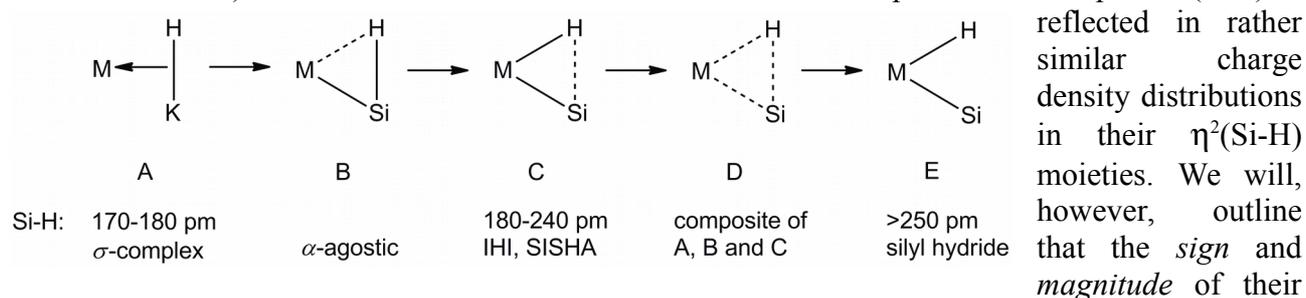


On the Saga of J(Si-H) coupling constants

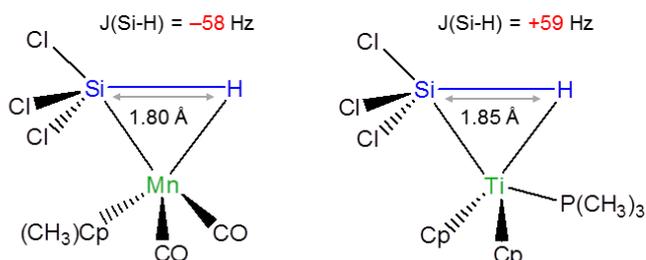
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The coordination of a transition metal atom (M) by a Si-H unit yields the perhaps largest spectrum of non-classical bonding types formed by a three-membered molecular moiety (Scheme; adopted from reference 1).^[1] The close structural and electronic relationship between complexes (A-E) is



$J(\text{Si-H})$ spin-spin coupling constants (SSCCs) can be used to discriminate between the various bonding modes (A-E). We will also show how the sign and magnitude of these SSCCs can be related to the charge and spin density distribution in (A-E) by considering the spin-induced core polarization at the silicon atoms.



Transition metal silane complexes as representatives of each bonding scenario (A-E) have been successfully isolated in the meantime and could be identified in many cases as key-intermediates of metal-catalyzed Si-H bond activation processes like hydrosilation or related metal-mediated transformations. An improved understanding of the origin and nature of the various non-classical bonding scenarios displayed by these complexes may thus assist in choice of suitable metal fragments and substrates in catalytic processes. We will therefore also outline charge density criteria, which provide the key parameters for the design and chemical control of catalysts for Si-H and related C-H activation processes.^[2]

[1] J. Y. Corey *Chem. Rev.* **2011**, 111, 863-1071.

[2] (a) W. Scherer, V. Herz, A. Brück, Ch. Hauf, F. Reiner, S. Altmannshofer, D. Leusser, D. Stalke, *Angew. Chem. Int. Ed.* **2011**, 50, 2845-2849; (b) W. Scherer, P. Meixner, J. E. Barquera-Lozada, C. Hauf, A. Obenhuber, A. Brück, D. J. Wolstenholme, K. Ruhland, D. Leusser, D. Stalke, *Angew. Chem. Int. Ed.* **2013**, 52, 6092-6096; (c) W. Scherer, A. C. Dunbar, J. E. Barquera-Lozada, D. Schmitz, G. Eickerling, D. Kratzert, D. Stalke, A. Lanza, P. Macchi, N. P. M. Casati, J. E. Allah, Ch. Kuntscher, *Angew. Chem. Int. Ed.* **2015**, 54, 2505-2509.