

Facile Access to Ni⁰ π -Complexes of Silicon-Heteroatom Multiple Bonds

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Classical transition-metal (TM) π -complexes of carbon-carbon and carbon-heteroatom multiple bonds are of paramount importance in a plethora of catalytic transformations, and are well understood on electronic grounds.^[1] On the contrary, heavier congeners of such complexes, involving Si-Pb, are poorly studied, with very few examples reported in the literature.^[2] We have now shown that, utilising acyclic-silylene Ni⁰ complex **1**,^[3] π -complexes involving Si=E bonds (E = C, N, P, As, and O) can be readily generated through direct addition of diazo or azide species, or *via* salt-metathesis methods.^[4] We have shown that these remarkable TM complexes undergo reactivity reminiscent of key steps in catalytic cycles, and in some cases undergo dynamic rearrangement processes in solution, for example forming a dimeric Ni-(sila)phosphindene complex. These results have shed further light on the stark contrasts between classical carbon-based TM π -complexes and their heavier congeners, and may lead us to a greater understanding of common catalytic cycles.

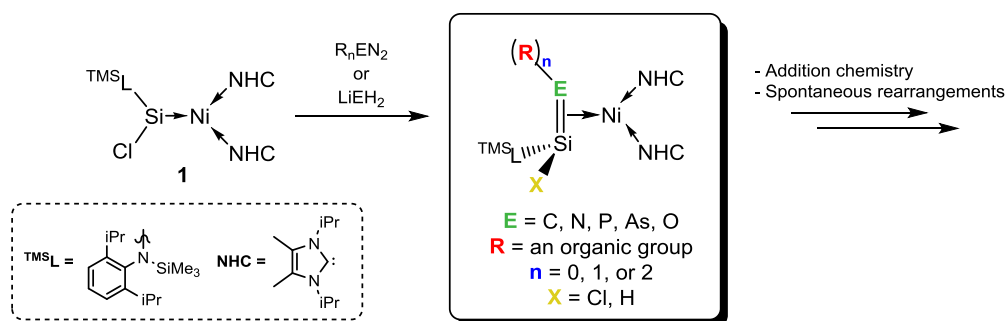


Figure 1. Accessing silene π -complexes, and their further reactivity.

[1] F. A. Cotton, G. Wilkinson; *Advanced Inorganic Chemistry* (Wiley, 1988).

[2] For examples, see: L. J. Procopio, P. J. Carroll, and D. H. Berry, *J. Am. Chem. Soc.*, **1991**, *113*, 1870; D. Bravo-Zhivotovskii, H. Peleg-Vasserman, M. Kosa, G. Molev, M. Botoshanskii, and Y. Apeloig, *Angew. Chem. Int. Ed.*, **2004**, *43*, 745.

[3] T. J. Hadlington, T. Szilvasi, and M. Driess, *Angew. Chem. Int. Ed.*, **2017**, *56*, 7470.

[4] T. J. Hadlington, T. Szilvasi, M. Driess, *Angew. Chem. Int. Ed.* **2017**, *56*, 14282.