

Pendant-phosphino Amides: A novel ligand class displaying diverse bonding capabilities

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Ligand design plays an undeniably central role in countless facets of chemistry, from templating materials to efficient catalytic regimens. Amongst the most prominent ligands utilized in organometallic chemistry are bulky amides,^{[1][2]} the most notable of which perhaps being the $[(\text{Me}_3\text{Si})_2\text{N}]^-$ fragment which is ubiquitous in low-valent metal systems. Such ligands are employed due to their inherent bulk, which kinetically stabilizes otherwise unattainable molecular species. Moving beyond the isolation of laboratory curiosities, the further reactivity of the stabilized species can be hampered by the excessive steric bulk of utilized ligands. To overcome this, we introduce a family of chelating phosphino-amide ligands,^{[3][4][5]} which present considerable steric protection whilst also demonstrating a high degree of binding fluxionality. This can lead to the activation of otherwise inert element-element bonds, lead to diverse bonding motifs, and even directly partake in bonding. A selection of case-studies will be discussed, demonstrating these points, and looking towards the future of this easily accessible, readily diversified ligand class.

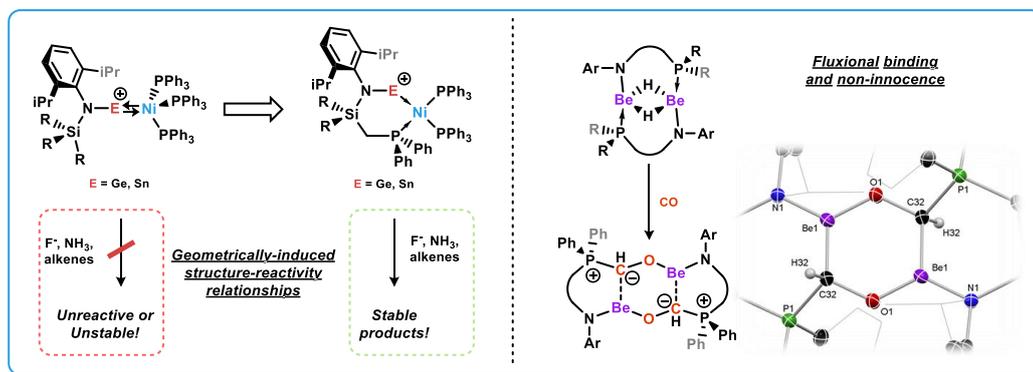


Figure 1. Demonstrating the utility of pendant-phosphino amide ligands

- [1] Lappert H, Protchenko A, Power P, Seeber A. Metal Amide Chemistry. John Wiley and Sons, Inc., New Jersey, 2009.
- [2] Kays DL. Extremely bulky amide ligands in main group chemistry. *Chem. Soc. Rev.* **2016**, *45*, 1004-1018.
- [3] Keil PM, Szilvasi T, Hadlington TJ. Reversible metathesis of ammonia in an acyclic germylene-Ni⁰ complex. *Chem. Sci.*, 2021,**12**, 5582-5590
- [4] Keil PM, Hadlington TJ. Geometrically Constrained Cationic Low-Coordinate Tetrylenes: Highly Lewis Acidic σ -Donor Ligands in Catalytic Systems. *Angew. Chemie. Int. Ed.*, **2021**, DOI: 10.1002/ange.202114143.
- [5] Hadlington TJ, Szilvasi T. Accessing the Main-Group Metal Formyl Scaffold through CO-Activation in Beryllium Hydride Complexes. *Nature Commun.*, **2021**, accepted article.