometallics* **2015**, *34* (1), 212–220. https://doi.org/10.1021/om501071n.

(206) Parks, D. J.; Piers, W. E. Tris(Pentafluorophenyl)Boron-Catalyzed Hydrosilation of Aromatic Aldehydes, Ketones, and Esters. *J. Am. Chem. Soc.* **1996**, *118* (39), 9440–9441. https://doi.org/10.1021/ja961536g.

(207) Parks, D. J.; Blackwell, J. M.; Piers, W. E. Studies on the Mechanism of $B(C_6F_5)_3$-Catalyzed Hydrosilation of Carbonyl Functions. *J. Org. Chem.* **2000**, *65* (10), 3090–3098. https://doi.org/10.1021/jo991828a.

(208) Rendler, S.; Oestreich, M. Conclusive Evidence for an S_N2-Si Mechanism in the $B(C_6F_5)_3$-Catalyzed Hydrosilylation of Carbonyl Compounds: Implications for the Related Hydrogenation. *Angew. Chem. Int. Ed.* **2008**, *47* (32), 5997–6000. https://doi.org/10.1002/anie.200801675.

(209) Nolin, K. A.; Krumper, J. R.; Pluth, M. D.; Bergman, R. G.; Toste, F. D. Analysis of an Unprecedented Mechanism for the Catalytic Hydrosilylation of Carbonyl Compounds. *J. Am. Chem. Soc.* **2007**, *129* (47), 14684–14696. https://doi.org/10.1021/ja074477n.

(210) Chung, L. W.; Lee, H. G.; Lin, Z.; Wu, Y.-D. Computational Study on the Reaction Mechanism of Hydrosilylation of Carbonyls Catalyzed by High-Valent Rhenium(V)−Di-Oxo Complexes. *J. Org. Chem.* **2006**, *71* (16), 6000–6009. https://doi.org/10.1021/jo060654b.

(211) Bleith, T.; Gade, L. H. Mechanism of the Iron(II)-Catalyzed Hydrosilylation of Ketones: Activation of Iron Carboxylate Precatalysts and Reaction Pathways of the Active Catalyst. *J. Am. Chem. Soc.* **2016**, *138* (14), 4972–4983. https://doi.org/10.1021/jacs.6b02173.

(212) Díez-González, S.; Kaur, H.; Zinn, F. K.; Stevens, E. D.; Nolan, S. P. A Simple and Efficient Copper-Catalyzed Procedure for the Hydrosilylation of Hindered and Functionalized Ketones. *J. Org. Chem.* **2005**, *70* (12), 4784–4796. https://doi.org/10.1021/jo050397v.

(213) Díez-González, S.; Stevens, E. D.; Scott, N. M.; Petersen, J. L.; Nolan, S. P. Synthesis and Characterization of [Cu(NHC)$_2$]X Complexes: Catalytic and Mechanistic Studies of Hydrosilylation Reactions. *Chem. - Eur. J.* **2008**, *14* (1), 158–168. https://doi.org/10.1002/chem.200701013.

(214) Vergote, T.; Nahra, F.; Merschaert, A.; Riant, O.; Peeters, D.; Leyssens, T. Mechanistic Insight into the (NHC)Copper(I)-Catalyzed Hydrosilylation of Ketones. *Organometallics* **2014**, *33* (8), 1953–1963. https://doi.org/10.1021/om401097q.

(215) Tran, B. L.; Pink, M.; Mindiola, D. J. Catalytic Hydrosilylation of the Carbonyl Functionality via a Transient Nickel Hydride Complex. *Organometallics* **2009**, *28* (7), 2234–2243. https://doi.org/10.1021/om801160j.

(216) Piers, E.; Lemieux, R. Platinum-Catalysed Addition of Trimethylgermane to 1-Trimethylsilylalk-1-Ynes: A Convenient Synthesis of Functionalised 2-Trimethylgermylalk-1-Enes. *J. Chem. Soc. Perkin 1* **1995**, No. 1, 3. https://doi.org/10.1039/p19950000003.

(217) Lakhtin, V. G.; Knyazev, S. P.; Pavlov, K. V.; Gusel’nikov, L. E.; Buravtseva, E. N.; Kuyantseva, N. A.; Parshkova, L. A.; Mid’ko, A. A.; Bykovchenko, V. G.; Kisin, A. V.; Chernyshev, E. A. Hydrogermylation of Silyl-Substituted Ethylenes with Trimethylgermane and Trichlorogermane Etherate. *Russ. J. Gen. Chem.* **2008**, *78* (5), 898–902. https://doi.org/10.1134/S1070363208050101.

(218) Ahrens, T.; Teltewskoi, M.; Ahrens, M.; Braun, T.; Laubenstein, R. Competing Reaction Pathways of 3,3,3-Trifluoropropene at Rhodium Hydrido, Silyl and Germyl Complexes: C–F Bond Activation versus Hydrogermylation. *Dalton Trans.* **2016**, *45* (43), 17495–17507. https://doi.org/10.1039/C6DT03027K.

(219) Marciniec, B.; Ławicka, H.; Majchrzak, M.; Kubicki, M.; Kownacki, I. Synthesis of Functionalized Vinylgermanes through a New Ruthenium-Catalyzed Coupling Reaction. *Chem. - Eur. J.* **2006**, *12* (1), 244–250. https://doi.org/10.1002/chem.200500670.

(220) Wolfsberger, W. Hydrogermylierungsreaktionen. *J. Für Prakt. ChemieChemiker-Ztg.* **1992**, *334* (6), 453–464. https://doi.org/10.1002/prac.19923340602.

(221) Biermann, U.; Klaassen, G.; Koch, R.; Metzger, J. O. Alkene Assisted Homolysis of the Si-H, Ge-H, and Sn-H Bond: New Examples of Molecule Assisted Homolysis (MAH): Alkene Assisted Homolysis of the Si-H, Ge-H, and Sn-H Bond: New Examples of Molecule Assisted Homolysis (MAH). *Eur. J. Org. Chem.* **2019**, *2019* (22), 3599–3604. https://doi.org/10.1002/ejoc.201900363.

(222) El Kadib, A.; Feddouli, A.; Rivière, P.; Delpech, F.; Rivière-Baudet, M.; Castel, A.; Ahra, M.; Hasnaoui, A.; Burgos, F.; Manriquez, J. M.; Chavez, I. Radical Hydrometalation of Functional Ethylenic Compounds: Radical Autoinhibition Changes the Regioselectivity. *Organometallics* **2005**, *24* (3), 446–454. https://doi.org/10.1021/om049525g.

(223) Zhang, J.; Lu, B.; Meng, L.; Li, X. Theoretical Investigations on Reactivity Influencing Factors of $^{\cdot}$Mn(CO)$_5$ Catalyzed Alkyne Hydrosilylation and Hydrogermylation. *New J. Chem.* **2023**, *47* (5), 2436–2443. https://doi.org/10.1039/D2NJ05342J.

(224) Yorimitsu, H.; Oshima, K. Recent Advances in the Use of Tri(2-Furyl)Germane, Triphenylgermane and Their Derivatives in Organic Synthesis. *Inorg. Chem. Commun.* **2005**, *8* (1), 131–142. https://doi.org/10.1016/j.inoche.2004.11.017.

(225) Summerscales, O. T.; Caputo, C. A.; Knapp, C. E.; Fettinger, J. C.; Power, P. P. The Role of Group 14 Element Hydrides in the Activation of C–H Bonds in Cyclic Olefins. *J. Am. Chem. Soc.* **2012**, *134* (35), 14595–14603. https://doi.org/10.1021/ja305853d.

(226) Jambor, R.; Lyčka, A. Organosilicon and -germanium Hydrides in Catalyst-Free Hydrometallation Reactions. *Eur. J. Inorg. Chem.* **2017**, *2017* (42), 4887–4898. https://doi.org/10.1002/ejic.201700630.

(227) Jana, A.; Ghoshal, D.; Roesky, H. W.; Objartel, I.; Schwab, G.; Stalke, D. A Germanium(II) Hydride as an Effective Reagent for Hydrogermylation Reactions. *J. Am. Chem. Soc.* **2009**, *131* (3), 1288–1293. https://doi.org/10.1021/ja808656t.

(228) Zhao, L.; Hermann, M.; Jones, C.; Frenking, G. Reaction Mechanism of the Hydrogermylation/Hydrostannylation of Unactivated Alkenes with Two-Coordinate E^{II} Hydrides (E=Ge, Sn): A Theoretical Study. *Chem. – Eur. J.* **2016**, *22* (33), 11728–11735. https://doi.org/10.1002/chem.201600666.

(229) Musaev, D. G.; Mebel, A. M.; Morokuma, K. An Ab Initio Molecular Orbital Study of the Mechanism of the Rhodium(I)-Catalyzed Olefin Hydroboration Reaction. *J. Am. Chem. Soc.* **1994**, *116* (23), 10693–10702. https://doi.org/10.1021/ja00102a039.

(230) Harrison, K. N.; Marks, T. J. Organolanthanide-Catalyzed Hydroboration of Olefins. *J. Am. Chem. Soc.* **1992**, *114* (23), 9220–9221. https://doi.org/10.1021/ja00049a083.

(231) Tamang, S. R.; Findlater, M. Iron Catalyzed Hydroboration of Aldehydes and Ketones. *J. Org. Chem.* **2017**, *82* (23), 12857–12862. https://doi.org/10.1021/acs.joc.7b02020.

(232) Braunschweig, H. Transition Metal Complexes of Boron. *Angew. Chem. Int. Ed.* **1998**, *37* (13–14), 1786–1801. https://doi.org/10.1002/(SICI)1521-3773(19980803)37:13/14<1786::AID-ANIE1786>3.0.CO;2-C.

(233) Zhang, L.; Peng, D.; Leng, X.; Huang, Z. Iron-Catalyzed, Atom-Economical, Chemo- and Regioselective Alkene Hydroboration with Pinacolborane. *Angew. Chem. Int. Ed.* **2013**, *52* (13), 3676–3680. https://doi.org/10.1002/anie.201210347.

(234) Burgess, K.; Van der Donk, W. A.; Westcott, S. A.; Marder, T. B.; Baker, R. T.; Calabrese, J. C. Reactions of Catecholborane with Wilkinson’s Catalyst: Implications for Transition Metal-Catalyzed Hydroborations of Alkenes. *J. Am. Chem. Soc.* **1992**, *114* (24), 9350–9359. https://doi.org/10.1021/ja00050a015.

(235) Hayashi, T.; Matsumoto, Y.; lto, Y. Asymmetric Hydroboration of Styrenes Catalyzed by Cationic Chiral Phosphine-Rhodium(I) Complexes. *Tetrahedron Asymmetry* **1991**, *2* (7), 601–612. https://doi.org/10.1016/S0957-4166(00)86112-1.

(236) Obligacion, J. V.; Chirik, P. J. Bis(Imino)Pyridine Cobalt-Catalyzed Alkene Isomerization–Hydroboration: A Strategy for Remote Hydrofunctionalization with Terminal Selectivity. *J. Am. Chem. Soc.* **2013**, *135* (51), 19107–19110. https://doi.org/10.1021/ja4108148.

(237) Chen, X.; Cheng, Z.; Lu, Z. Cobalt-Catalyzed Asymmetric Markovnikov Hydroboration of Styrenes. *ACS Catal.* **2019**, *9* (5), 4025–4029. https://doi.org/10.1021/acscatal.8b05135.

(238) Carroll, A.-M.; O'Sullivan, T.; Guiry, P. The Development of Enantioselective Rhodium-Catalysed Hydroboration of Olefins. *Adv. Synth. Catal.* **2005**, *347* (5), 609–631. https://doi.org/10.1002/adsc.200404232.

(239) Yang, Z.; Zhong, M.; Ma, X.; De, S.; Anusha, C.; Parameswaran, P.; Roesky, H. W. An Aluminum Hydride That Functions like a Transition-Metal Catalyst. *Angew. Chem. Int. Ed.* **2015**, *54* (35), 10225–10229. https://doi.org/10.1002/anie.201503304.

(240) Brown, H.; Rao, B. C. Communications - Selective Conversion of Olefins into Organoboranes Through Competitive Hydroboration, Isomerization and Displacement Reactions. *J. Org. Chem.* **1957**, *22* (9), 1137–1138. https://doi.org/10.1021/jo01360a626.

(241) Glowacki, D. R.; Liang, C. H.; Marsden, S. P.; Harvey, J. N.; Pilling, M. J. Alkene Hydroboration: Hot Intermediates That React While They Are Cooling. *J. Am. Chem. Soc.* **2010**, *132* (39), 13621–13623. https://doi.org/10.1021/ja105100f.

(242) Brown, H. C.; Wang, K. K.; Chandrasekharan, J. Hydroboration Kinetics. 7. Kinetics and Mechanism of the Reduction of Aldehydes and Ketones with 9-Borabicyclo[3.3.1]Nonane Dimer. *J. Am. Chem. Soc.* **1983**, *105* (8), 2340–2343. https://doi.org/10.1021/ja00346a038.

(243) Nagase, S.; Ray, N. K.; Morokuma, K. Reaction Mechanism of Hydroboration. Ab Initio MO Study on the C_2H_4 + BH_3 Reaction. *J. Am. Chem. Soc.* **1980**, *102* (13), 4536–4537. https://doi.org/10.1021/ja00533a048.

(244) Streitwieser, A.; Verbit, L.; Bittman, R. Stereochemistry of the Primary Carbon. XVI. Optically Active 1-Butanol-1-*d* by Hydroboration. *J. Org. Chem.* **1967**, *32* (5), 1530–1532. https://doi.org/10.1021/jo01280a050.

(245) Jones, P. R. Symmetry Considerations and the Mechanism of the Hydroboration Reaction. Nature of π-Complexes. *J. Org. Chem.* **1972**, *37* (12), 1886–1889. https://doi.org/10.1021/jo00977a007.

(246) Brown, H. C.; Chandrasekharan, J.; Wang, K. K. Hydroboration-Kinetics and Mechanism. *Pure Appl. Chem.* **1983**, *55* (9), 1387–1414. https://doi.org/10.1351/pac198355091387.

(247) Vishwakarma, L. C.; Fry, A. Relative Rates and Regioselectivity in the Hydroboration of Substituted Styrenes with 9-Borabicyclo[3.3.1]Nonane in Tetrahydrofuran. *J. Org. Chem.* **1980**, *45* (26), 5306–5308. https://doi.org/10.1021/jo01314a017.

(248) Wang, K. K.; Brown, H. C. Hydroboration Kinetics. 2. Improved Procedure for Following the Kinetics for the Reaction of Alkenes with 9-Borabicyclo[3,3,1]Nonane. Further Evidence for the Dissociation Mechanism. *J. Org. Chem.* **1980**, *45* (26), 5303–5306. https://doi.org/10.1021/jo01314a016.

(249) Brown, H. C.; Chandrasekharan, J. Mechanism of Hydroboration of Alkenes with Borane-Lewis Base Complexes. Evidence That the Mechanism of the Hydroboration Reaction Proceeds through a Prior Dissociation of Such Complexes. *J. Am. Chem. Soc.* **1984**, *106* (6), 1863–1865. https://doi.org/10.1021/ja00318a066.

(250) Heiden, Z. M.; Lathem, A. P. Establishing the Hydride Donor Abilities of Main Group Hydrides. *Organometallics* **2015**, *34* (10), 1818–1827. https://doi.org/10.1021/om5011512.

(251) Query, I. P.; Squier, P. A.; Larson, E. M.; Isley, N. A.; Clark, T. B. Alkoxide-Catalyzed Reduction of Ketones with Pinacolborane. *J. Org. Chem.* **2011**, *76* (15), 6452–6456. https://doi.org/10.1021/jo201142g.

(252) Zhu, Z.; Wu, X.; Xu, X.; Wu, Z.; Xue, M.; Yao, Y.; Shen, Q.; Bao, X. *N*-Butyllithium Catalyzed Selective Hydroboration of Aldehydes and Ketones. *J. Org. Chem.* **2018**, *83* (17), 10677–10683. https://doi.org/10.1021/acs.joc.8b01495.

(253) Wu, Y.; Shan, C.; Ying, J.; Su, J.; Zhu, J.; Liu, L. L.; Zhao, Y. Catalytic Hydroboration of Aldehydes, Ketones, Alkynes and Alkenes Initiated by NaOH. *Green Chem.* **2017**, *19* (17), 4169–4175. https://doi.org/10.1039/C7GC01632H.

(254) Vasilenko, V.; Blasius, C. K.; Wadepohl, H.; Gade, L. H. Mechanism-Based Enantiodivergence in Manganese Reduction Catalysis: A Chiral Pincer Complex for the Highly Enantioselective Hydroboration of Ketones. *Angew. Chem. Int. Ed.* **2017**, *56* (29), 8393–8397. https://doi.org/10.1002/anie.201704184.

(255) Vijjamarri, S.; O'Denius, T. M.; Yao, B.; Kubátová, A.; Du, G. Highly Selective Hydroboration of Carbonyls by a Manganese Catalyst: Insight into the Reaction Mechanism. *Organometallics* **2020**, *39* (18), 3375–3383. https://doi.org/10.1021/acs.organomet.0c00448.

(256) Harder, S.; Spielmann, J. Calcium-Mediated Hydroboration of Alkenes: "Trojan Horse" or "True" Catalysis? *J. Organomet. Chem.* **2012**, *698*, 7–14. https://doi.org/10.1016/j.jorganchem.2011.09.025.

(257) Burgess, K.; Jaspars, M. Hydroboration Reactions Mediated by Bis(Mesityl)Niobium: Beware of the Trojan Horse. *Tetrahedron Lett.* **1993**, *34* (43), 6813–6816. https://doi.org/10.1016/S0040-4039(00)91802-1.

(258) Bage, A. D.; Nicholson, K.; Hunt, T. A.; Langer, T.; Thomas, S. P. The Hidden Role of Boranes and Borohydrides in Hydroboration Catalysis. *ACS Catal.* **2020**, *10* (22), 13479–13486. https://doi.org/10.1021/acscatal.0c04051.

(259) Marciniec, B. Catalysis by Transition Metal Complexes of Alkene Silylation–Recent Progress and Mechanistic Implications. *Coord. Chem. Rev.* **2005**, *249* (21–22), 2374–2390. https://doi.org/10.1016/j.ccr.2005.02.025.

(260) Lipke, M. C.; Liberman-Martin, A. L.; Tilley, T. D. Electrophilic Activation of Silicon-Hydrogen Bonds in Catalytic Hydrosilations. *Angew. Chem. Int. Ed.* **2017**, *56* (9), 2260–2294. https://doi.org/10.1002/anie.201605198.

(261) Iglesias, M.; Fernández-Alvarez, F. J.; Oro, L. A. Non-Classical Hydrosilane Mediated Reductions Promoted by Transition Metal Complexes. *Coord. Chem. Rev.* **2019**, *386*, 240–266. https://doi.org/10.1016/j.ccr.2019.02.003.

(262) Schneider, N.; Finger, M.; Haferkemper, C.; Bellemin-Laponnaz, S.; Hofmann, P.; Gade, L. H. Multiple Reaction Pathways in Rhodium-Catalyzed Hydrosilylations of Ketones. *Chem. - Eur. J.* **2009**, *15* (43), 11515–11529. https://doi.org/10.1002/chem.200901594.

(263) Iglesias, M.; Fernández-Alvarez, F. J.; Oro, L. A. Outer-Sphere Ionic Hydrosilylation Catalysis. *ChemCatChem* **2014**, *6* (9), 2486–2489. https://doi.org/10.1002/cctc.201402355.

(264) Dobbs, A. P.; Chio, F. K. I. 8.25 Hydrometallation Group 4 (Si, Sn, Ge, and Pb). In *Comprehensive Organic Synthesis II*; Elsevier, 2014; pp 964–998. https://doi.org/10.1016/B978-0-08-097742-3.00827-2.

(265) Chen, J.-B.; Whiting, A. Recent Advances in Copper-Catalyzed Asymmetric Hydroboration of Electron-Deficient Alkenes: Methodologies and Mechanism. *Synthesis* **2018**, *50* (19), 3843–3861. https://doi.org/10.1055/s-0037-1609583.

(266) Widauer, C.; Grützmacher, H.; Ziegler, T. Comparative Density Functional Study of Associative and Dissociative Mechanisms in the Rhodium(I)-Catalyzed Olefin Hydroboration Reactions. *Organometallics* **2000**, *19* (11), 2097–2107. https://doi.org/10.1021/om9909946.

(267) Perrin, L.; Carr, K. J. T.; McKay, D.; McMullin, C. L.; Macgregor, S. A.; Eisenstein, O. Modelling and Rationalizing Organometallic Chemistry with Computation: Where Are We? In *Computational Studies in Organometallic Chemistry*; Macgregor, S. A., Eisenstein, O., Eds.; Structure and Bonding; Springer International Publishing: Cham, 2015; Vol. 167, pp 1–37. https://doi.org/10.1007/430_2015_176.

(268) Cheng, G.-J.; Zhang, X.; Chung, L. W.; Xu, L.; Wu, Y.-D. Computational Organic Chemistry: Bridging Theory and Experiment in Establishing the Mechanisms of Chemical Reactions. *J. Am. Chem. Soc.* **2015**, *137* (5), 1706–1725. https://doi.org/10.1021/ja5112749.

(269) Marciniec, B.; Kownacka, A.; Kownacki, I.; Hoffmann, M.; Taylor, R. Hydrosilylation vs. Dehydrogenative Silylation of Styrene Catalysed by Iron(0) Carbonyl Complexes with Multivinylsilicon Ligands – Mechanistic Implications. *J. Organomet. Chem.* **2015**, *791*, 58–65. https://doi.org/10.1016/j.jorganchem.2015.04.051.

(270) MacGregor, S. A.; Eisenstein, O. *Computational Studies in Organometallic Chemistry*; Springer, 2016.

(271) Malacea, R.; Poli, R.; Manoury, E. Asymmetric Hydrosilylation, Transfer Hydrogenation and Hydrogenation of Ketones Catalyzed by Iridium Complexes. *Coord. Chem. Rev.* **2010**, *254* (5–6), 729–752. https://doi.org/10.1016/j.ccr.2009.09.033.

Articles and Supplementary information can be found at the following web addresses:

1. Nowicki, M.; Zaranek, M.; Pawluć, P.; Hoffmann, M. DFT Study of Trialkylborohydride-Catalysed Hydrosilylation of Alkenes – the Mechanism and Its Implications. *Catal. Sci. Technol.* **2020**, *10* (4), 1066–1072. (**Appendix A1**)
   https://doi.org/10.1039/C9CY02261A
2. Nowicki, M.; Zaranek, M.; Grzelak, M.; Pawluć, P.; Hoffmann, M. Mechanism of Silylation of Vinyl Arenes by Hydrodisiloxanes Driven by Stoichiometric Amounts of Sodium Triethylborohydride – a Combined DFT and Experimental Study. *Int. J. Mol. Sci*. **2023**, 24, 4924. (**Appendix A2**)
   https://doi.org/10.3390/ijms24054924
   IF = 6.208, MEiN = 140
3. Zaranek, M.; Nowicki, M.; Andruszak, P.; Hoffmann, M.; Pawluć, P. Hydrogermylation Initiated by Trialkylborohydrides: A Living Anionic Mechanism. *Chem. Commun.* **2022**, *58* (100), 13979–13982. (**Appendix A3**)
   https://doi.org/10.1039/D2CC05567H
4. Nowicki, M.; Kuciński, K.; Hreczycho, G.; Hoffmann, M. Catalytic and Non-Catalytic Hydroboration of Carbonyls: Quantum-Chemical Studies. *Org. Biomol. Chem.* **2021**, *19* (13), 3004–3015. (**Appendix A4**)
   https://doi.org/10.1039/D1OB00037C.

Mgr Mateusz Nowicki
Faculty of Chemistry
Adam Mickiewicz University in Poznań

DECLARATION

I declare, that in the following articles:

(1) Nowicki, M.; Zaranek, M.; Pawluć, P.; Hoffmann, M. DFT Study of Trialkylborohydride-Catalysed Hydrosilylation of Alkenes – the Mechanism and Its Implications. *Catal. Sci. Technol.* **2020**, *10* (4), 1066–1072. https://doi.org/10.1039/C9CY02261A,

(2) Nowicki, M.; Zaranek, M.; Grzelak, M.; Pawluć, P.; Hoffmann, M. Mechanism of Silylation of Vinyl Arenes by Hydrodisiloxanes Driven by Stoichiometric Amounts of Sodium Triethylborohydride – a Combined DFT and Experimental Study. *Int. J. Mol. Sci.* Accepted on 02 March **2023**,

(3) Zaranek, M.; Nowicki, M.; Andruszak, P.; Hoffmann, M.; Pawluć, P. Hydrogermylation Initiated by Trialkylborohydrides: A Living Anionic Mechanism. *Chem. Commun.* **2022**, *58* (100), 13979–13982. https://doi.org/10.1039/D2CC05567H,

(4) Nowicki, M.; Kuciński, K.; Hreczycho, G.; Hoffmann, M. Catalytic and Non-Catalytic Hydroboration of Carbonyls: Quantum-Chemical Studies. *Org. Biomol. Chem.* **2021**, *19* (13), 3004–3015. https://doi.org/10.1039/D1OB00037C,

which are parts of the doctoral dissertation entitled:

Transition metal–free hydroelementation of C=C and C=O bonds with p-block elements – a quantum chemical mechanistic study

my own contribution includes:

(1) – conceptualization,

– methodology,
– formal analysis,
– investigation,
– resources,
– data curation,
– visualization,
– writing – original draft preparation (with M.Z.),

(2) – conceptualization (experimental part),
– methodology (experimental part),
– formal analysis (experimental part),
– investigation (experimental part),
– resources (experimental part),
– data curation (experimental part),
– visualization (experimental part),
– writing – original draft preparation (experimental part),

(3) – conceptualization (experimental part),
– methodology (experimental part),
– formal analysis (experimental part),
– investigation (experimental part),
– resources (experimental part),
– data curation (experimental part),
– visualization (experimental part),
– writing – original draft preparation (experimental part),

(4) – conceptualization,
– methodology,
– formal analysis,
– investigation,
– resources,
– data curation,
– visualization,
– writing – original draft preparation (with K.K.).

………………………………………

mgr Mateusz Nowicki

Dr Maciej Zaranek
Centre for Advanced Technologies
Adam Mickiewicz University in Poznań

DECLARATION

I declare, that in the following articles:

(1) Nowicki, M.; Zaranek, M.; Pawluć, P.; Hoffmann, M. DFT Study of Trialkylborohydride-Catalysed Hydrosilylation of Alkenes – the Mechanism and Its Implications. *Catal. Sci. Technol.* **2020**, *10* (4), 1066–1072. https://doi.org/10.1039/C9CY02261A,

(2) Nowicki, M.; Zaranek, M.; Grzelak, M.; Pawluć, P.; Hoffmann, M. Mechanism of Silylation of Vinyl Arenes by Hydrodisiloxanes Driven by Stoichiometric Amounts of Sodium Triethylborohydride – a Combined DFT and Experimental Study. *Int. J. Mol. Sci.* Accepted on 02 March **2023**

(3) Zaranek, M.; Nowicki, M.; Andruszak, P.; Hoffmann, M.; Pawluć, P. Hydrogermylation Initiated by Trialkylborohydrides: A Living Anionic Mechanism. *Chem. Commun.* **2022**, *58* (100), 13979–13982. https://doi.org/10.1039/D2CC05567H,

which are parts of the doctoral dissertation entitled:

Transition metal–free hydroelementation of C=C and C=O bonds with p-block elements – a quantum chemical mechanistic study

my own contribution includes:

(1) – visualization,
– writing – original draft preparation (with M.N.),

(2) – conceptualization (experimental part),
– methodology (experimental part),
– investigation (experimental part),

– resources (experimental part),
– data curation (experimental part),
– visualization (experimental part),
– writing – original draft preparation (experimental part),

(3) – conceptualization (experimental part),
– methodology (experimental part,
– investigation (experimental part),
– resources (experimental part),
– data curation (experimental part),
– writing – original draft preparation (experimental part).

Maciej Zaranek
dr Maciej Zaranek

Dr Magdalena Grzelak
Centre for Advanced Technologies
Adam Mickiewicz University in Poznań

DECLARATION

I declare, that in the following article:

> Nowicki, M.; Zaranek, M.; Grzelak, M.; Pawluć, P.; Hoffmann, M. Mechanism of Silylation of Vinyl Arenes by Hydrodisiloxanes Driven by Stoichiometric Amounts of Sodium Triethylborohydride – a Combined DFT and Experimental Study. *Int. J. Mol. Sci.* Accepted on 02 March **2023**

which is a part of the doctoral dissertation entitled:

> *Transition metal–free hydroelementation of C=C and C=O bonds with p-block elements – a quantum chemical mechanistic study*

my own contribution includes:

- – investigation (experimental part),
- – writing – review and editing (experimental part).

Magdalena Grzelak
....
dr Magdalena Grzelak

Mgr Piotr Andruszak
Faculty of Chemistry
Adam Mickiewicz University in Poznań

DECLARATION

I declare, that in the following article:

> Zaranek, M.; Nowicki, M.; Andruszak, P.; Hoffmann, M.; Pawluć, P. Hydrogermylation Initiated by Trialkylborohydrides: A Living Anionic Mechanism. *Chem. Commun.* **2022**, *58* (100), 13979–13982. https://doi.org/10.1039/D2CC05567H,

which is a part of the doctoral dissertation entitled:

> *Transition metal–free hydroelementation of C=C and C=O bonds with p-block elements – a quantum chemical mechanistic study*

my own contribution includes:

- investigation (experimental part),
- data curation (experimental part).

Andruszak
....
mgr Piotr Andruszak

Dr Krzysztof Kuciński
Faculty of Chemistry
Adam Mickiewicz University in Poznań

DECLARATION

I declare, that in the following article:

> Nowicki, M.; Kuciński, K.; Hreczycho, G.; Hoffmann, M. Catalytic and Non-Catalytic Hydroboration of Carbonyls: Quantum-Chemical Studies. *Org. Biomol. Chem.* **2021**, *19* (13), 3004–3015. https://doi.org/10.1039/D1OB00037C,

which is a part of the doctoral dissertation entitled:

> *Transition metal–free hydroelementation of C=C and C=O bonds with p-block elements – a quantum chemical mechanistic study*

my own contribution includes:

- – visualization,
- – writing – original draft preparation (with M.N.).

....

dr Krzysztof Kuciński

Prof. dr hab. Grzegorz Hreczycho
Faculty of Chemistry
Adam Mickiewicz University in Poznań

DECLARATION

I declare, that in the following article:

> Nowicki, M.; Kuciński, K.; Hreczycho, G.; Hoffmann, M. Catalytic and Non-Catalytic Hydroboration of Carbonyls: Quantum-Chemical Studies. *Org. Biomol. Chem.* **2021,** *19* (13), 3004–3015. https://doi.org/10.1039/D1OB00037C,

which is a part of the doctoral dissertation entitled:

> *Transition metal–free hydroelementation of C=C and C=O bonds with p-block elements – a quantum chemical mechanistic study*

my own contribution includes:

- – writing – review and editing,
- – funding acquisition,
- – supervision.

....
prof. dr hab. Grzegorz Hreczycho

Prof. dr hab. Piotr Pawluć
Faculty of Chemistry
Adam Mickiewicz University in Poznań

DECLARATION

I declare, that in the following articles:

(1) Nowicki, M.; Zaranek, M.; Pawluć, P.; Hoffmann, M. DFT Study of Trialkylborohydride-Catalysed Hydrosilylation of Alkenes – the Mechanism and Its Implications. *Catal. Sci. Technol.* **2020**, *10* (4), 1066–1072. https://doi.org/10.1039/C9CY02261A,

(2) Nowicki, M.; Zaranek, M.; Grzelak, M.; Pawluć, P.; Hoffmann, M. Mechanism of Silylation of Vinyl Arenes by Hydrodisiloxanes Driven by Stoichiometric Amounts of Sodium Triethylborohydride – a Combined DFT and Experimental Study. *Int. J. Mol. Sci.* Accepted on 02 March **2023**

(3) Zaranek, M.; Nowicki, M.; Andruszak, P.; Hoffmann, M.; Pawluć, P. Hydrogermylation Initiated by Trialkylborohydrides: A Living Anionic Mechanism. *Chem. Commun.* **2022**, *58* (100), 13979–13982. https://doi.org/10.1039/D2CC05567H,

which are parts of the doctoral dissertation entitled:

Transition metal–free hydroelementation of C=C and C=O bonds with p-block elements – a quantum chemical mechanistic study

my own contribution includes:

- – writing – review and editing,
- – funding acquisition,
- – supervision.

prof. dr hab. Piotr Pawluć

3.03.2023r

Prof. dr hab. Marcin Hoffmann
Faculty of Chemistry
Adam Mickiewicz University in Poznań

DECLARATION

I declare, that in the following articles:

(1) Nowicki, M.; Zaranek, M.; Pawluć, P.; Hoffmann, M. DFT Study of Trialkylborohydride-Catalysed Hydrosilylation of Alkenes – the Mechanism and Its Implications. *Catal. Sci. Technol.* **2020**, *10* (4), 1066–1072. https://doi.org/10.1039/C9CY02261A,

(2) Nowicki, M.; Zaranek, M.; Grzelak, M.; Pawluć, P.; Hoffmann, M. Mechanism of Silylation of Vinyl Arenes by Hydrodisiloxanes Driven by Stoichiometric Amounts of Sodium Triethylborohydride – a Combined DFT and Experimental Study. *Int. J. Mol. Sci.* Accepted on 02 March **2023**

(3) Zaranek, M.; Nowicki, M.; Andruszak, P.; Hoffmann, M.; Pawluć, P. Hydrogermylation Initiated by Trialkylborohydrides: A Living Anionic Mechanism. *Chem. Commun.* **2022**, *58* (100), 13979–13982. https://doi.org/10.1039/D2CC05567H,

(4) Nowicki, M.; Kuciński, K.; Hreczycho, G.; Hoffmann, M. Catalytic and Non-Catalytic Hydroboration of Carbonyls: Quantum-Chemical Studies. *Org. Biomol. Chem.* **2021,** *19* (13), 3004–3015. https://doi.org/10.1039/D1OB00037C,

which are parts of the doctoral dissertation entitled:

Transition metal–free hydroelementation of $C=C$ and $C=O$ bonds with p-block elements – a quantum chemical mechanistic study

my own contribution includes:

– writing – review and editing,

– funding acquisition,

– supervision.

Hoffmann

....

prof. dr hab. Marcin Hoffmann