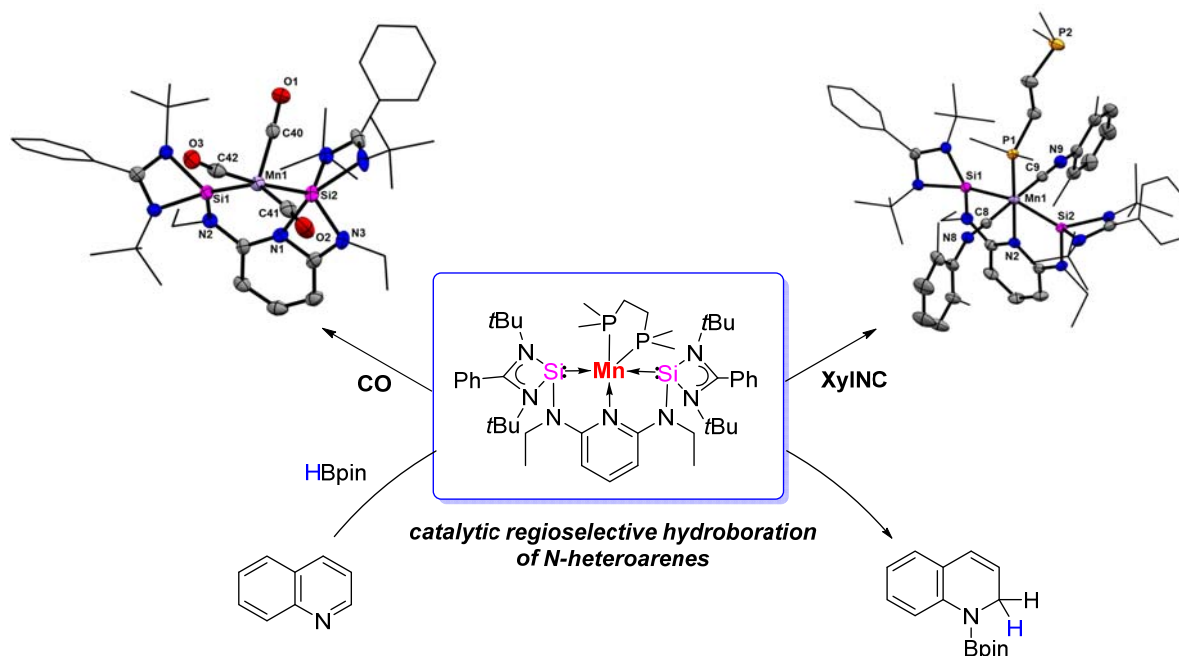


Synthesis and reactivity of bis(silylene)pyridine stabilized low-valent manganese complex: A bis(silylene) analogue of Mn(CO)₅ radical

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Bis-silylenes are known to serve as effective ligands to stabilize even the first-row metal centers Fe, Co, Ni in low oxidation states.^{1,2} Despite of numerous reports on silylene-TM(0) complexes, examples of Mn(0) complexes are rare. Here in this work, using the potentially tridentate *N,N'*-bis(*N*-heterocyclic silylene)pyridine [SiNSi] pincer-type ligand, 2,6-*N,N'*-diethyl-bis[*N,N'*-di-tert-butyl(phenylamindinato)silylene] diaminopyridine, led to the first isolable bis(silylene)pyridine-stabilized manganese(0) complex, {κ³-[SiNSi]Mn(dmpe)} (**4**) (dmpe = (Me₂P)₂C₂H₄), which represents an isolobal 17 VE analogue of the elusive Mn(CO)₅ radical. The compound is accessible through the reductive dehalogenation of the corresponding dihalido (SiNSi)Mn(II) complexes **1** (Cl) and **2** (Br) with potassium graphite. Exposing **4** towards the stronger π-acceptor ligands CO and 2,6-dimethylphenyl isocyanide afforded the related Mn(0) complexes κ²-[SiNSi]Mn(CO)₃ (**5**) and κ³-[SiNSi]Mn(CNXyl)₂(κ¹-dmpe) (**6**), respectively. Remarkably, the stabilization of Mn(0) in the coordination sphere of the [SiNSi] ligand favors the d⁷ low-spin electronic configuration, as suggested by EPR spectroscopy and SQUID measurements. The suitability of **4** acting as a superior pre-catalyst in regioselective hydroboration of quinolines has also been studied.



References:

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