Low-Valent Group 14 Hydride Chemistry: Towards Catalysis

Journal:	*Chemical Society Reviews*
Manuscript ID	CS-SYN-09-2017-000649.R2
Article Type:	Review Article
Date Submitted by the Author:	06-Apr-2018
Complete List of Authors:	Jones, Cameron; Monash University, School of Chemistry Hadlington, Terrance; Metallorganics and Inorganic Materials, Institute of Chemistry Driess, Matthias; Metallorganics and Inorganic Materials, Institute of Chemistry

Low-Valent Group 14 Element Hydride Chemistry: Towards Catalysis

Terrance J. Hadlington,*,† Matthias Driess,† and Cameron Jones*,‡

†Department of Chemistry, Metalorganics and Inorganic Materials, Techniche Universitat Berlin, Strasse des 17. Juni 135, Sekr. C2, 10623 Berlin, Germany

‡School of Chemistry, Monash University, P.O. Box 23, Melbourne, VIC 3800, Australia

Abstract

The chemistry of group 14 element(II) hydride complexes has rapidly expanded since the first stable example of such a compound was reported in 2000. Since that time it has become apparent that these systems display remarkable reactivity patterns, in some cases mimicking those of late transition-metal (TM) hydride compounds. This is especially so for the hydroelementation of unsaturated organic substrates. Recently, this aspect of their reactivity has been extended to the use of group 14 element(II) hydrides as efficient, "TM-like" catalysts in organic synthesis. This review will detail how the chemistry of these hydride compounds has advanced since their early development. Throughout, there is a focus on the importance of ligand effects in these systems, and how ligand design can greatly modify a coordinated complex's electronic structure, reactivity, and catalytic efficiency.

Low-Valent Group 14 Element Hydride Chemistry: Towards Catalysis

Terrance J. Hadlington,*,† Matthias Driess,† and Cameron Jones*,‡

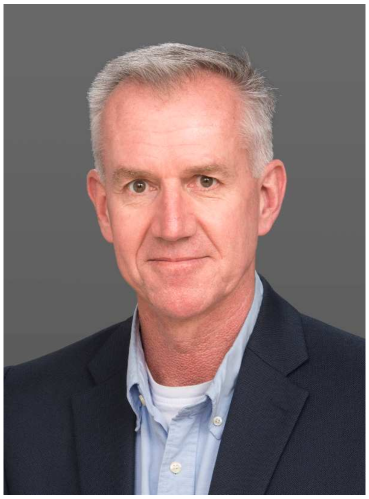
†Department of Chemistry, Metalorganics and Inorganic Materials, Techniche Universitat Berlin, Strasse des 17. Juni 135, Sekr. C2, 10623 Berlin, Germany

‡School of Chemistry, Monash University, P.O. Box 23, Melbourne, VIC 3800, Australia

Author Biographies:

Terrance Hadlington completed his MChem(Hons) at the University of Bath, UK, in 2011. He then attained his PhD from Monash University, Australia, in 2015, working under Professor Cameron Jones, with a short research stay at Oxford University (UK) working with Professor Simon Aldridge. This work led to developments in the stabilisation of low-valent group 14 element complexes, and their reactivity directed towards transition-metal like catalytic transformations. He has been a postdoctoral fellow of the Cluster of Excellence UniCat, TU Berlin (Germany), since May 2016, working with Professor Matthias Driess. His research interests currently lie in the synergistic interplay between transition-metal fragments and low-valent group 14 ligands, low-valent main-group compounds as ligands in catalysis, and main-group element centered catalysis.

Matthias Driess obtained his Ph.D. degree in 1988 and completed his habilitation at the University of Heidelberg (Germany) in 1993. Since 2004, he is full professor of metalorganics and inorganic materials at the Department of Chemistry of the Technische Universität Berlin. He serves as spokesperson of the Cluster of Excellence UniCat, co-director of the UniCat-BASF joint laboratory (BasCat) and director of Chemical Invention Factory (CIF) in the Berlin area. He has received several awards, including the Alfred Stock Memorial Award of the German Chemical Society in 2010 and the Wacker Silicone Award in 2011. He is a member of the German National Academy of Sciences (Leoplodina) and of the Berlin-Brandenburg Academy of Sciences and Humanities. His current research interests include coordination chemistry of main-group elements and transition-metals in unusual coordination and oxidation states and synthesis of functional inorganic materials, for example, heterobimetallic oxide nanoparticles, employing molecular architecture for catalysis.



Cameron Jones obtained his BSc(Hons) degree at the University of Western Australia (1984). His PhD degree (1992) was gained from Griffith University, Brisbane, under the supervision of Professor Colin Raston. He then moved to a postdoctoral fellowship (1992–1994) at Sussex University under the supervision of Professor John Nixon FRS. From 1994 he held a lectureship at The University of Wales, Swansea before moving to a Readership in Inorganic Chemistry at Cardiff University (1998). There, he was promoted to a Personal Chair in 2002. In 2007 he moved to Monash University, Melbourne, where he is currently Professor of Chemistry, in addition to being the Director of the Monash Centre for Catalysis (MonCat). His research interests include the stabilisation of low oxidation state and hydrido s- and p-block metal complexes, and their application to synthesis, small molecule activations and catalysis.

1. Introduction

Our fundamental understanding of the reactive capacity of the main-group (MG) elements has been challenged and significantly developed over recent decades. Only in 1976 was the ‘*Double-Bond Rule*’ disproved,[1] with the publication of the first heavier MG multiple bond described by M. F. Lappert, in $[\{(Me_3Si)_2CH\}_2Sn]_2$.[2] This was soon followed by related low-valent Si^{II} and P^{I} compounds (*viz*. $[\{(Mes)_2Si\}_2]$ and $[\{(Mes^*)_2P\}_2]$; Mes = C_6H_2-Me_3-2,4,6; Mes* = C_6H_2-Bu^t_3-2,4,6) in 1981, both of which are heavier element π-bonded systems.[3] Since that time, synthetic inorganic chemists have achieved numerous breakthroughs in heavier group 14 element chemistry. For example, heavier alkene and alkyne analogues have been described for Si-Pb,[4] in addition to monomeric heavier tetrylenes, [R_2E:] (E = Si-Pb).[5] Their reactivity has been shown to be extremely far removed from that of their E^{IV} analogues. For example, the facile activation of synthetically important small molecules such as dihydrogen,[6] ethylene,[7] and both C^{II} and C^{IV} oxides[8] has been effected by heavier group 14 element compounds in the +1 and +2 oxidation states, bringing this fascinating area of research into the spotlight since the turn of the millennium. This remarkable reactivity has led to direct comparisons between the chemistry of the transition-metals (TMs) and the group 14 elements.[9] This, of course, goes hand-in-hand with the underlying concepts of catalysis: TMs are extremely important for otherwise challenging organic transformations, and rely heavily on oxidative-addition/reductive elimination cycles to achieve this.[10] These key reactions have now been observed at low-valent group 14 centres.[11,12] This comes at a time where combating man-made environmental issues is at the core of research efforts across the globe, with the potential toxicity and high cost of precious *d*-block elements fuelling the search for benign yet efficient catalytic systems. Frustrated Lewis Pairs (FLPs) have proven powerful towards this end, since the first demonstration of their ability to cleave typically unreactive small-molecules.[13] Broadly studied on a more fundamental basis, low-valent E-H complexes (E = group 14 element) have shown great promise, with their hydridic reactivity far more pronounced than classical E^{IV} congeners, allowing for direct hydroelementation of even unactivated alkenes, in some cases reversibly.[14] In 2015, our (the Jones) group extended such systems to catalytic hydroboration reactions,[15] marking the beginning of what we believe will be a fruitful area of MG catalysis into the future. This review aims to discuss progress towards the application of low-valent group 14 element hydride species in hydrofunctionalisation catalysis. This will firstly address the fundamental electronic features of tetrylenes which can lead to extremely reactive hydride complexes and related catalytically significant transformations. This should act as a guide for the synthetic chemist in the design of novel low-valent group 14 complexes which extend the catalytic potential of such species. A discussion of the advances in the literature towards the synthesis and reactivity of hydrido tetrylenes will highlight key points in accessing isolable, yet highly reactive systems of this type, leading to how these factors have allowed for efficient catalysis to be achieved at a low-valent heavier group 14 centre. Throughout, there will be a focus on the importance of ligand effects in these systems, and how ligand design can greatly modify a coordinated complex's electronic structure, reactivity, and dynamic solution processes.

2. Frontier Orbitals for Small-Molecule Activation

The most stable electronic ground-state of the heavier parent tetrylenes (i.e. $[H_2E]$) is the singlet state, whereby E holds a lone-pair of electrons (the HOMO) and a vacant *p*-orbital (the LUMO), as calculated by Trinquier for the parent tetrylenes.[16] The same is typically observed for $[L_2E]$ species, where L is a monoanionic ligand.[5] The stability of the monomeric singlet state increases as group 14 is descended due to the inert pair effect, which in turn reduces the degree of *sp*-mixing at E with increasing quantum number. The important interactions between a singlet tetrylene and small-molecules (e.g. H_2, C_2H_4; Figure 1) can be compared with those for a TM fragment, the mechanisms for the latter being typically very well-established (e.g. the Dewar-Chatt-Duncason model).[17,18] As early as 1977, Lappert *et al.* reported that organic halides, acid anhydrides, and related species can be readily oxidatively cleaved at Ge^{II} and Sn^{II} centres.[19] Ligand modifications have since allowed for tuning of the HOMO-LUMO gap in such systems, leading to the metal-free oxidative activation of benign molecules such as H_2 and CO,[6,7,8] even at low-valent carbon centres.[17]

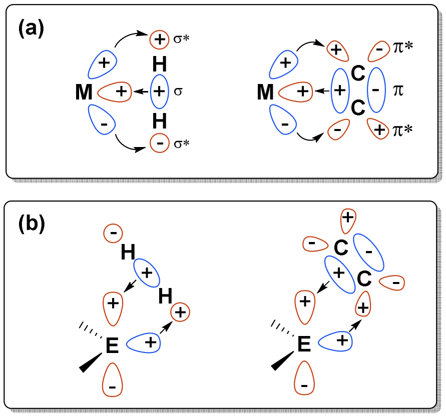


Figure 1. (a) Frontier orbital interactions between a transition metal fragment and dihydrogen (left) and ethylene (right); (b) Frontier orbital interactions between a singlet tetrylene and dihydrogen (left) and ethylene (right). M = transition metal; E = Si-Pb.

Small-molecule activation by tetrylenes, of course, will play a pivotal role in their efficacy as hydrofunctionalisation catalysts. Figure 2 highlights key transitions for the first insertion step (i.e. Step A) and a following turn-over step (i.e. Step B). Step A can occur *via* a two-step process; that is formally a [1+2] cycloaddition reaction of an unsaturated organic bond to a singlet hydrido-tetrylene, followed by hydride migration, generating a new functionalised tetrylene. This chemistry has been directly observed for Si^{II} systems.[14(a)] Jones, Frenking *et al.* have also shown that a contrasting mechanism can be more favourable for the reaction of low-coordinate hydrido-tetrylenes with alkenes, which involves a single [2+2] cycloaddition transition state.[20] In this mechanism, the weakening and polarisation of the C=C bond is instigated through a coordinative interaction, which then allows for hydride transfer to the β-C of the alkene, forming a new alkyl tetrylene. It has been shown experimentally that lower coordinate hydrido tetrylenes are more potent in such reactivity; *pseudo*-two coordinate (amido)(hydrido) tetrylenes (E = Ge, Sn) reported by Frenking, Jones *et al.* immediately react quantitatively with unactivated alkenes at ambient temperature,[14(b)] whilst base-stabilised diketiminato hydrido-tetrylenes reported by Roesky *et al.* react with only activated alkynes.[21] This would indicate that a based-stabilised hydrido-tetrylene complex, which ostensibly lacks a vacant *p*-orbital, is hindered towards activation of less reactive unsaturated substrates. This, then, is the first hint in designing reactive E^{II} hydride systems for challenging catalytic functionalisation processes. Whilst higher coordinate ligand systems stabilise the reactive E-H fragment, subsequent chemistry may be hindered. Expansion towards a broader library of mono-anionic, extremely bulky ligands is of paramount importance for the further development of this aspect of group 14 catalysis.

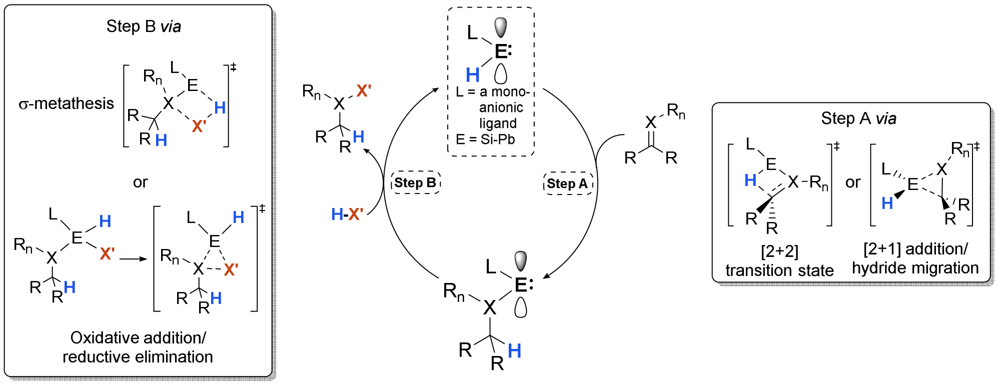
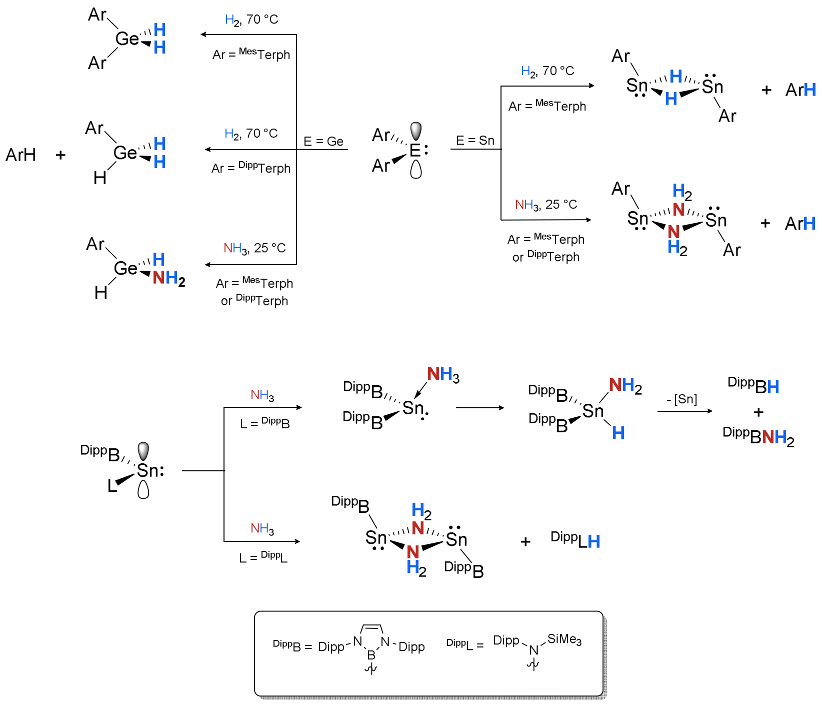


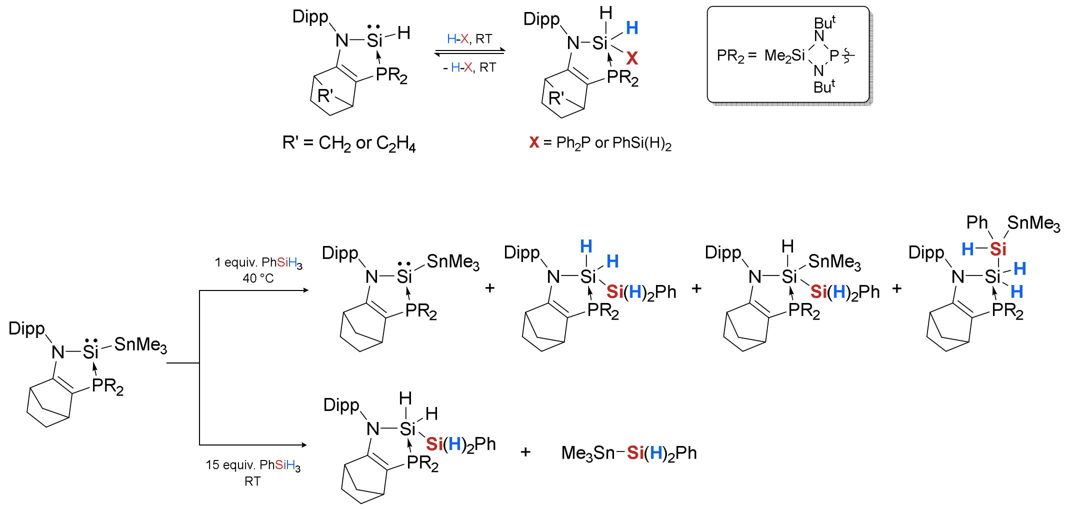
Figure 2. A hypothetical catalytic cycle for the hydrofunctionalisation of unsaturated C=X bonds by a hydrido tetrylene, with key transitions inset. X = C, N, or O; X' = R_3Si, R_2B, or H).

In order to extend such reactivity to hydroelementation catalysis, one must design a system which can subsequently metathesise an X'-H bond (i.e. Step B, Figure 2; X' = R_3Si, R_2B, or H), overall functionalising the unsaturated substrate, and regenerating the active E^{II} hydride catalyst. Two plausible mechanisms can be considered here: direct σ-bond metathesis, or an oxidative addition/reductive elimination pathway; both have been observed for low-valent group 14 systems. Reports from Power *et al*. have shown that bis(aryl) tetrylenes, $[(Ar)_2E]$ (E = Ge, Sn; Ar = ^{Mes}Terph or ^{Dipp}Terph; ^{Mes}Terph = C_6H_3-Mes_2-2,6; ^{Dipp}Terph = C_6H_3-$Dipp_2$-2,6; Dipp = C_6H_3-Pr^i_2-2,6), can react with H_2 in the formation of either Sn^{II} or Ge^{IV} hydride species, possibly through an oxidative addition-reductive elimination process, indicated to some degree by product distributions (Scheme 1).[11] Related work by Aldridge *et al.* has shown similar reactivity of bis(boryl)- and (amido)(boryl)-stannylenes, $[(^{Dipp}B)_2Sn:]$ and $[(^{Dipp}B)(^{Dipp}L)Sn:]$ (^{Dipp}B = $[B\{N(Dipp)C(H)\}_2]$; ^{Dipp}L = $[N(Dipp)(SiMe_3)]$) , towards N-H bonds, where both oxidative addition and reductive elimination products were isolated and fully characterised (Scheme 1).[22]



Scheme 1. *Above:* Reactions of bis(aryl)tetrylenes with dihydrogen or ammonia, leading to oxidative addition or ligand metathesis; *Below:* Reactions of a bis(boryl)stannylene and a (boryl)(amido)stannylene with ammonia, showing stages or oxidative addition and reductive elimination.

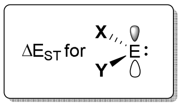
Further exciting results on this theme have been reported by Baceiredo, Kato *et al.*. It was shown that hydrido and stannyl divalent silicon complexes were capable of the reversible oxidative addition of Si^{IV}-H and P^{III}-H bonds at room temperature (Scheme 2).[12] In a remarkable set of experiments, it was found that, where a stannyl silylene was employed in this reactivity, the stannyl group underwent a scrambling process with the hydride of the silane substrate. More simply, a stannyl silylene was converted into a hydrido silylene *via* an oxidative addition/reductive elimination process (Scheme 2). This demonstrates that true precious-metal-type catalysis could be accessible at a low-valent group 14 centre. Key features in these systems are the strong σ-donor properties and the steric encumbrance of the utilised ligand systems, the former of which reduces the HOMO-LUMO gap by destabilisation of the HOMO, and the latter aiding in reductive elimination through destabilisation of the E^{IV} compound on steric grounds. Base-induced reductive elimination can also play a key role here (*vide infra*), which, too, can be an important point in TM catalysis.[23]



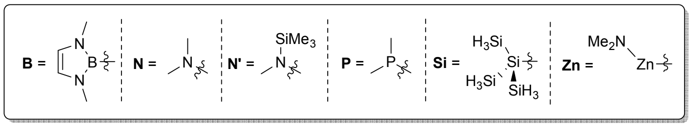
Scheme 2. *Above*: Reversible oxidative addition of a silane or phosphine to a hydrido silylene; *Below*: Ligand scrambling through reversible oxidative addition of phenyl silane to a stannyl silylene.

Three important Density Functional Theory (DFT) investigations have given some insight into the above two points. Aldridge *et al.* investigated the effects of ligand electronics (i.e. σ- and π-donor strength) on the singlet-triplet gap (ΔE_{ST}) of heavier tetrylenes, a value which relates to the potential for oxidative bond scission at a low-valent element centre (i.e. a narrower ΔE_{ST} generally gives rise to a more reactive element centre; Table 1).[22] First of all, the authors found that ΔE_{ST} increased on descending the group, a generally accepted phenomenon based on the inert pair effect. More importantly, strongly σ-donating ligands, such as boryl or silyl substituents, reduce ΔE_{ST} due to destabilisation of the HOMO. Strongly π-donating ligands have the opposite effect, increasing ΔE_{ST} through stabilisation of the LUMO. Related calculations from Frenking, Jones *et al.*, which focused on ligand modifications at Ge^{II}, have shown that small ΔE_{ST} values are attained for the metallated germylene, [(TBoN){(Me$_2$N)Zn}Ge:] (Table 1; TBoN = [N(SiMe$_3$){B(DippNCH)$_2$}]).[6(f)] This was demonstrated experimentally, by the facile cleavage of H_2 by the isolable zincagermylene, [(TBoN){(L*)Zn}Ge:] (L* = N(Ar*)(SiMe$_3$), Ar* = $C_6H_2Me\{C(H)Ph_2\}_2$-4,2,6), which had not been achieved under ambient conditions (i.e. 1 atm H_2, 25 °C) at a Ge^{II} centre previously.

Table 1. Calculated Singlet-Triplet energy separation for singlet two-coordinate tetrylenes.



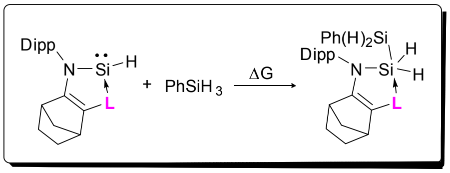
M	X	Y	ΔE_{ST} (kcal/mol)
Sn	**B**	**B**	12.8[a]
Sn	**B**	**N'**	23.5 [a]
Sn	**B**	**P**	14.8 [a]
Sn	**Si**	**Si**	14.5 [a]
Sn	**Si**	**N'**	24.5 [a]
Ge	**B**	**B**	10.5 [a]
Ge	**B**	**N'**	24.2 [a]
Ge	**N**	*H*	40.1 [b]
Ge	**N**	*Cl*	53.7 [b]
Ge	**N**	*Me*	41.3 [b]
Ge	**N**	**N**	47.7 [b]
Ge	**N**	**B**	28.6 [b]
Ge	**N**	**Zn**	24.0 [b]
Si	**B**	**B**	7.8 [a]
Si	**B**	**N'**	21.4[a]

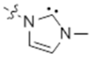
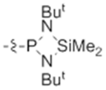
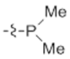
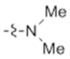
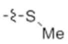


[a] Values taken from ref. 22; [b] Values taken from ref. 6(f).

Baceiredo, Kato *et al.* also reported on DFT investigations into the effects of chelating monoanionic donor ligands on oxidative addition process at a Si^{II} centre.[12] Overall, chelation disfavours oxidative addition to a Si^{II} centre, therefore favouring the reverse process, i.e. reductive elimination from Si^{IV}. The calculated energy of this process can be tweaked by modification of the donor strength of the chelating ligand (Table 2). These two computational studies give a fantastic depth of insight into the design of effective ligands for low-valent group 14 catalytic systems.

Table 2. Calculated Gibbs free energy for the oxidative addition of $PhSiH_3$ to an (amido)(hydrido)silylene



L						
ΔG (kcal/mol)	6.3	-6.5	-11.1	-17.2	-19.3	-28.1

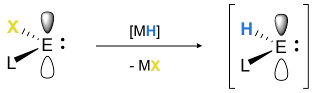
In the Jones group, we have achieved the 'turn-over' step (i.e. Figure 2, Step B) of the catalytic cycle through a σ-metathesis mechanism of a Ge-OR fragment with pinacol borane (HBpin), which is likely favoured due to the polar nature of the bonds involved.[15] Such a mechanism, however, is important in alkaline-earth and lanthanide mediated catalysis,[24] and can allow for the metathesis of unpolarised H-H bonds at a MG metal centre.[25] Taken as a whole, these experimental studies display the importance of ligand design to achieve catalytically relevant reactions at E^{II} centres; *viz.* tuning of ΔE_{ST} at an E^{II} centre through ligand sterics and electronics gives a poignant basis on which to design successful ligand systems for use in low-valent group 14 centred catalysis.

3. Accessing Low-Valent Group 14 Hydride Systems

Numerous methods have been developed to access divalent group 14 hydride complexes, since the first example was reported in 2000.[26] The most common methods for these synthetic transformations will be summarised briefly here.

3.1 Salt-Metathesis

The first example of a divalent group 14 hydride complex was reported only 18 years ago, and was accessed through a salt-metathesis reaction of an (aryl)(chloro)stannylene. Subsequently, numerous Ge^{II} and Sn^{II} hydride complexes have been synthesised using this method. Metathesis reagents used range from DIBAL through to Li[BH_4] and the more selective Li[BBu^sH]. It is worthy of note that in some cases irreversible BH_3 coordination was observed, and so the use of M[BH_4] (M = Li-K) salts should be avoided.

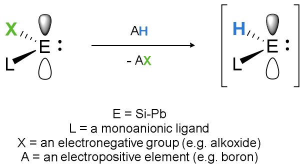


E = Si-Pb
L = a monoanionic ligand
X = a halide
M = a metal

Scheme 3. General scheme for a salt-metathesis route to a hydrido tetrylene.

3.2 σ-Metathesis

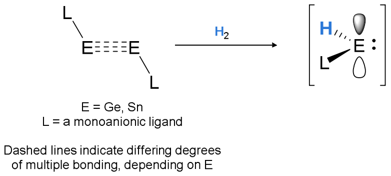
The σ-metathesis reaction is favourable due to its mild nature, allowing for potentially rapid yet selective generation of desired hydride complexes. Indeed, such a method was employed in order to access the first and only example of a Pb^{II} hydride species. Such reactivity is also important in a catalytic context, as discussed within this review.



Scheme 4. General scheme for a σ-metathesis route to a hydrido tetrylene.

3.3 Oxidative Routes

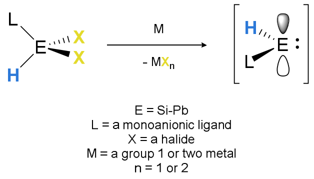
Since 2000, numerous examples of heavier alkyne analogues (i.e. tetrylynes) have been isolated and characterised. Remarkably, a number of these species are capable of the facile activation of dihydrogen in the absence of any catalyst, in some cases giving clean access to E^{II} hydride complexes. This activation of H_2 in the formation of E^{II} hydride species represents a formal oxidative synthetic route, and is beneficial on the basis of atom economy.



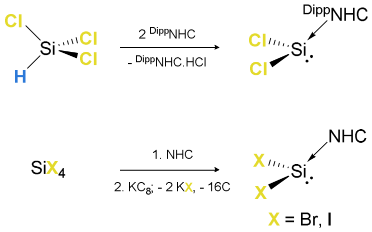
Scheme 5. General scheme for an oxidative route to a hydrido tetrylene.

3.4 Reductive Routes

For the synthesis of reactive Si^{II} hydrides, the reduction of halosilanes has been met with considerable success. Baceiredo has reported that the reduction of chelating-(amido)(phosphino) dichloro silanes with elemental Mg generates the corresponding Si^{II} hydrides in good yields, whilst in other cases more potent reducing agents are required (e.g. Li-naphthalenide). Indeed, such routes have been necessary for Si chemists largely due to the lack of readily available Si^{II} precursors. However, with the report of easily-synthesised divalent N-heterocyclic carbene (NHC) stabilised silicon halides, [^{Dipp}NHC•SiX$_2$] (X = Cl-I; ^{Dipp}NHC = [:C{N(Dipp)C(H)}$_2$]),[27] perhaps the synthetic scope towards Si^{II} hydride species will grow over coming years. A similar method has been employed to synthesise NHC-stabilised Si^{II} hydride complexes (*vide infra*).



Scheme 6. General scheme for reductive route to a hydrido tetrylene.



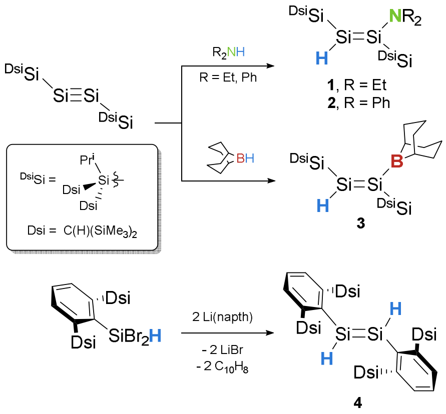
Scheme 7. Synthesis of NHC-stabilised di(halo)silylenes.

4. Divalent Silicon Hydride Chemistry

Si^{II} hydride chemistry came to fruition somewhat later than related chemistry of Ge^{II} and Sn^{II}, perhaps due to the lower stability of Si^{II} species relative to those of the heavier group 14 elements.[16] Nevertheless, developments in kinetic and coordinative stabilisation have allowed for the isolation of some interesting and highly reactive Si^{II} hydride species. Silicon is the second most abundant element on Earth, surpassed only by oxygen. Achieving TM-like catalysis at a silicon centre, then, would be an enormous step forward not just for MG chemistry, but for the chemical community as a whole. Traditionally, silicon is employed in silanes for TM-metal catalysed hydrosilylation of unsaturated organic bonds.[28] Here, steps toward uncatalysed hydrosilylation will be discussed, which should pave the way towards greater prospects in silicon catalysis.

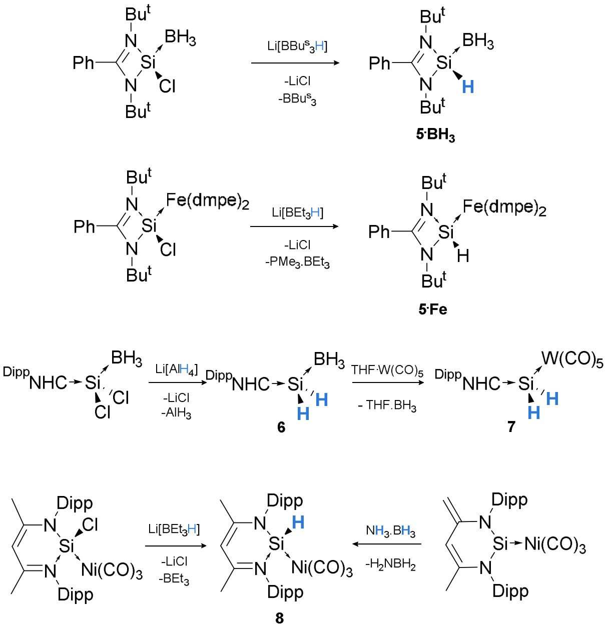
4.1 Synthesis

The initial publication of a Si^{II} hydride came from the Sekiguchi *et al.* in 2010, and involved the formal oxidation of a triply-bonded disilyne, [[{(Dsi)$_2$(Pr^i)Si}Si]$_2$] (Dsi = C(H)(SiMe$_3$)$_2$).[29] Addition of amines or boranes to this Si^I analogue led to addition of the N-H or B-H bonds across the Si-Si triple bond, akin to the addition reaction of alkynes (**1**-**3**, Scheme 8).[30] A related 1,2-diaryl-1,2-dihydrodisilene, [{(Bbp)(H)Si}$_2$] (**4**, Scheme 8; Bbp = C$_6$H$_3$-(Dsi)$_2$-2,6) was reported by Sasamori, Tokitoh *et al.*, which was accessed *via* reduction of the aryldibromosilane, [(Bbp)SiBr$_2$H], with lithium naphthalenide.[31]



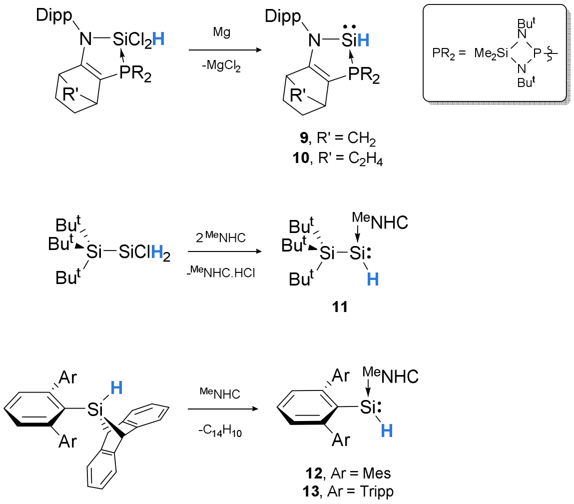
Scheme 8. Synthesis of compounds **1**-**4**.

The first mononuclear Si^{II} hydride complex was published by Roesky, Stalke *et al.* in 2011, synthesised utilising their previously reported Si^{II} chloride complex, [(^{But}Am)(Cl)Si:] (^{But}Am = [PhC{N(Bu^t)}$_2$]$^-$).[32] In order to protect the reactive Si^{II} centre, 'push-pull' stabilisation was employed; the chelating amidinate ligand fills the empty *p*-orbital at silicon, whilst the lone-pair of electrons is quenched by the Lewis-acidic BH$_3$ fragment. Subsequent reaction with Li[BBu$^s_3$H] led to the four coodindate Si^{II} hydride, [(^{But}Am)SiH•BH$_3$] (**5•BH$_3$**, Scheme 9). The same chloro silylene was also utilised by Inoue, Driess *et al.*, who were able to isolate the related Si^{II} hydride complex stabilised by a Lewis-acidic Fe^{0} fragment (**5•Fe**, Scheme 9). This hydrido silylene proved to be of particular importance in silylene-ligated iron hydrosilylation catalysis (*vide infra*).[33] A similar 'push-pull' method was used by Rivard *et al.* in the stabilisation of the parent methylene analogue, [^{Dipp}NHC•SiH$_2$•BH$_3$], first through coordination of the known dichlorosilylene, [^{Dipp}NHC•SiCl$_2$], with BH$_3$, followed by reaction with Li[AlH$_4$] (**6**, Scheme 9).[34] It was also demonstrated that the borane fragment could be displaced with an alternative Lewis-acidic fragment, namely [W(CO)$_5$] (**7**, Scheme 9). Driess et al. also reported on a related Lewis-acid stabilised BDI-stabilised Si^{II} hydride, [(^{Dipp}BDI)(H)Si:] (**8**, Scheme 9; ^{Dipp}BDI = [(DippNCMe)$_2$CH]) which utilised [Ni(CO)$_3$] as the Lewis-acidic fragment.[35]



Scheme 9. Synthesis of compounds **5-8**.

Five examples of three-coordinate Si^{II} hydride systems have reported, two of which contain a stabilising NHC ligand, and all of which were generated through reductive synthetic routes. Kato, Baceiredo *et al.* have reported two derivatives of (phosphino)(amido) silicon(II) hydride complexes, which employ bulky chelating ligands to protect the monomeric Si^{II} centre. These hydride complexes were accessed *via* reduction of the dichlorosilane precursors, with elemental Mg (**9** and **10**, Scheme 10).[14(a)] Inoue *et al.* and Müller *et al.* have both reported on the reductive synthesis of Si^{II} hydride complexes induced by an NHC donor ligand, namely ^{Me}NHC (^{Me}NHC = [:C{N(Me)C(Me)}$_2$]. The former reported that the addition of two molar equivalents of ^{Me}NHC to $[(Bu^t_3Si)SiClH_2]$ proceeds *via* loss of ^{Me}NHC•HCl, generating $[(Bu^t_3Si)(H)Si•^{Me}NHC]$ (**11**, Scheme 10).[36] Müller *et al.* reported that the addition of one molar equivalent of ^{Me}NHC to the anthacenyl-silanes, $[(^{Mes}Terph)(H)Si(\eta^2\text{-anth})]$ and $[(^{Tripp}Terph)(H)Si(\eta^2\text{-anth})]$ ($^{Tripp}Terph = C_6H_3\text{-Tripp}_2\text{-2,6}$; Tripp = $C_6H_2\text{-}Pr^i_3\text{-2,4,6}$; anth = $C_{14}H_{10}$), results in elimination of anthracene and formation of the Si^{II} hydride complexes, $[(^{Mes}Terph)(H)Si•^{Me}NHC]$ and $[(^{Tripp}Terph)(H)Si•^{Me}NHC]$, respectively (**12** and **13**, Scheme 10).[37]



Scheme 10. Synthesis of compounds **9-13**.

Table 3. Key spectroscopic data for the Si-H moiety in compounds **1-13**.

	1	**2**	**3**	**4**	**5•BH$_3$**	**5•Fe**	**6**	**7**	**8**	**9**	**10**
$^1H_{Si\text{-}H}$ (ppm)	2.97	4.54	6.21	6.08	6.12	6.88	3.76	4.16	6.15	5.59 5.76	5.46
$^{29}Si_{Si\text{-}H}$ (ppm)	-39.3	66.6	151.0	63.3	54.3	63.6	-55.6	-71.6	45.1	-44.8 -38.0	-63.7
$^1J_{SiH}$ (Hz)	157	160	157	216	235	-	-	164	154	-	85.6
ν_{SiH} (cm^{-1})	-	-	-	2160	2107	-	2096	2086	-	1954	1951

2108

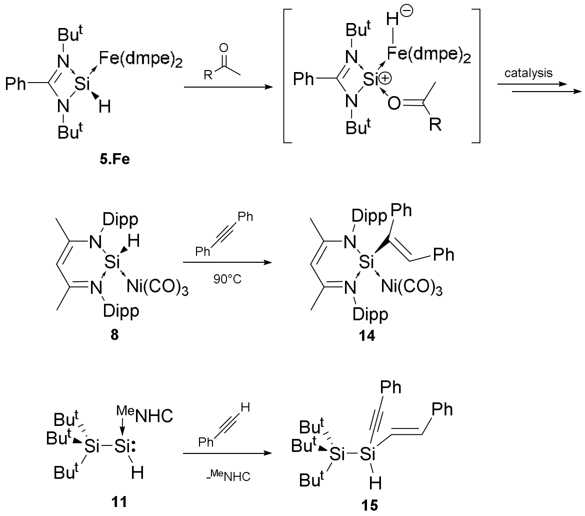
Table 3 cont.

	11	**12**	**13**
$^{1}H_{Si\text{-}H}$ (ppm)	3.17	4	3.88
$^{29}Si_{Si\text{-}H}$ (ppm)	-137.8	-87.6	-80.5
$^{1}J_{SiH}$ (Hz)	101.3	103.3	104.9
ν_{SiH} (cm^{-1})	1984	1970	1970

Key spectroscopic data for Si^{II} hydrides are summarised in Table 3. Generally, Si-H IR stretching vibrational frequencies do not deviate from those typically observed in Si^{IV} hydride species, and range from 1950 to 2160 cm^{-1}, with higher values for higher coordinate systems. Conversely, a wide range of ^{1}H NMR spectroscopic shifts have been reported for Si^{II} hydride complexes, from $\delta = 2.97$ ppm, up to $\delta = 6.20$ ppm. Their $^{1}J_{SiH}$ values are higher for higher coordinate systems (i.e. **1-8**), in line with observed IR stretching frequencies. This seems counter-intuitive, and may be due to increased polarisation at Si^{II} upon becoming higher coordinate. Finally, ^{29}Si NMR shifts for compounds **1-13** vary widely, likely due to the vast differences in ligand electronics.

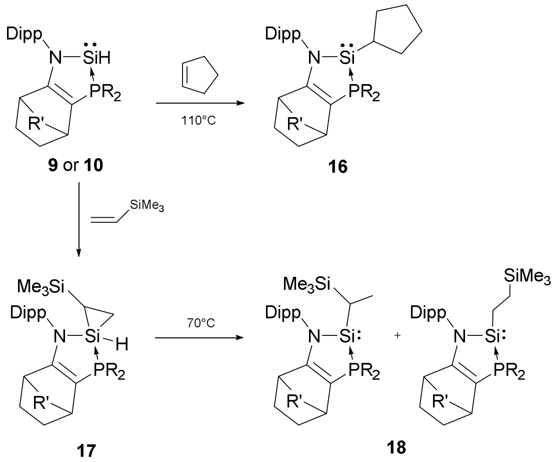
4.2 Reactivity

The uncatalysed insertion of an unsaturated C-E bond (E = C, N, O, etc.) into and Si-H bond is an extremely important reaction if we are to effect catalytic transformations using silicon. Despite this, broader studies on the reactivity of Si^{II} hydrides are lacking relative to those of Ge^{II} and Sn^{II} hydrides (*vide infra*). This is in part due to the challenges in synthesising such species, and in particular, low-coordinate derivatives. Surprisingly, the reaction of iron complex **5•Fe** from Inoue, Dries *et al.* with ketones did not lead to insertion into the Si-H bond. Rather, DFT calculations suggested that coordination of the ketone at Si^{II} instead formed a cationic complex, with hydride migration to Fe. This was found to be a key intermediate in the catalytic cycle using **5•Fe** as a precatalyst for the efficient hydrosilylation of ketones.[33] In contrast to this, in the initial report of Ni-stabilised **8**, reported by the same group, it was described that its reaction with diphenyl acetylene led to stoichiometric insertion of the C-C triple bond into the Si-H bond, forming the alkenyl-silylene **14** (Scheme 11).[35] DFT studies showed that the reaction in fact proceeded through alkyne coordination to the [$Ni(CO)_3$] fragment prior to Si-H insertion, and so is metal-assisted. The related reaction of NHC-stabilised **11** with phenyl acetylene, however, proceeds metal-free, and results in the hydrosilylation of the C-C triple bond, but also C-H oxidative addition at silicon, and loss of ^{Me}NHC, overall resulting in a novel asymmetric silane **15** (Scheme 11).[38]

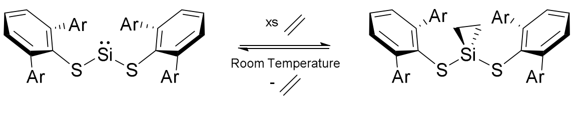


Scheme 11. Reactions of stabilised Si^{II} hydride complexes **5.Fe**, **8**, and **11**.

An exemplary display of the potential reactivity of a Si^{II} hydride was reported by Baceiredo, Kato *et al.*, giving examples of the uncatalysed addition of Si-H bonds across the C=C bond of unactivated alkenes (Scheme 12). This was achieved with Si^{II} hydride compounds **9** and **10**, which react with both cyclopentene (**16**) and 1-trimethylsilylethylene (**18**) at elevated tempreatures (70-110 °C).[14] Further, for 1-trimethylsilylethylene, sila-cyclopropane intermediates **17** were isolated, which were shown to undergo clean Si-*H* migration upon heating to 70 °C (Scheme 12), yielding **18**. This demonstrates the importance of substrate activation prior to Si-*H* migration in such systems. Closely related work reported by the same group as well as from Power *et al.* has demonstrated that such [2+1] cycloaddition reactions can be reversible, lending further comparison to the chemistry of these remarkable low-valent MG compounds and TMs (Scheme 13).[39,40] Such redox activity is vital for the prospect of catalysis, and, alongside related chemistry discussed earlier in this review, is an extremely promising observation, leading towards the achievement of this milestone at a Si^{II} centre.



Scheme 12. Reactions of **9** and **10** with alkenes. R = $[Me_2Si(NBu^t)_2]$; R' = CH_2 or C_2H_4.



Scheme 13. The reversible [2+1] cycloaddition of an acyclic silylene with ethylene. Ar = Mes or Dipp.

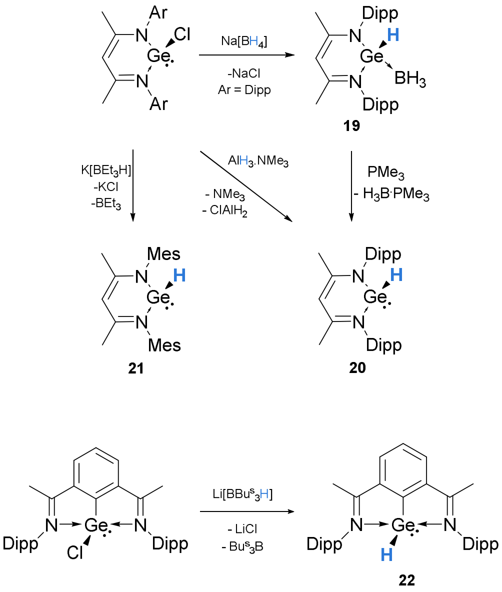
5. Divalent Germanium Hydride Chemistry

The chemistry of low-valent germanium has perhaps been the most prominent amongst the heavier group 14 elements, particularly so in hydride chemistry. The enthusiasm in this topic was sparked by the publication by Roesky *et al.* of the first example of an isolable divalent germanium hydride complex in 2001, $[(^{Dipp}BDI)(H)Ge{\bullet}BH_3]$, the borane-free derivative of which was later shown to be highly reactive relative to higher valent derivatives (*vide infra*). Soon after, Power et al. published a

1,2-dihydrodigermene, a heavy alkene analogue, and described its isomerisation characteristics, a sign that the electronic structure of these species deviates considerably from that of classical hydroalkenes such as ethylene. Now, Ge^{II} hydride complexes can be accessed cleanly through the facile activation of H_2. Thus, the chemistry of germanium hydrides has since seen much attention, allowing for their application as catalysts in well-defined catalytic processes.

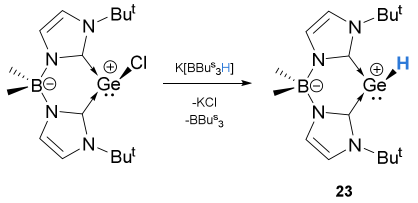
5.1 Synthesis

Roesky's landmark Ge^{II} hydride complex, [(^{Dipp}BDI)(H)Ge•BH_3] (**19**), was synthesised in high yield by addition of [$NaBH_4$] to the Ge^{II} halide species, [(^{Dipp}BDI)(Cl)Ge:] (Scheme 14).[41] In the same publication, it was shown that the coordinated BH_3 could be readily removed by the addition of PMe_3, yielding [(^{Dipp}BDI)(H)Ge:] (**20**). A later publication from the same group described that **20** could be directly accessed by reaction of [(^{Dipp}BDI)(Cl)Ge:] with [Me_3N•AlH_3], as could the Sn^{II} congener, [(^{Dipp}BDI)(H)Sn:] (*vide supra*).[42] One further derivative of **20** ([(^{Mes}BDI)(H)Ge:], **21**) was later reported by Frenking, Jones *et al.*, and was accessed *via* salt-metathesis of a related Ge^{II} chloride complex with [$KBEt_3H$] (Scheme 14).[43] Roesky, Stalke *et al.* have published one further example of a monomeric Ge^{II} hydride, utilising a di(imino)benzene ligand, [(^{Dipp}DIB)(H)Ge:] (**22**, Scheme 14; ^{Dipp}DIB = [C_6H_3-{(Dipp)NC(Me)}$_2$-2,6]), which features a 4-coordinate Ge^{II} centre.[44]

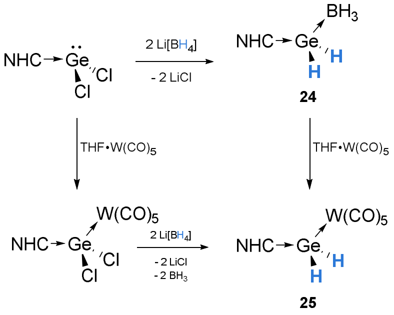


Scheme 14. Synthesis of compounds **19-22**.

Driess *et al.* have reported an example of a monomeric Ge^{II} hydride complex which stands as the only example of a germyliumylidene complex, $[\{^{Ph}B(NHC)_2\}\{Ge(H)\}]$ (**23**, Scheme 15; $^{Ph}B(NHC)_2$ = $[Ph_2B(^{tBu}NHC)_2]$; ^{tBu}NHC = $:C[N(Bu^t)\{C(H)\}_2N]$), which employs a chelating monoanionic bis(carbene)borate ligand scaffold to stabilise the reactive $[:GeH]^+$ fragment.[45] The 'push-pull' stabilised parent germylene, $[^{Dipp}NHC{\bullet}GeH_2{\bullet}BH_3]$ **24**,[46] has also been reported by Rivard *et al.*, as well as the related tungsten stabilised derivative, $[^{Dipp}NHC{\bullet}GeH_2{\bullet}W(CO)_5]$ **25**,[47] both of which were synthesised in a similar manner to the Si^{II} derivative described previously in this review (Scheme 16). Further examples stabilised by Wittig reagents and N-heterocyclic olefins have also be synthesised *via* similar routes.[48]



Scheme 15. Synthesis of compound **23**.



Scheme 16. Synthesis of compounds **24** and **25**.

Considerable efforts have been made in studying the isomeric forms of dimeric Ge^{II} and Sn^{II} hydrides. Whilst an in-depth discussion of this is beyond the scope of this review, previous publications on this topic are available.[16,49] A general overview of potential isomeric forms is shown in Figure 3. Compared with alkenes, which are planar molecules, tetra-hydrido heavier alkenes (i.e. $[(H_2E)_2]$, E = Si-Pb) were found to be more stable in trans-pyramidal (for Si and Ge, **A**) or trans-bridged (for Sn and Pb, **B**) forms. Further, mixed-valence isomer **C** is also a minimum on the potential energy surface, whilst electronic and steric forces could lead to stable monomeric singlet tetrylenes (**D**). Notably, 'push-pull' stabilised derivatives of the parent isomeric form **A** have been reported, giving insights into the electronic structure of such species.[50]

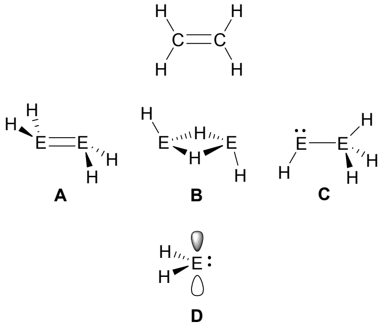
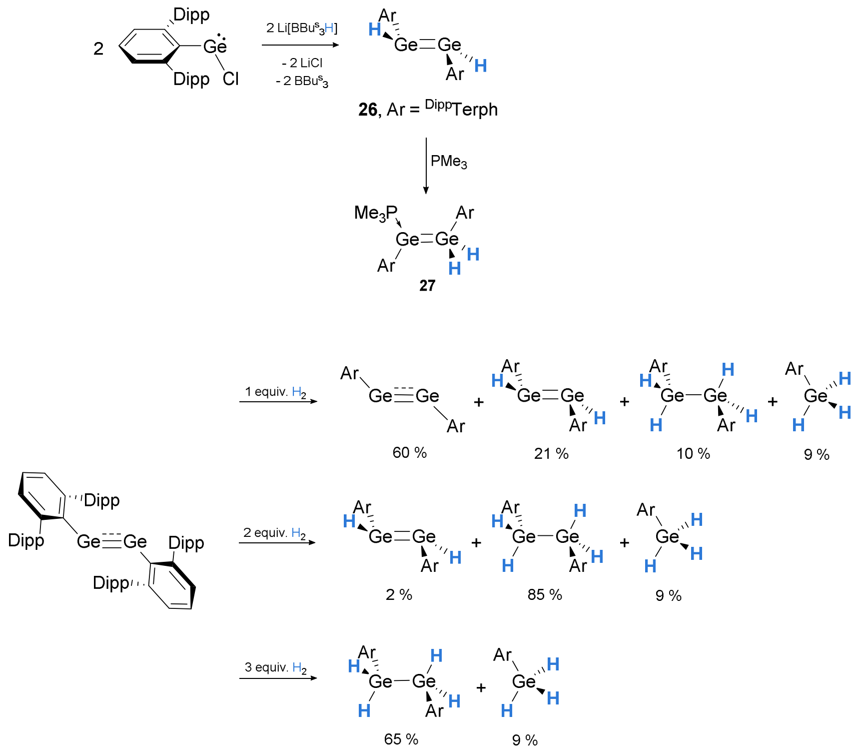


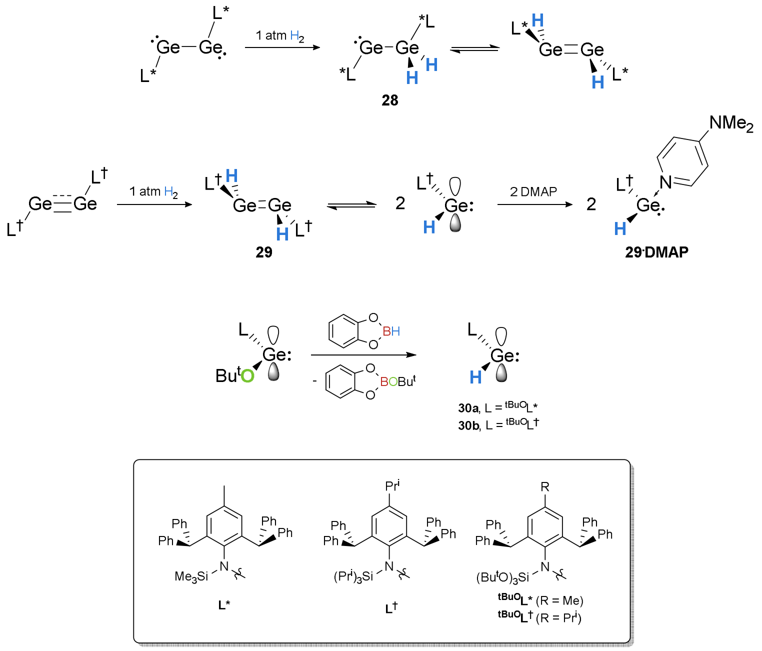
Figure 3. Isomeric forms of heavy ethylene analogues; E = Si-Pb.

The past decade has led to huge steps forward in this arena, with all of the above isomeric forms now known for [LGeH] complexes (L = a monodentate, monoanionic ligand). Power *et al.* reported that the dimeric 1,2-dihydro-1-2-diaryl digermene, $[\{(^{Dipp}Terph)(H)Ge\}_2]$ (**26**) is formed upon salt-metathesis of the monomeric $[(^{Dipp}Terph)(Cl)Ge:]$ with $[LiBBu^s{}_3H]$, which isomerises to the mixed-valence isomer upon coordination with PMe_3 (Scheme 17; $[\{(^{Dipp}Terph)(PMe_3)Ge\{Ge(H)_2(^{Dipp}Terph)\}]$, **27**).[51] Notably, **26** was formed as a mixture with related Ge^{III} and Ge^{IV} compounds upon H_2 activation by the digermyne, $[\{(^{Dipp}Terph)Ge\}_2]$ (Scheme 17) in a landmark demonstration of small-molecule activation by a MG compound.[6(a)]



Scheme 17. *Above*: Synthesis of compounds **26** and **27**; *Below*: Product distribution resulting from the reaction of a 1,2-diaryldigermyne with one, two, or three equivalents of dihydrogen. Ar = ^{Dipp}Terph.

In the Jones group, we have also achieved dihydrogen activation utilising low-valent germanium stabilised by extremely bulky amide ligands, allowing for the synthesis of singly ([(L*Ge)$_2$]; L* = [N(Ar*)(SiMe$_3$)], Ar* = [$C_6H_2Me\{C(H)Ph_2\}_2$-4,2,6]) and doubly ([(L†Ge)$_2$]; L† = [N(Ar†)(SiPr$^i_3$)], Ar† = [$C_6H_2Pr^i\{C(H)Ph_2\}_2$-4,2,6]) bonded digermynes through minor ligand modifications. Contrary to Power's aryl digermyne, the amido derivatives quantitatively formed the respective Ge^{II} hydride complexes upon exposure to one atmosphere of dihydrogen (Scheme 18).[6(c),52] Slight ligand differences in the formed hydride complexes resulted in considerably different isomeric forms for these species in the solid state: hydrogenation of [(L*Ge)$_2$] led to the mixed-valence isomer **C**, in [(L*)GeGe(H)$_2$(L*)] (**28**), whilst hydrogenation of [(L†Ge)$_2$] led to the *trans*-pyramidalised conformer **A**, in [{(L†)(H)Ge}$_2$] (**29**). Both **28** and **29** showed dynamic conformational behaviour in solution, **28** existing in equilibrium with the *trans*-pyramidalised isomeric form **A**, whilst **29** readily establishes a mono-dimer equilibrium, both processes being temperature dependant. In the latter case, this was due to both steric and electronic properties of the amide donor ligand, which disfavoured dimerisation through N→Ge π-donation, and employment of the large [(Pr^{i})$_3$Si] group in the L† relative to the [Me$_3$Si] group in L*. (Scheme 18). Evidence for this dynamic process was given by the 'trapping' of the monomer upon coordination by the Lewis-base, DMAP (**29•DMAP**; Scheme 18). It was later shown that further increasing the steric bulk of the ligand in ^{tBuO}L* and ^{tBuO}L† allowed for the isolation of what are still the only examples of two-coordinate hydrido tetrylenes, [(^{tBuO}L*)(H)Ge:] (**30a**) and [(^{tBuO}L†)(H)Ge:] (**30b**; Scheme 18).[53] The monomer-dimer nature of **29** was later shown to be extremely important in its reactivity, and ultimately for its applications in catalysis (*vide infra*).



Scheme 18. Synthesis of compounds **28-30**, and the solution dynamics of **28** and **29**.

Key spectroscopic data for described Ge^{II} hydride species are summarised in Table 4. Ge-H IR stretching frequencies can be observed at lower wavenumbers when compared with related Si^{II} complexes, testament to the weaker Ge-H bond. Importantly, the IR spectra of the two-coordinate species **30a** and **30b** show stretching vibrational bands at high wavenumbers relative to base-stabilised derivatives, possibly due to lower electron density at Ge^{II} for lower-coordinate species. The effect of coordination number is also clear in related ^{1}H NMR spectral data; compounds **29**, **30a**, and **30b**, which are monomeric in solution, show characteristic low-field resonances, with the variable temperature ^{1}H NMR spectrum of **29** demonstrating that increasing the temperature to 100 °C in toluene results in a low-field shift of the Ge-*H* signal to ~ δ 10.5 ppm, due to an increase in dissociation to the monomer.[52]

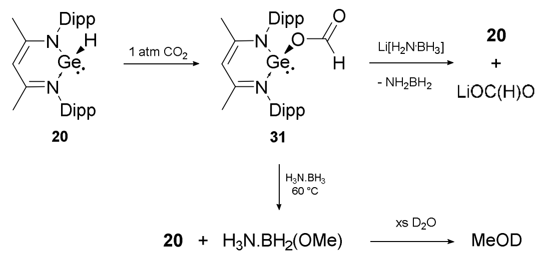
Table 5. Key spectroscopic data for the Ge-H moiety in compounds **20-30**. All values reported at ambient temperature.

	20	**21**	**22**	**23**	**24**	**25**	**26**	**27**	**28**	**29**	**30a**	**30b**
$^1H_{Ge\text{-}H}$ (ppm)	8.08	8.25	6.69	5.69	3.92	4.23	3.48	3.81	6.13	8.21	10.00	10.02
ν_{GeH} (cm^{-1})	1733	1722	1985	1809	1987	1981	1785	1905	1990 2031	1961	2083	2057

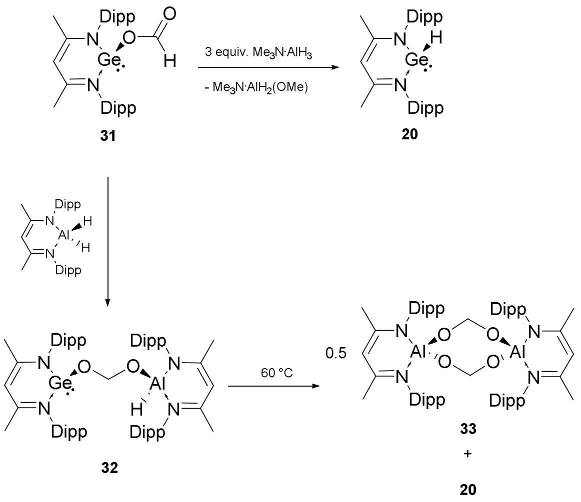
5.2 Reactivity

Considerable contributions have been made towards the reactivity of divalent germanium hydride complexes, ultimately allowing for remarkable reactivity such as the rapid, reversible hydrogermylation of unactivated internal alkenes. More recently, this has even led to efficient, well-defined organic transformations utilizing Ge^{II} complexes as catalysts. Substantial work towards the former has been reported by Roesky *et al.*, who have shown, in a series of publications, that complex **20** is capable of the hydrogermylation of a number of unsaturated organic bonds.[21] In an initial report on the reactivity of **20**, its Ge-H fragment was shown to readily undergo addition across C-O double bonds in non-enolisable ketones, and perhaps more importantly, in CO_2.[54] This reaction marked the first uncatalysed hydroelementation of CO_2 by a group 14 hydride. Further, the reaction was rapid, being complete in just 15 minutes at ambient temperature and pressure, quantitatively furnishing the Ge^{II} formate, [(^{Dipp}BDI)Ge{OC(H)O}] (**31**, Scheme 19). This was taken one step further some years later, when it was shown that **20** could be regenerated through reaction of **31** with either Li[$H_2N{\bullet}BH_3$]

or [$H_3N{\bullet}BH_3$], although catalysis was not achieved in this case.[55] Nevertheless, quenching the reaction mixture with D_2O allowed for the generation of MeOD in a 46 % yield. A related study from Driess *et al.* found similar results using [$Me_3N{\bullet}AlH_3$] as the reducing agent.[56] Insights into this process of CO_2 reduction were given by the reaction of equimolar quantities of the Ge^{II} formate **31** with the hindered alane, [(^{Dipp}BDI)AlH_2], which proceeded to generate the [$OC(H)_2O$] bridged dimer, **32** (Scheme 20). Heating a solution of **32** at 60 °C led to a redistribution reaction, forming the homoleptic, doubly bridged alane dimer, **33**, and regenerating the Ge^{II} hydride complex, **20**. Again, catalysis was not achieved here, but concepts leading to such an end were clearly at play.

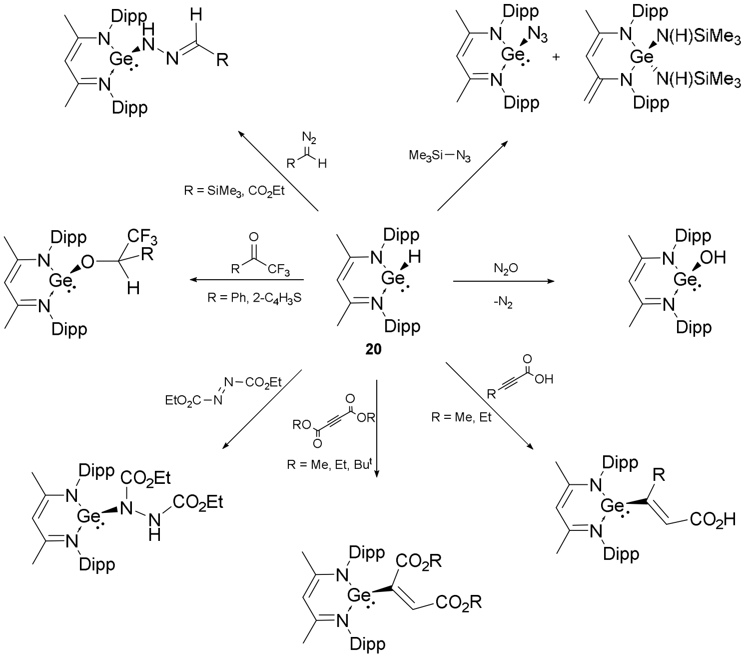


Scheme 19. Reactivity of **20** with CO_2, and subsequent regeneration of **20** with ammonia borane and derivatives.



Scheme 20. Reactivity of **31** towards [($^{\mathrm{Dipp}}$BDI)AlH$_2$].

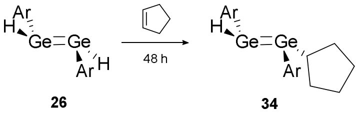
Roesky, Schulzke *et al.* also showed that **20** exhibited insertion reactivity towards azo dicarboxylate, diazo, azide, and alkyne compounds, as well as with N$_2$O (Scheme 21).[57] Whilst not all reactions were quantitative, generally this collection of results demonstrates the functional group tolerance and potential synthetic utility of **20** in substrate functionalisation. Notably, alkynes underwent rapid addition reactions, and were selective for mono-insertion, leading exclusively to vinyl germylenes.



Scheme 21. Diverse reactivity of **20** towards unsaturated substrates.

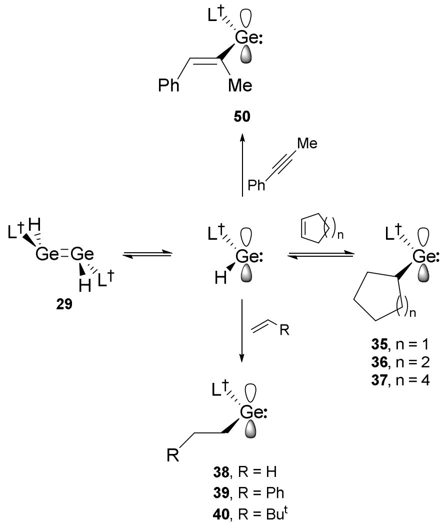
The dimeric Ge$^{\mathrm{II}}$ hydride, **26**, reported by Power *et al.*, shows markedly enhanced reactivity relative to base-stabilised **20**. This was displayed through the reaction of the former with cyclopentene, which proceeded over the course of 48 h to generate the 1-hydro-2-alkyl digermene, **34** (Scheme 22).[58]

Whilst this reaction was slow, it highlights the possible potency of a group 14 hydride, as well as the benefits of monodentate, monoanionic ligands in such systems.

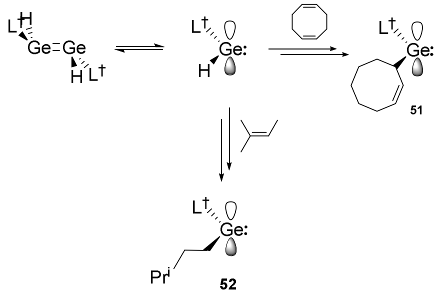


Scheme 22. Reactivity of **26** towards cyclopentene. Ar = $^{\mathrm{Dipp}}$Terph.

Work from our (the Jones) group has taken this reactivity a step further. As mentioned, utilising extremely bulky monodentate amide ligands has allowed for the isolation of 2-coordinate, divalent germanium hydride systems. This allows the frontier orbitals of the germylene to remain vacant, relative to higher coordinate hydrogermylenes discussed above, and has led to more potent hydridic reactivity. That is, **29** reacts with unactivated internal alkenes essentially instantly at ambient temperature.[14(b)] The monomeric nature of the hydride precursor was somewhat confirmed in the products, in that all examples yielded monomeric, 2-coordinate (amido)(alkyl)germylenes or (amido)(vinyl)germylenes (Scheme 23). Despite the facile nature of these transformations, some reactions were in fact found to be reversible. For example, cyclohexyl germylene, **36**, formed an equilibrium mixture of **29**, **36**, and cyclohexene at ambient temperature. A further demonstration of this reversibility came from reaction of **29** with either 1,5-cyclooctadiene (COD) or 2-methyl-2-butene. Both reactions led to isomerised alkyl products (**51** and **52**), which proceeded *via* a series of insertion-elimination steps (Scheme 24). As such, these reactions demonstrated the role of low-valent group 14 hydrides in alkene isomerisation processes. Unactivated alkynes were also hydrogermylated by **29**, selectively giving access to the monomeric, 2-coordinate vinyl germylene **50** (Scheme 23).



Scheme 23. Reactivity of **29** towards various unactivated alkenes and 1-phenyl propyne.



Scheme 24. Isomerisation/hydrogermylation of alkenes with **29**.

The mechanism for this reactivity was investigated by Jones, Frenking *et al.*, who showed that a formal [2+2] addition reaction arises *via* a single transition state which leads directly to the insertion products, with the reverse reaction, formally *β*-hydride elimination, responsible for the aforementioned alkene isomerisation processes (Figure 4).[20] This is in contrast to hydrosilylation reactions described by Baceiredo, Kato *et al.*,[14(a)] in which a Si^{IV} [2+1] cycloaddition intermediate could be isolated prior to formal insertion. The [2+2] transition state found for reactions of **29** with alkenes relies heavily on the availability of frontier orbitals of monomeric **29**, namely a vacant *p*-

orbital and an *s*-based lone-pair of electrons. Thus, the low coordinate nature of **29** is paramount to its high reactivity, an important lesson in the design of reactive low-valent group 14 hydride systems.

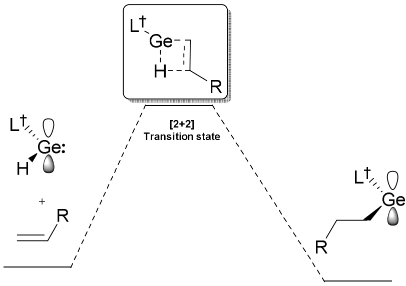


Figure 4. Calculated [2+2] transition state for alkene hydrogermylation by **29**.

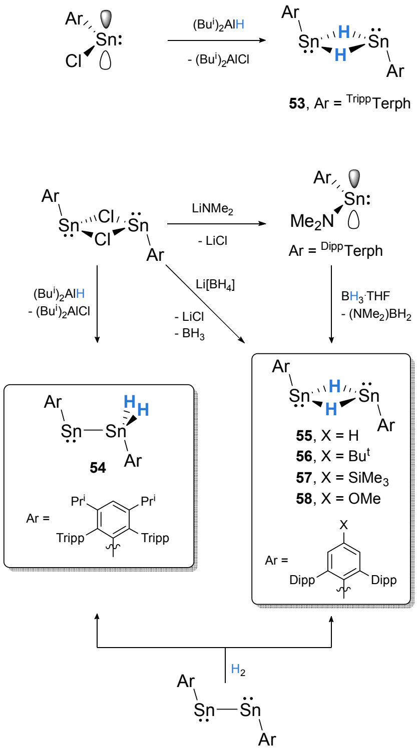
6. Divalent Tin Hydride Chemistry

As with germanium, tin(II) hydrides have seen considerable attention over the last two decades, with the first tin(II) hydride reported by Power *et al.* in 2000, representing the first entry into divalent group 14 hydride complexes. Over the last 2 decades, many studies have revealed interesting dynamic solution behaviour of these divalent tin species, as well as C-H activation and potent hydrostannylation capacities.

6.1 Synthesis

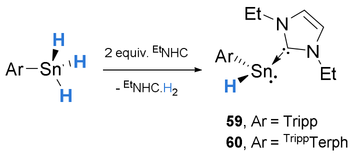
The synthetic route to the first example of a Sn^{II} hydride, $[\{(^{Tripp}Terph)Sn(\mu\text{-}H)\}_2]$ **53**, involved the metathesis reaction of $[(Bu^i)_2AlH]$ with $[\{(^{Tripp}Terph)(Cl)Sn:]$ (Scheme 25).[26] A lower yield route to the related deuteride was described utilising $Li[AlD_4]$ in a salt metathesis reaction. In 2007, five further examples of bulky-aryl stabilised tin(II) hydride complexes were reported *via* similar salt-metathesis synthetic routes (**54-58**, Scheme 25), also with one example synthesised *via* formal *σ*-metathesis of an (aryl)(amido)stannylene with borane.[59] One year later, the same group reported that some examples of these hydride complexes could also be accessed by H_2 activation by Sn^I dimers (distannynes) which had been reported some years before. Interestingly, in all cases the 1,2-

diaryldistannynes exclusively reacted with a single equivalent of H_2 to form Sn^{II} hydride complexes, in contrast to their Ge^{I} congeners.[60]

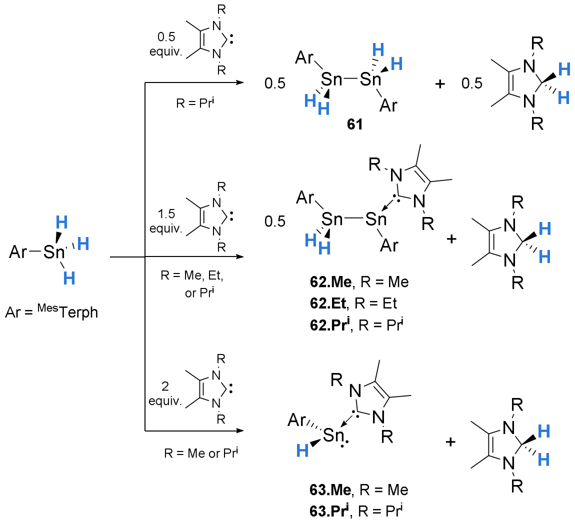


Scheme 25. Synthesis of compounds **53-58**.

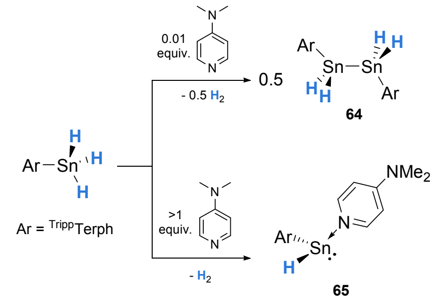
Monomeric, base-stabilised Sn^{II} hydrides related to the dimeric aryl derivatives described above have also been reported by Wesermann *et al.*. Remarkably, these were synthesised by base-induced reductive elimination of H_2 from bulky-aryl stannanes (Scheme 26). In an initial contribution on this chemistry, addition of two molar equivalents of ^{Et}NHC (^{Et}NHC = [:C{N(Et)C(H)}$_2$] to aryl stannanes, [(Tripp)SnH_3] and [(^{Tripp}Terph)SnH_3], led to formation of ^{Et}NHC•H_2 and [(Tripp)(H)Sn•^{Et}NHC] (**59**) or [(^{Tripp}Terph)(H)Sn•^{Et}NHC] (**60**), respectively.[61] More recently, investigations varying the stoichiometry of NHC added to a related stannane, [(^{Mes}Terph)SnH_3], showed that dimeric stannane **61**, mono base-stabilised distannene **62**, or monomeric base-stabilised stannylene **63** can selectively be formed (Scheme 27).[62] The same group has also shown that nitrogen bases could be used to achieve similar results, with direct loss of H_2 gas. Using DMAP, distannane or monomeric base-stabilised stannylenes were obtained, the former generated using essentially catalytic quantities of base (**64** and **65**, Scheme 28). A broad investigation utilising various nitrogen bases demonstrated that distannane, distannene, or monomeric base-stabilised stannylenes could be selectively generated.[63] These results are a poignant display of the ability of Sn^{IV} to undergo reductive elimination reactivity, which will undoubtedly prove extremely important for TM-like catalysis at a Sn^{II} centre.



Scheme 26. Synthesis of **59** and **60**.

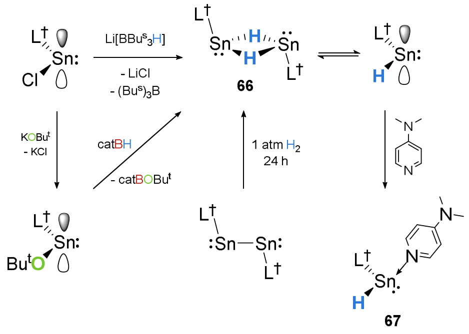


Scheme 27. Synthesis of compounds **61-63**.



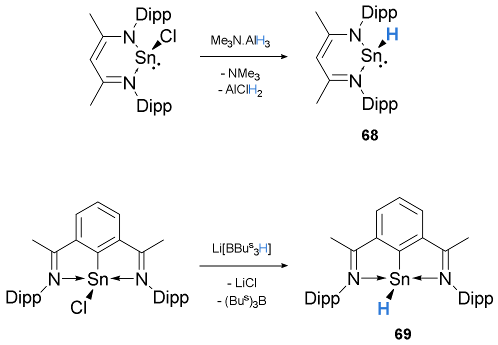
Scheme 28. Synthesis of compounds **64** and **65**.

In our (the Jones) group, bulky amide ligands have been applied to the synthesis of a Sn^{II} hydride complex. This was accessed *via* the salt metathesis of the Sn^{II} halide complex, $[(L^\dagger)(Cl)Sn:]$, with Li[BBu$^s{}_3$H], leading to the hydride bridged dimer, $[\{(L^\dagger)Sn(\mu\text{-}H)\}_2]$ (**66**, Scheme 29) .[52] The same complex can also be formed by the activation of H_2 by the 1,2-diamido distannyne, $[\{(L^\dagger)Sn\}_2]$, or the σ-bond metathesis reaction of $[(L^\dagger)(OBu^t)Sn:]$ with pinacol borane (HBpin).[6(e),15] As with the Ge^{II} derivative, **66** exists in equilibrium with the monomeric, 2-coordinate divalent tin hydride, which can be trapped by addition of DMAP, to form $[(L^\dagger)(H)Sn{\bullet}DMAP]$ (**67**).[52] This monomer-dimer equilibrium for **66** is extremely important for its reactivity on the basis of availability of frontier orbitals, and will be discussed below.

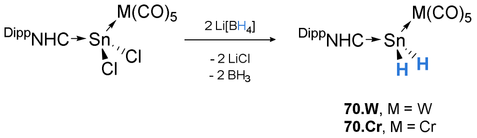


Scheme 29. Synthesis of compounds **66** and **67**.

Roesky, Stalke *et al.* have also reported the synthesis for the ^{Dipp}BDI and ^{Dipp}DIP stabilised tin analogues of their reported Ge^{II} hydrides, namely $[(^{Dipp}BDI)(H)Sn:]$ (**68**) and $[(^{Dipp}DIB)(H)Sn:]$ (**69**), accessed *via* the same routes as the Ge^{II} congeners (Scheme 30).[42,44] Finally, Rivard *et al.* successfully isolated the 'push-pull' stabilised parent stannylene, [^{Dipp}NHC•SnH$_2$•W(CO)$_5$] (**70•W**), published alongside its Ge^{II} congener, which was synthesised in the same manner (Scheme 31).[47] Subsequently, the chromium stabilised derivative, [^{Dipp}NHC•SnH$_2$•Cr(CO)$_5$] (**70•Cr**), was also published (Scheme 31).[64]



Scheme 30. Synthesis of compounds **68** and **69**.



Scheme 31. Synthesis of compound **70**.

Table 5. Key spectroscopic data for discussed Sn^{II} hydride complexes.

	53	**54**	**55**	**56**	**57**	**58**	**59**	**60**	**62.Me**	**62.Et**	**62.Pr^{i}**
^{1}H (ppm)	7.87	7.92	9.13	9.11	9.12	9.28	7.59 [c]	6.93	3.02	4.58	4.86
									4.43	3.71	4.53
^{119}Sn (ppm)	699	1727	657	667	87	687	-	338	-247	-227	-192
		38 [b]							-371	-363	-364
$^{1}J_{HSn}$ (Hz)[a]	592	528	89	87	-	95	162 [c]	237	1434	1450	1424
									1050	1066	1058
ν_{SnH} (cm^{-1})	1828	1810	-	-	-	-	-	1759	1852	-	1778

1771 1783 1761

[a] Where ^{119}Sn and ^{117}Sn values were given, only the ^{119}Sn values are shown here. [b] Value recorded at -80 °C; [c]Values recorded at -40 °C.

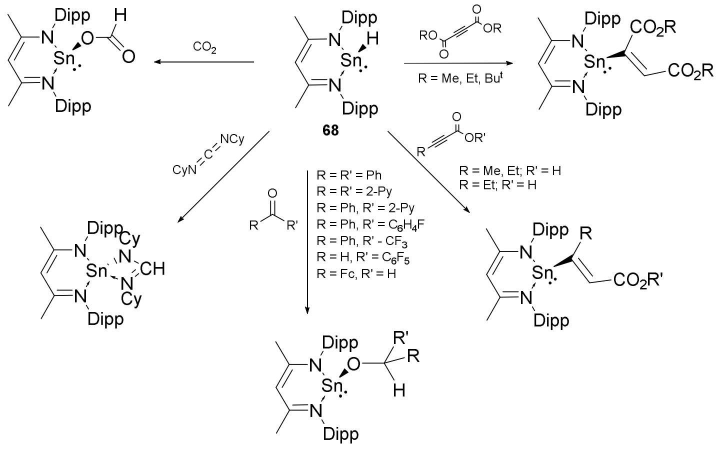
***Table 5** continued*

	63.Me	**63.Pr^{i}**	**65**	**66**	**67**	**68**	**69**	**70•W**	**70•Cr**
$^{1}H_{Sn\text{-}H}$ (ppm)	6.91	7.23	11.64	17.20	15.01	13.8	10.59	5.55	5.51
$^{119}Sn_{Sn\text{-}H}$ (ppm)	-349	-291	225	-	-	224	-114	-309	-107
$^{1}J_{SnH}$ (Hz)	210	192	118	-	-	64	112	1159	1181
ν_{SnH} (cm^{-1})	1653	1632	-	1800	1759	1859	1826	1786	1772

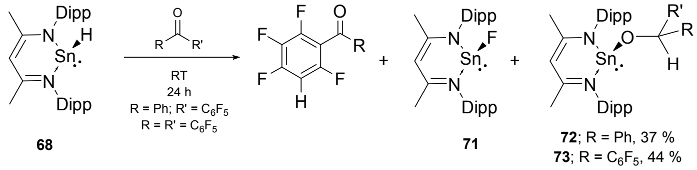
Key spectroscopic data for reported divalent tin hydride complexes are given in Table 5. Typically, monomeric, and in particular low-coordinate, systems exhibit considerable low-field ^{1}H NMR chemical shifts, emphasised by compound **66** (δ = 17.20 ppm), which is essentially two coordinate in solution. As is common with ^{119}Sn NMR spectroscopy, reported resonances range from δ = +1727 ppm to δ = -371 ppm, with lower-field resonances observed for Power's hydride-bridged systems that are considered to show monomeric character in solution. Reported $^{1}J_{SnH}$ coupling constants also vary enormously, with higher-coordinate Sn^{II} centres typically exhibiting higher coupling constants.

6.2 Reactivity

As with the BDI-stabilised Ge^{II} hydride complex **20**, the reactivity of the Sn^{II} congener, **68**, has been extensively studied by Roesky *et al.*. Compound **68** was observed to be very reactive towards addition across C=O bonds in several unactivated ketones, which were rapidly hydrostannylated at ambient temperature.[65] This is in contrast with the reactivity of **20**, which only reacted with activated ketones under similar conditions. As with **20**, **68** was also capable of the facile hydrostannylation of CO_2, as well as activated alkynes and a carbodimide.[65] This collection of reactivity is summarised in Scheme 32. Interestingly, it was noted that C-F activation is observed where perfluorophenyl ketones were employed, testament perhaps to the greater polarity of the Sn-H bond relative to that of the Ge-H bond.[66] The major product of these reactions was the fluoro stannylene [(^{Dipp}BDI)(F)Sn:] (**71**), formed in up to 63 % yield (Scheme 33).

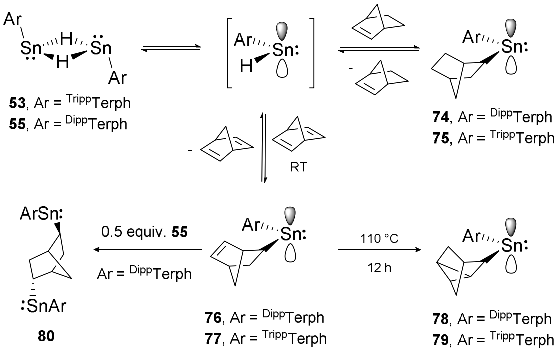


Scheme 32. Diverse reactivity of **68** towards unsaturated compounds.



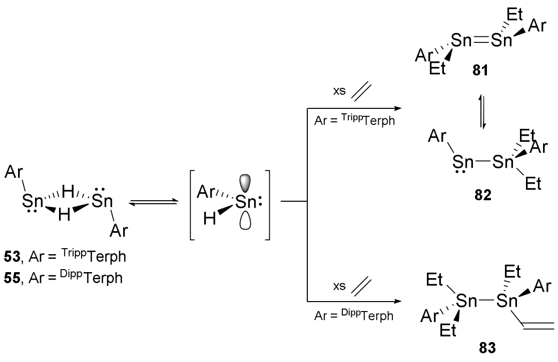
Scheme 33. Reactivity of **68** towards fluorinated ketones.

Power *et al.* have recently reported on interesting observations resulting from the reactions of the aryl Sn^{II} hydride systems, **53** and **55**, with unactivated alkenes. In one report, they described the reversible hydrostannylation of norbornene and norbornadiene with both species, which proceeded rapidly at ambient temperature to yield (aryl)(alkyl) stannylenes **74-77** (Scheme 34),[67] the monomeric nature of which may suggest that the reactive hydride species are in fact monomeric in solution, i.e. [(Ar)(H)Sn:] (*viz.* reactivity of (amido)(hydrido)tetrylenes from the Jones group). Remarkably, it was also found that these tin hydride species promote the rearrangement of norbornadiene to the nortricyclic group, slowly at ambient temperature, but in 12 h when heated to 110 °C, generating monomeric nortricyclic-stannylenes **78** and **79**. It was also shown that the double hydrostannylation of norbornadiene was possible with **55**, despite the steric bulk of the terphenyl ligand utilised in this system (Scheme 34).

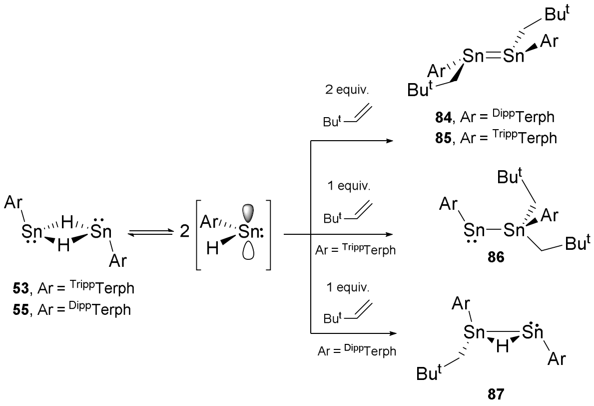


Scheme 34. The role of Sn^{II} hydrides, **53** and **55**, in the rearrangement of norbornadiene.

In a related publication, the same group showed that both **53** and **55** readily undergo insertion reactions with the unactivated alkenes ethylene and 3,3-dimethylbut-1-ene. Compound **53** reacted with an excess of ethylene over the course of 12 h to yield ethylene insertion products as a mixture of structural isomers, namely the distannene, $[\{(^{Tripp}Terph)(Et)Sn\}_2]$ **81**, and the stannylstannylene $[\{(^{Tripp}Terph)(Et)_2Sn\}(^{Tripp}Terph)Sn:]$ **82** (Scheme 35).[68] Notably, in attempting to synthesise similar species from the reaction of **55** with ethylene, the Sn^{III} product, a di*stannane* (*viz.* $[(^{Tripp}Terph)(Et)_2SnSn(Et)(CHCH_2)(^{Tripp}Terph)]$, **83**, Scheme 35) was isolated. The process *via* which **83** is formed was speculated to involve a C-H activation step. The reactions of two molar equivalents of 3,3-dimethylbut-1-ene with either **53** or **55** proceed in both cases to yield symmetrical dimeric stannylenes, **88** and **85** (Scheme 36). It was also shown that the 1:1 reactions resulted in mono-insertion products. Interestingly, the slight differences in steric encumbrance of the aryl ligands at tin resulted in different isomeric forms in the dimeric products. Whilst $[^{Tripp}Terph]$ led to the formation of the known stannylstannylene structure in **86**, $[^{Dipp}Terph]$ led to the mono-hydride bridged structure in **87**, as shown in Scheme 36. This gives further testament to the significant effects induced by small ligand modifications in these reactive systems.

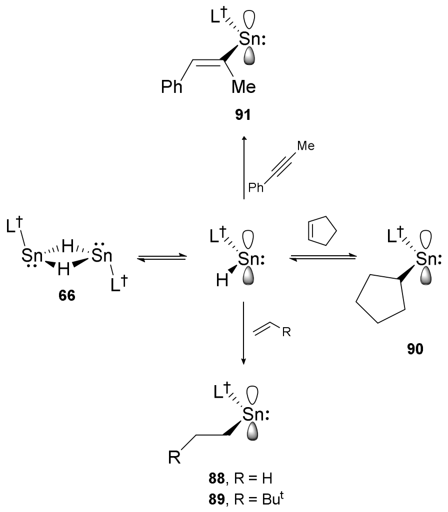


Scheme 35. Reactivity of **53** and **55** towards ethylene.



Scheme 36. Reactivity of **53** and **55** towards 3,3-dimethylbutene.

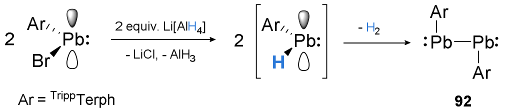
In the Jones group, we have shown that the *pseudo*-monomeric amido Sn^{II} hydride **66** is considerably more reactive than higher coordinate derivatives, and can essentially hydrostannylate unactivated internal alkenes immediately at ambient temperature.[14(b)] As with related reactions involving the Ge^{II} derivative, reactions of **66** with alkenes led exclusively to monomeric stannylene products, outlined in Scheme 37. Further, the hydrostannylation of cyclopentene was found to be reversible, in-line with results found for the analogous Ge^{II} system. Taken as a whole, the work from the groups of Power and Jones has demonstrated that low-coordinate hydridotetrylenes show a markedly greater reactive potency relative to their higher coordinate congeners. The low-coordinate nature of these systems has also led to the observation of remarkable solution-state dynamics, such as monomer-dimer equilibria and spontaneous isomerisation processes.



Scheme 37. Reactivity of **66** towards unactivated alkenes and 3-phenyl propyne.

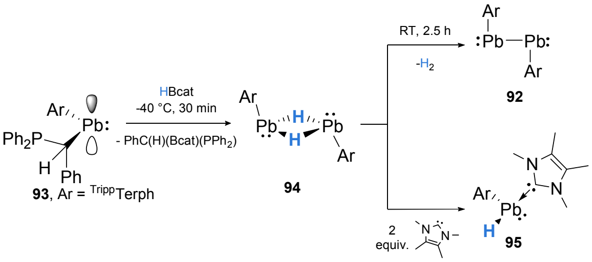
7. Divalent Lead Hydride Chemistry

Lead hydride chemistry is typically thwarted by the relative instability of Pb-H bonds, which leads to the formation of elemental lead and dihydrogen, e.g. when plumbane, PbH_4, is warmed to reasonable working temperatures.[69] Thus, plumbane has only been synthesised and spectroscopically characterised in matrix isolation studies,[70] whilst organoplumbanes are typically generated *in situ* and can be utilised in hydroplumbylation reactions below -20 °C.[71] In 2000, Power *et al.* reported that the attempted synthesis of the aryl lead(II) hydride, [(^{Dipp}Terph)(H)Pb], from the corresponding lead(II) bromide and [$LiAlH_4$], led instead to the formation of the first example of a heavier alkyne analogue, the lead(I) dimer, [{(^{Dipp}Terph)Pb}$_2$] **92** (Scheme 38).[72] The reaction was postulated to occur through reductive elimination of H_2 from a dimeric form of [(^{Dipp}Terph)(H)Pb], but evidence for this was not observed. Now, utilising an alternative σ-metathesis route, Wesemann *et al.* have succeeded in the synthesis and isolation of the first example of a lead hydride complex, dimeric [{(^{Dipp}Terph)Pb(μ-H)}$_2$] (**94**).[73] The (aryl)(phosphinobenzyl)plumbylene, **93**, reacts with HBcat at -40 °C within 30 min, generating **94** and [(Ph_2P)C(H)(Ph)(Bcat)] (Scheme 39). Compound **94** displays a remarkably down-field shift for its hydride ligand, at $\delta = 35.8$ ppm ($^1J_{PbH} = 734$ Hz), due to spin-orbit deshielding, a result of relativistic effects of the heavy lead atom.[74] Over the course of 2.5 h in solution, **94** loses H_2 and forms the previously reported diplumbyne, **92**, supporting the hypothesised mechanism for the formation of that compound in its original publication. The addition of an NHC to **94** results in the cleavage of the dimer, and the formation of the monomeric, 3-coordinate Pb^{II} hydride, **95** (Scheme 39). Indeed, related reactivity has been observed for Ge^{II} and Sn^{II} hydride complexes, as discussed in previous chapters. No further reactivity of either the dimeric or monomeric lead hydrides, **94** and **95**, has been reported as yet. Due to both their thermolability and the toxicity of lead, it is unlikely that they will find particular synthetic utility in regards to catalysis.



92

Scheme 38. Attempted synthesis of a Pb^{II} hydride, resulting in the diplumbyne, **92**.

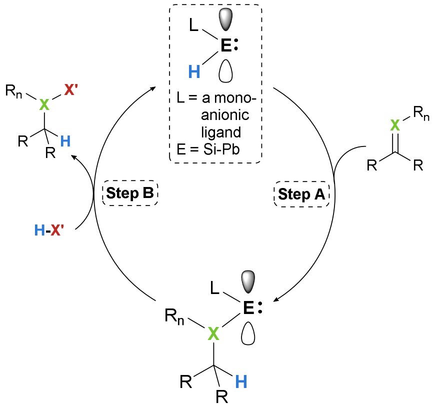


Scheme 39. Successful synthesis of a Pb^{II} hydride dimer **94**, and its base-induced cleavage to the monomeric **95**.

8. Low-valent Group 14 Hydrides in Catalysis

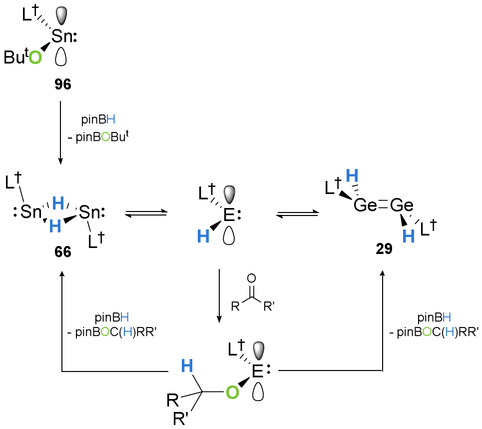
The majority of the discussed reactive chemistry of low-valent group 14 hydrides directly relates to the first step of a hydroelementation catalytic cycle, that is substrate insertion into the E-H bond (E = Si-Sn, Scheme 40). As we have seen, this is now possible for the majority of unsaturated organic bonds, and as it stands is a well understood process for the heavier group 14 hydrides. The remaining steps of such a catalytic cycle, however, have not featured so prominently in the reactivity of heavier tetrylenes. As discussed in an earlier chapter, the groups of Power, Aldridge, and Baceiredo have shown that net metathesis is possible at heavier tetrylene centres.[11,14,22] Here, the initial examples of hydrido tetrylenes acting as efficient, well-defined catalysts in organic transformations will be discussed.

Computational investigations reported in 2011 by Sakaki *et al.* suggested that the catalytic hydrosilylation of C-O and C-N double bonds should be possible at a Ge^{II} centre, more specifically, using the germanium hydride complex reported by Roesky (**20**) as a model.[75] Notably, in-depth mechanistic investigations implied that substrate coordination at germanium is a key step in such a cycle for both substrate insertion (i.e. Step A, Scheme 40) and subsequent metathesis (i.e. Step B, Scheme 40), where the same investigation found very similar intermediates in the analogous reactions catalysed by Rh^{I}. Of course, this study investigated the reactivity of a base-stabilised hydride complex, which leads to a degree of quenching of the frontier orbitals at Ge^{II}. One would postulate that a lower coordinate derivative should therefore act as a more potent catalyst.

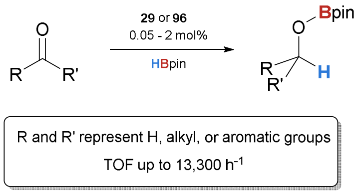


Scheme 40. Catalytic cycle for the hydrofunctionalisation of unsaturated organic bonds at a hydrido tetrylene. X = C, N, O; X' = H, SiR_3, BR_2, etc.; R = an organic group.

In the Jones group, we found that this is true for 2-coordinate (amido)(alkoxy)germylenes, which could be efficiently generated by the reaction of **29** with aldehydes or ketones (Scheme 41).[15] Further reaction of these germylenes with pinacol borane (HBpin) led, in some cases immediately, to the regeneration of germanium hydride **29** and concomitant formation of pinacolboronate esters, pinBOR (Scheme 41, R = an alkyl group). Similar chemistry is possible using the Sn^{II} hydride, **66**, with reactions generally being much more rapid. This ultimately led to complexes **29** and **66** being applied as efficient precatalysts for the hydroboration of aldehydes and ketones. Due to the thermal instability of **66**, however, a precursor to this hydride was employed (*viz.* $[(L^{\dagger})(Bu^{t}O)Sn:]$, **96**), which reacts with HBpin *in-situ* to generate the active hydride species. The mechanism for this catalytic cycle was elucidated through both experimental and computational means. The latter indicated that this occurs *via* a σ-bond metathesis mechanism, rather than through formal B-H oxidative addition, and subsequent reductive elimination of the pinacolboronate ester products. This is likely due to both the polarity of the Ge-O bond in (amido)(alkoxy)germylenes, as well as the oxophilicity of boron in HBpin. Importantly, kinetic investigations for the Ge^{II} reaction indicated that the rate determining step for this cycle is the σ-metathesis reaction between (amido)(alkoxy)germylenes and HBpin, and not the insertion reaction of the carbonyl substrate into the Ge-H bond. Thus, in order to extend this hydroboration catalysis to more challenging substrates (i.e. alkenes, alkynes, etc.), or to hydrosilylation and hydrogenation catalysis, then reactivity of the tetrylene intermediates should be addressed. Nevertheless, with Turn Over Frequencies (TOFs) of up 13,300 h^{-1}, the activity of these low-coordinate tetrylene catalysts rivals those of TM catalysts for related reactions (Scheme 42).[76]



Scheme 41. Reaction pathways for stoichiometric reactions replicating a catalytic cycle, using **96** and **29**.

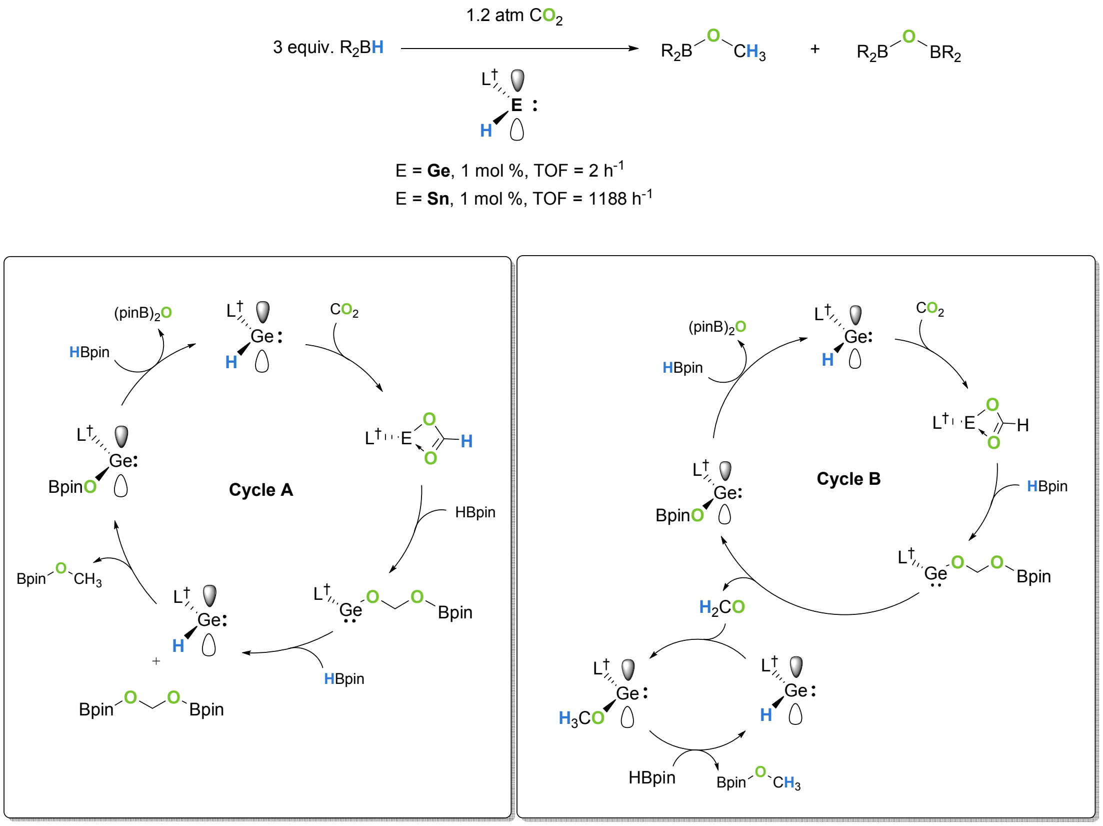


Scheme 42. General scheme for the hydroboration of aldehydes and ketones catalysed by **29** or **96**.

Due to warming of the Earth's atmosphere, which is has been linked to human-driven release of CO_2,[77] the utilisation of this green-house gas as a chemical feed stock has seen extreme attention over recent years.[78] Previously, single-site MG catalysts have been applied to the reduction of this gas, employing HBpin as the reductant, with Mg(II) and Ca(II) examples reported by Hill et al. (Mg: 10 mol% catalyst loading, 60 °C, TOF = 0.07 h^{-1}; 10 mol% catalyst loading, 60 °C, TOF = 0.1 h^{-1}), and one Ga(III) example reported by Aldridge et al. (10 mol% catalyst loading, 60 °C, TOF = 2.5 h^{-}

^{1}).[76(c),79] Tripodal-amine ligated alkali-metal tetraphenylborates have also been shown to catalyse the same reaction at ambient temperature, with TOFs of up to 10 h^{-1} at 10 mol% catalyst loading.[80] In this light, complexes **29** and **66** have been utilised in the catalytic hydroboration of CO_2 to [pinBOCH$_3$] or [catBOCH$_3$], with TOFs which parallel those for the most efficient TM systems, and far exceed those for related single-site MG catalysts discussed above (Scheme 43). For precatalyst **96** at 1 mol% loading, TOFs of up to 1188 h^{-1} were achieved, with HBcat as the reductant. To put this in context, a recently reported palladium thiolate catalyst was capable of reaching TOFs of 1780 h^{-1} (0.2 mol% catalyst loading).[81] Related nickel(II) thiolate complexes have recently been shown to be similarly as efficient in this reaction, with TOFs of up to 2400 h^{-1} (0.2 mol% catalyst loading).[82] Nevertheless, these TM complexes remain the most efficient catalysts for the chemical reduction of CO_2.

The mechanism for the catalytic reduction of CO_2 to methanol equivalents by **29** or **66** was subjected to an in-depth analysis both synthetically and computationally, elucidating two competing catalytic cycles, A and B, summarised in Scheme 43. Two points are of note: a) many transition states in both cycles rely on the low-coordinate nature of the catalyst centre, which allows for coordinative activation of intermediates and HBpin/cat; and b) intermediary [(L†)(pinBO)E:] (E = Ge or Sn) is common to both cycles, and ultimately its metathesis with one further equivalent of borane is paramount to the success of this cycle. Again, these aspects highlight the necessary points of design for tetrylene catalysts: low-coordination number to effect substrate activation and subsequent intermediate reactivity (also effected by ligand electronics).



Scheme 43. Completing catalytic cycles for the hydroboration of CO_2 using Ge^{II} hydride complex **29** (BR_2 = Bpin or Bcat).

9. Conclusions and Outlook

Catalysis will continue to be at the core of the synthetic chemical industry, and thus a prolific research area in both academic and industrial settings. Whilst countless research groups worldwide are focused on utilising TM-based catalytic systems, relatively few have taken a similar approach to MG systems, and in particular to heavier tetrylene-centred catalysis. Alongside the low toxicity and higher natural abundance of heavier tetrel elements, and in particular silicon, relative to commonly employed catalytically active precious metals, it certainly seems that the fascinating chemistry of the former elements should be exploited towards catalytic applications. Indeed, as has been summarised in this review, individual processes at the centre of TM catalysis, such as reversible alkene insertion, oxidative addition and reductive elimination reactions, have now been achieved in group 14 chemistry. Add to this our relatively recent knowledge of the effects of ligand design in direct relation to such chemistry, it seems that the stage is set for the development of group 14 based systems for TM-like catalytic transformations. We hope that this review helps to drive efforts in this direction.

Conflicts of Interest

There are no conflicts to declare.

Acknowledgements

CJ gratefully acknowledges funding from the Australian Research Council and The U.S. Air Force Asian Office of Aerospace Research and Development (grant FA2386-18-1-0125). TJH and MD thank Deutsche Forschungsgemeinschaft, DR 226/19-1 and Cluster of Excellence UniCat (ExC 314)

Notes and References

---

[1] P. Jutzi, *Angew. Chem Int. Ed.*, 1975, **14**, 232-245.

[2] D. E. Goldberg, D. H. Harris, M. F. Lappert, K. M. Thom, *J. Chem. Soc., Chem. Commun.*, 1976, **120**, 261-262.

[3] (a) R. West, M. J. Fink, and J. Michl, *Science*, 1981, **214**, 1343-1344; (b) M. Yoshifuji, I. Shima, and N. Inamoto, *J. Am. Chem. Soc.*, 1981, **103**, 4587-4589.

[4] (a) R. C. Fischer, and P. P. Power, *Chem. Rev.*, 2010, **110**, 3877–3923; (b) E. Rivard, *Chem. Soc. Rev.*, 2016, **45**, 989-1003.

[5] (a) Y. Mizuhata, T. Sasamori, and N. Tokitoh, *Chem. Rev.*, 2009, **109**, 3479–3511; (b) M. Asay, C. Jones, and M. Driess, *Chem. Rev.*, 2011, **111**, 354–396; (c) C. Marschner, *Eur. J. Inorg. Chem.*, 2015, 3805–3820.

[6] (a) G. H. Spikes, J. C. Fettinger, and P. P. Power, *J. Am. Chem. Soc.*, 2005, **127**, 12232–12233; (b) Y. Peng, M. Brynda, B. D. Ellis, J. C. Fettinger, E. Rivard, and P. P. Power, *Chem. Commun.*, 2008, 6042–6044; (c) J. Li, C. Schenk, C. Goedecke, G. Frenking, and C. Jones, *J. Am. Chem. Soc.*, 2011, **133**, 18622–18625; (d) A. V. Protchenko, K. H. Birjkumar, D. Dange, A. D. Schwarz, D. Vidovic, C. Jones, N. Kaltsoyannis, P. Mountford, and S. Aldridge, *J. Am. Chem. Soc.*, 2012, **134**, 6500–6503; (e) T. J. Hadlington, and C. Jones, *Chem. Commun.*, 2014, **50**, 2321-2323; (f) M. M. Juckel, J. Hicks, D. Jiang, L. Zhao, G. Frenking, and C. Jones, *Chem. Commun.*, 2017, **53**, 12692-12695.

---

[7] (a) Y. Peng, B. D. Ellis, X. Wang, J. C. Fettinger, and P. P. Power, *Science*, 2009, **325**, 1668-1670; (b) R. Rodriguez, D. Gau, T. Kato, N. Saffon-Merceron, A. D. Cozar, F. P. Cossio, and A. Baceiredo, *Angew. Chem. Int. Ed.*, 2011, **50**, 10414–10416; (c) T. J. Hadlington, J. Li, M. Hermann, A. Davey, G. Frenking, and C. Jones, *Organometallics*, 2015, **34**, 3175−3185; (d) T. Sasamori, T. Sugahara, T. Agou, K. Sugamata, J.-D. Guo, S. Nagase, and N. Tokitoh, *Chem. Sci.*, 2015, **6**, 5526–5530.

[8] (a) X. Wang, Z. Zhu, Y. Peng, H. Lei, J. C. Fettinger, and P. P. Power, *J. Am. Chem. Soc.*, 2009, **131**, 6912–6913; (b) D. Gau, R. Rodriguez, T. Kato, N. Saffon-Merceron, A. Czar, F. P. Cosso, and A. Baceiredo, *Angew. Chem.Int. Ed.*, 2011, **123**, 1124–1128; (c) J. Li, H. Hermann, G. Frenking, and C. Jones, *Angew. Chem. Int. Ed.*, 2012, **51**, 8611–8614.

[9] P. P. Power, *Nature*, 2010, **463**, 171–177.

[10] J. Zhao, A. S. Goldman, and J. F. Hartwig, *Science*, 2005, **307**, 1080-1082.

[11] (a) Y. Peng, B. D. Ellis, X. Wang, and P. P. Power, *J. Am. Chem. Soc.*, 2008, **130**, 12268–12269; (b) Y. Peng, J.-D. Guo, B. D. Ellis, Z. Zhu, J. C. Fettinger, S. Nagase, and P. P. Power, *J. Am. Chem. Soc.*, 2009, **131**, 16272–16282.

[12] R. Rodriguez, Y. Contie, R. Nougué, A. Baceiredo, N. Saffon-Merceron, J.-M. Sotiropoulos, and T. Kato, *Angew. Chem. Int. Ed.*, 2016, **55**, 14355 –14358.

[13] (a) G. C. Welch, R. R. San Juan, J. D. Masuda, and D. W. Stephan, *Science*, 2006, **314**, 1124-1126; (b) G. Erker, and D. W. Stephan, *Frustrated Lewis Pairs II: Expanding the Scope*, Springer, Heidelberg, 2013; (c) D. W. Stephan, and G. Erker, *Angew. Chem. Int. Ed.*, 2015, **54**, 6400–6441

[14] (a) R. Rodriguez, D. Gau, Y. Contie, T. Kato, N. Saffon-Merceron, and A. Baceiredo, *Angew. Chem. Int. Ed.*, 2011, **50**, 11492 –11495; (b) T. J. Hadlington, M. Hermann, G. Frenking, and C. Jones, *Chem. Sci.*, 2015, **6**, 7249–7257; (c)

[15] T. J. Hadlington, M. Hermann, G. Frenking, and C. Jones, *J. Am. Chem. Soc.*, 2014, **136**, 3028−3031.

[16] (a) G. Trinquier, *J. Am. Chem. Soc.*, 1990, **112**, 2130-2131; (b) Y. Apeloig, R. Pauncz, M. Karni, R. West, W. Steiner, and D. Chapman, *Organometallics*, 2003, **22**, 3250-3256.

[17] G. D. Frey, V. Lavallo, B. Donnadieu, W. W. Schoeller, and G. Bertrand, *Science*, 2007, **316**, 439-441.

[18] G. J. Kubas, R. R. Ryan, B. I. Swanson, P. J. Vergamini, and H. J. Wasserman, *J. Am. Chem. Soc.*, 1984, **106**, 451-452;

[19] For examples, see: (a) M. J. S. Gynane, M. F. Lappert, S. J. Miles, A. J. Carty, and N. J. Taylor, *J. Chem. Soc., Dalton Trans.*, 1977, **6**, 2009-2015; (b) M. F. Lappert, M. C. Misra, M. Onyszchuk, R. S. Rowe, P. P. Power, and M. J. Slade, *J. Orgonomet. Chem.*, 1987, **330**, 31-46.

[20] L. Zhao, M. Hermann, C. Jones, and G. Frenking, *Chem. Eur. J.*, 2016, **22**, 11728 –11735.

[21] S. K. Mandal, and H. W. Roesky, *Acc. Chem. Res.*, 2012, **45**, 298-307.

[22] A. V. Protchenko, J. I. Bates, L. M. A. Saleh, M. P. Blake, A. D. Schwarz, E. L. Kolychev, A. L. Thompson, C. Jones, P. Mountford, and S. Aldridge, *J. Am. Chem. Soc.*, 2016, **138**, 4555−4564.

[23] (a) J. F. Hartwig, *Inorg. Chem.*, 2007, **46**, 1936−1947; (b) P. L. Arrechea, and S. L. Buchwald, *J. Am. Chem. Soc.*, 2016, **138**, 12486−12493

[24] (a) S. Hong, and T. J. Marks, *Acc. Chem. Res.*, 2004, **37**, 673-686; (b) A. G. M. Barrett, M. R. Crimmin, M. S. Hill, and P. A. Procopiou, *Proc. R. Soc. A*, 2010, **466**, 927-963; (c) C. J. Weiss, and T. J. Marks, *Dalton Trans.*, 2010, **39**, 6576–6588.

[25] H. Bauer, M. Alonso, C. Färber, H. Elsen, J. Pahl, A. Causero, G. Ballmann, F. D. Proft, and S. Harder, *Nat. Catal.*, 2018, **1**, 40-47.

[26] B. E. Eichler, P. P. Power, *J. Am. Chem. Soc.*, 2000, **122**, 8785-8786.

[27] (a) R. S. Ghadwal, H. W. Roesky, S. Merkel, J. Henn, and D. Stalke, *Angew. Chem. Int. Ed.*, 2009, **121**, 5793–5796; (b) O. Chernov, G. Schnakenburg, and A. C. Filippou, *Angew. Chem. Int. Ed.*, 2009, **121**, 5797-5800; (c) R. S. Ghadwal, R. Azhakar, and H. W. Roesky, *Acc. Chem. Res.*, 2013, **46**, 444–456; (d) A. C. Filippou, Y. N. Lebedev, O. Chernov, M. Straßmann, and G. Schnakenburg, *Angew. Chem. Int. Ed.*, 2013, **52**, 6974 –6978.

[28] B. Marciniec, *Hydrosilylation*, Springer, Netherlands, **2009**.

[29] R. Kinjo, M. Ichinohe, and A. Sekiguchi, *J. Am. Chem. Soc.*, 2007, **129**, 26–27.

---

[30] K. Takeuchi, M. Ikoshi, M. Ichinohe, and A. Sekiguchi, *J. Am. Chem. Soc.*, 2010, **132**, 930–931

[31] T. Agou, Y. Sugiyama, T. Sasamori, H. Sakai, Y. Furukawa, N. Takagi, J.-D. Guo, S. Nagase, D. Hashizume, and N. Tokitoh, *J. Am. Chem. Soc.*, 2012, **134**, 4120−4123.

[32] A. Jana, D. Leusser, I. Objartel, H. W. Roesky, and D. Stalke, *Dalton Trans.*, 2011, **40**, 5458–5463.

[33] B. Blom, S. Enthaler, S. Inoue, E. Irran, and M. Driess, *J. Am. Chem. Soc.*, 2013, **135**, 6703−6713.

[34] S. M. I. Al-Rafia, A. C. Malcolm, R. McDonald, M. J. Ferguson, and E. Rivard, *Chem. Commun.*, 2012, **48**, 1308–1310.

[35] M. Stoelzel, C. Präsang, S. Inoue, S. Enthaler, and M. Driess, *Angew. Chem. Int. Ed.*, 2012, **51**, 399–403.

[36] S. Inoue, and C. Eisenhut, *J. Am. Chem. Soc.*, 2013, **135**, 18315−18318.

[37] D. Lutters, C. Severin, M. Schmidtmann, and T. Müller, *J. Am. Chem. Soc.*, 2016, **138**, 6061−6067.

[38] C. Eisenhut, N. C. Breit, T. Szilvási, E. Irran, and S. Inoue, *Eur. J. Inorg. Chem.*, 2016, 2696–2703.

[39] R. Rodriguez, D. Gau, T. Kato, N. Saffon-Merceron, A. D. Cózar, F. P. Cossío, and A. Baceiredo, *Angew. Chem. Int. Ed.*, 2011, **123**, 10598–10600.

[40] F. Lips, J. C. Fettinger, A. Mansikkamaki, H. M. Tuononen, and P. P. Power, *J. Am. Chem. Soc.*, 2014, **136**, 634−637.

[41] Y. Ding, H. Hao, H. W. Roesky, M. Noltemeyer, and H.-G. Schmidt, *Organometallics*, 2001, **20**, 4806-4811.

[42] L. W. Pineda, V. Jancik, K. Starke, R. B. Oswald, and H. W. Roesky, *Angew. Chem. Int. Ed.*, 2006, **45**, 2602–2605.

[43] S. L. Choong, W. D. Woodul, C. Schenk, A. Stasch, A. F. Richards, and C. Jones, *Organometallics*, 2011, **30**, 5543–5550.

[44] S. Khan, P. P. Samuel, R. Michel, J. M. Dieterich, R. A. Mata, J.-P. Demers, A. Lange, H. W. Roesky, and D. Stalke, *Chem. Commun.*, 2012, **48**, 4890–4892.

[45] Y. Xiong, T. Szilvasi, S. Yao, G. Tan, and M. Driess, *J. Am. Chem. Soc.*, 2014, **136**, 11300−11303.

[46] K. C. Thimer, S. M. I. Al-Rafia, M. J. Ferguson, R. McDonald and E. Rivard, *Chem. Commun.*, 2009, 7119–7121.

[47] S. M. I. Al-Rafia, A. C. Malcolm, S. K. Liew, M. J. Ferguson, and E. Rivard, *J. Am. Chem. Soc.*, 2011, **133**, 777–779.

[48] (a) A. K. Swarnakar, S. M. McDonald, K. C. Deutsch, P. Choi, M. J. Ferguson, R. McDonald, and E. Rivard, *Inorg. Chem.*, 2014, **53**, 8662−8671; (b) S. M. I. Al-Rafia, A. C. Malcolm, S. K. Liew, M. J. Ferguson, R. McDonald and E. Rivard, *Chem. Commun.*, 2011, **47**, 6987–6989.

[49] E. Rivard and P. P. Power, *Dalton Trans.*, 2008, 4336–4343.

[50] (a) S. M. I. Al-Rafia, A. C. Malcolm, R. McDonald, M. J. Ferguson, and E. Rivard, *Angew. Chem. Int. Ed.*, 2011, **50**, 8354–8357; (b) S. M. I. Al-Rafia, M. R. Momeni, M. J. Ferguson, R. McDonald, A. Brown, and E. Rivard, *Organometallics*, 2013, **32**, 6658−6665.

[51] A. F. Richards, A. D. Phillips, M. M. Olmstead, and P. P. Power, *J. Am. Chem. Soc.*, 2003, **125**, 3204-3205.

[52] T. J. Hadlington, M. Hermann, J. Li, G. Frenking, and C. Jones, *Angew. Chem. Int. Ed.*, 2013, **52**, 10199 –10203.

[53] T. J. Hadlington, B. Schwarze, E. I. Izgorodina, and C. Jones, *Chem. Commun.*, 2015, **51**, 6854—6857.

[54] A. Jana, D. Ghoshal, H. W. Roesky, I. Objartel, G. Schwab, and D. Stalke, *J. Am. Chem. Soc.*, 2009, **131**, 1288–1293.

[55] A. Jana, G. Tavcar, H. W. Roesky, and M. John, *Dalton Trans.*, 2010, **39**, 9487–9489.

[56] G. Tan, W. Wang, B. Blom, and M. Driess, *Dalton Trans.*, 2014, **43**, 6006–6011.

[57] A. Jana, H. W. Roesky, and C. Schulzke, *Dalton Trans.*, 2010, **39**, 132–138.

[58] O. T. Summerscales, C. A. Caputo, C. E. Knapp, J. C. Fettinger, and P. P. Power, *J. Am. Chem. Soc.*, 2012, **134**, 14595−14603.

[59] E. Rivard, R. C. Fischer, R. Wolf, Y. Peng, W. A. Merrill, N. D. Schley, Z. Zhu, L. Pu, J. C. Fettinger, S. J. Teat, I. Nowik, R. H. Herber, N. Takagi, S. Nagase, and P. P. Power, *J. Am. Chem. Soc.*, 2007, **129**, 16197-16208.

[60] Y. Peng, M. Brynda, B. D. Ellis, J. C. Fettinger, E. Rivard, and P. P. Power, *Chem. Commun.*, 2008, 6042–6044.

[61] C. P. Sindlinger, and L. Wesermann, *Chem. Sci.*, 2014, **5**, 2739–2746.

[62] C. P. Sindlinger, W. Grahneis, F. S. W. Aicher, and L. Wesemann, *Chem. Eur. J.*, 2016, **22**, 7554–7566.

[63] C. P. Sindlinger, A. Stasch, H. F. Bettingerc, and L. Wesemann, *Chem. Sci.*, 2015, **6**, 4737–4751.

---

[64] S. M. I. Al-Rafia, O. Shynkaruk, S. M. McDonald, S. K. Liew, M. J. Ferguson, R. McDonald, R. H. Herber, and E. Rivard, *Inorg. Chem.*, 2013, **52**, 5581−5589.

[65] A. Jana, H. W. Roesky, C. Schulzke, and A. Dring, *Angew. Chem. Int. Ed.*, 2009, **48**, 1106–1109.

[66] A. Jana, H. W. Roesky, C. Schulzke, and P. P. Samuel, *Organometallics*, 2010, **29**, 4837–4841.

[67] S. Wang, M. L. McCrea-Hendrick, C. M. Weinstein, C. A. Caputo, E. Hoppe, J. C. Fettinger, M. M. Olmstead, and P. P. Power, *J. Am. Chem. Soc.*, 2017, **139**, 6596−6604.

[68] S. Wang, M. L. McCrea-Hendrick, C. M. Weinstein, C. A. Caputo, E. Hoppe, J. C. Fettinger, M. M. Olmstead, and P. P. Power, *J. Am. Chem. Soc.*, 2017, **139**, 6586−6595.

[69] Cotton, F. A.; Wilkinson, G.; Murillo, C. A.; Bochmann, M. *Advanced Inorganic Chemistry*, 6th ed., Wiley: New York, 1999.

[70] X. Wang, and L. Andrews, *J. Am. Chem. Soc.*, 2003, **125**, 6581-6587.

[71] W. P. Neumann, and K. Kühlein, *Angew. Chem., Int. Ed. Engl.*, 1965, **4**, 784−785.

[72] L. Pu, B. Twamley, and P. P. Power, *J. Am. Chem. Soc.*, 2000, **122**, 3524-3525.

[73] J. Schneider, C. P. Sindlinger, K. Eichele, H. Schubert, and L. Wesemann, *J. Am. Chem. Soc*., 2017, **139**, 6542−6545.

[74] J. Vícha, R. Marek, and M. Straka, *Inorg. Chem.*, 2016, **55**, 10302−10309.

[75] N. Takagi, and S. Sakaki, *J. Am. Chem. Soc.*, 2013, **135**, 8955−8965.

[76] (a) L. Koren-Selfridge, I. P. Query, J. A. Hanson, N. A. Isley, I. A. Guzei, and T. B. Clark, *Organometallics*, 2010, **29**, 3896-3900; (b) A. A. Oluyadi, S. Ma, and C. N. Muhoro, *Organometallics*, 2013, **32**, 70-78; (c) C. C. Chong, and R. Kinjo, *ACS Catal.*, 2015, **5**, 3238−3259.

[77] (a) *Climate Change 2007: Synthesis Report*. Intergovernmental Panel on Climate Change: Geneva, 2007; (b) K. S. Lackner, S. Brennan, J. M. Matter, A.-H. A. Park, A. Wright, and B. van der Zwaan, *Proc. Natl. Acad. Sci. USA*, 2012, **109**, 13156−13162.

[78] M. Aresta, *Carbon Dioxide as a Chemical Feedstock*, WileyVCH, Weinheim, Germany, 2010.

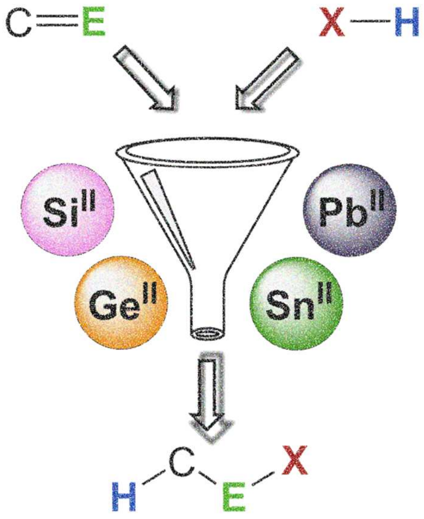
[79] (a) M. D. Anker, M. Arrowsmith, P. Bellham, M. S. Hill, G. KociokKohn, D. J. Liptrot, M. F. Mahon, and C. Weetman, *Chem. Sci.*, 2014, **5**, 2826–2830; (b) J. A. B. Abdalla, I. M. Riddlestone, R. Tirfoin, and S. Aldridge, *Angew. Chem., Int. Ed.*, 2015, **54**, 5098−5102.

[80] D. Mukherjee, H. Osseili, T. P. Spaniol, and J. Okuda, *J. Am. Chem. Soc.*, 2016, **138**, 10790−10793.

[81] Q.-Q. Ma, T. Liu, S. Li, J. Zhang, X. Chen, and H. Guan, *Chem. Commun.*, 2016, **52**, 14262−14265.

[82] T. Liu, W. Meng, Q.-Q. Ma, J. Zhang,* H. Li, S. Li, Q. Zhao, and X. Chen, *Dalton Trans.*, 2017, **46**, 4504–4509.

ToC Entry



This review summarises advances in the chemistry of group 14 element(II) hydride complexes, including their recent introduction as efficient, "transition metal-like" catalysts in organic synthesis.