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, \( \kappa^3\text{-[SiNSi]Mn(dmpe)} \) (4) (dmpe = \((\text{Me}_2\text{P})_2\text{C}_2\text{H}_4\)), 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 \( \pi \)-acceptor ligands CO and 2,6-dimethylphenyl isocyanide afforded the related Mn(0) complexes \( \kappa^2\text{-[SiNSi]Mn(CO)}_3 \) (5) and \( \kappa^3\text{-[SiNSi]Mn(CNXyl)}_2(\kappa^1\text{-dmpe}) \) (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: