

## GROUP 14 TRANSITION METAL MIMICRY

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### INTRODUCTION

Transition metals have been privileged in their use in catalysis throughout modern chemistry. Main group compounds however have been relegated to use as transmetalating reagents, substrates, ligands, and additives. It is generally considered that main group compounds have difficulty activating small molecules making them ineffective as catalysts. In the last 20 years group 14 complexes have championed the main group and demonstrated their ability to perform migratory insertion, oxidative addition, and perform allylation.

### DIVALENT GROUP 14 HYDRIDES

In 2000, Power *et al.* reported the first Sn(II) hydride species taking advantage of *m*-terphenyl ligand to yield a trans dihydrogen bridged  $M_2H_2L_2$  dimer.<sup>1)</sup> The dimer was generated by the addition of a hydride source to a solution of (*m*-terphenyl)SnCl, this result fits the trend observed that low valent group 14 elements are stabilized by increasing the bulk of the organic substituents.<sup>2</sup> These metal hydride dimers are profound in existence but provide no useful reactivity. Shortly after this report Roesky *et al.* corresponding with Power reported Sn(II) and Ge(II) hydrides with diketiminato ligands.<sup>3</sup> The diketiminato tetragen

hydrides performed hydrostannylation of  $CO_2$ , ketones, activated alkynes, and cyanamides at ambient temperatures.<sup>4</sup> In 2010, Rivard *et al.* reported both Sn(II) and Ge(II) hydrides stabilized with a NHC ligand and a Lewis acid.<sup>4</sup> The NHC stabilized Sn(II) hydride executes hydrostannylation of ketones but continues and does migratory insertion across ketones with the NHC ligand. The diketiminato ligand system was adapted to for the isolation of a monomeric Si(II) hydride.<sup>6</sup> The reactivity is diminished towards hydrometallation but the increase in chemo selectivity is promising for diamine tetragen hydride catalysis.

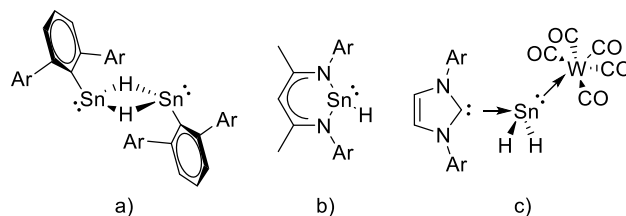


Figure 1: Group 14 hydrides, a) Ar = 2,4,6-tri-isopropylphenyl, b) and c) Ar = 2,6-di-isopropylphenyl

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### REACTIONS OF $\pi$ -SYSTEMS WITH TETRALENES

The first report of a silirane was in 1972 by Seyferth *et al.* and was accomplished by the intramolecular Grignard reaction of a dialkyl silane.<sup>7</sup> This was followed by the first example of silacyclopropenes created by the addition of silenes to alkynes.<sup>8</sup> For many years the use of acyclic silenes

to do oxidative cyclization with alkenes and alkynes was performed. Recent reports of acyclic silenes were explored to generate silacyclopropenes from alkynes.<sup>9</sup> The more interesting aspect of this reaction is the transformation with diphenyl acetylenes and dienes, yielding disubstituted silacyclopropenes and silacyclopentenes respectively. These cycles are made under mild conditions and can then be further elaborated to interesting compounds.

## ALLYLATION

The allylation of carbonyls has been known for a significant period and demonstrated with many Group-14 elements as handles. Most of these transformations are what is called type 2 allylation with an acyclic transition state. Type 1 allylation with Si was developed in the 90's and was even rendered asymmetric.<sup>10</sup> The use of transition metal catalysis overtook these reactions as state of the art providing better enantioselectivity and similar yields. In 2002 through the use of 5 membered Si heterocycle reagent based off pseudoephedrine the enantioselective allylation of aldehydes was achieved.<sup>11</sup> This reaction has been applied in multiple total synthesis since.

## CONCLUSION

The still limited transformations afforded by modern group 14 complexes provide reasonable alternatives to classical transition metal transformations in a few cases granting improved reactivity but in most just reducing the cost of performing the transformation.

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