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Preliminary communication

COORDINATION CHEMISTRY OF SILOLES: SYNTHESIS AND REACTIVITY OF NEW SILICON-DISUBSTITUTED (η^4-SILOLE) COMPLEXES

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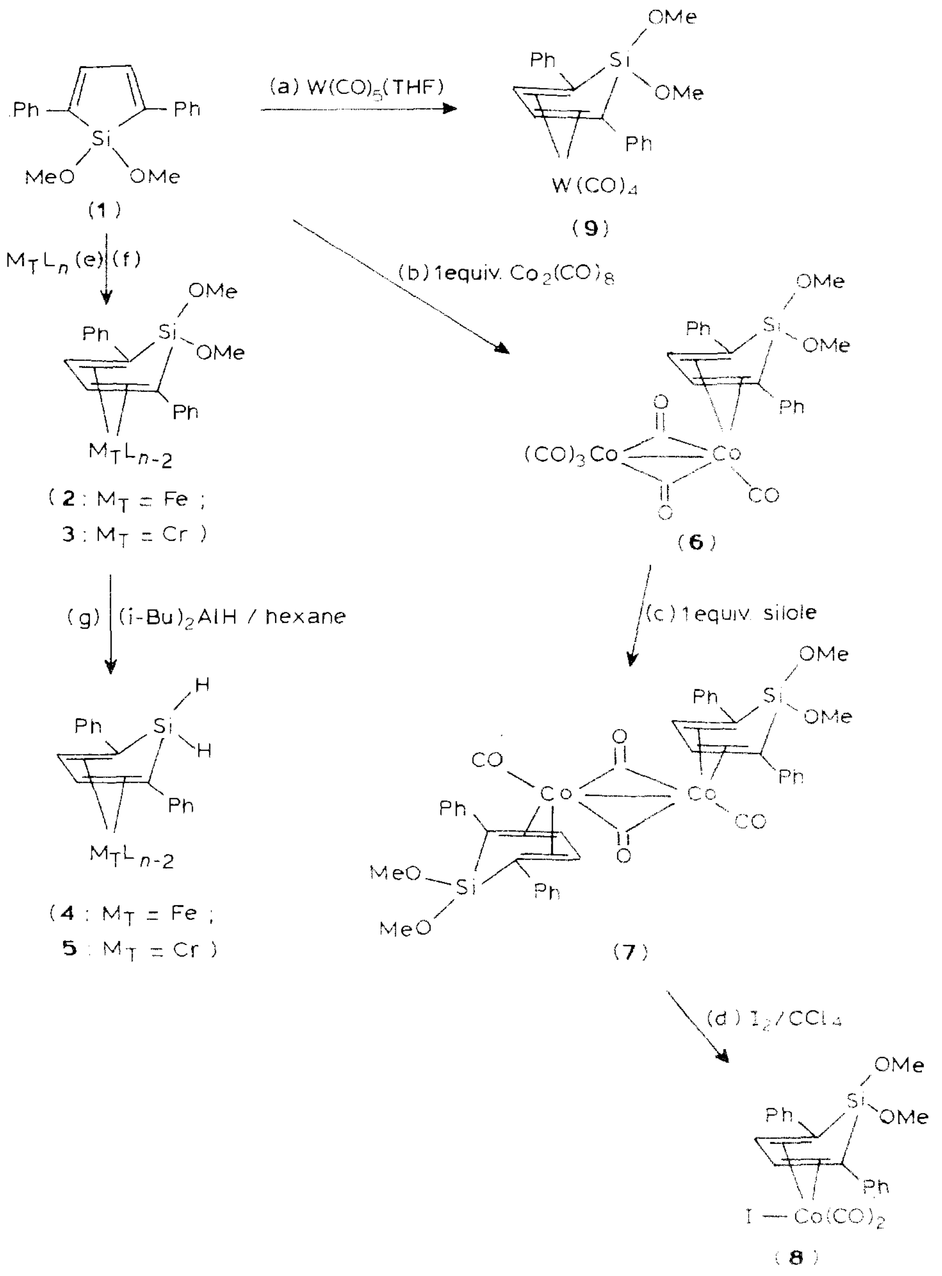
Summary

The synthesis of some new silicon-disubstituted (η^4-2,5-diphenylsilacyclopentadiene)tricarbonyliron complexes are described. Stable complexes with various functional groups attached at silicon have been isolated. The *exo* position shows an enhanced reactivity, and cleavage of an Si–H bond at this position occurs selectively with retention.

There is interest in the possibility of generating or detecting a (η^5-silacyclopentadiene) metal complex by reaction of a coordinated η^4-silole [1]. In this context, we recently reported the synthesis of functional 2,5-diphenylsiloles [2] and their use as η^4-ligands [3]. Herein, we describe the synthesis of silicon-disubstituted η^4-silole complexes and preliminary results on the reactivity at the silicon atom.

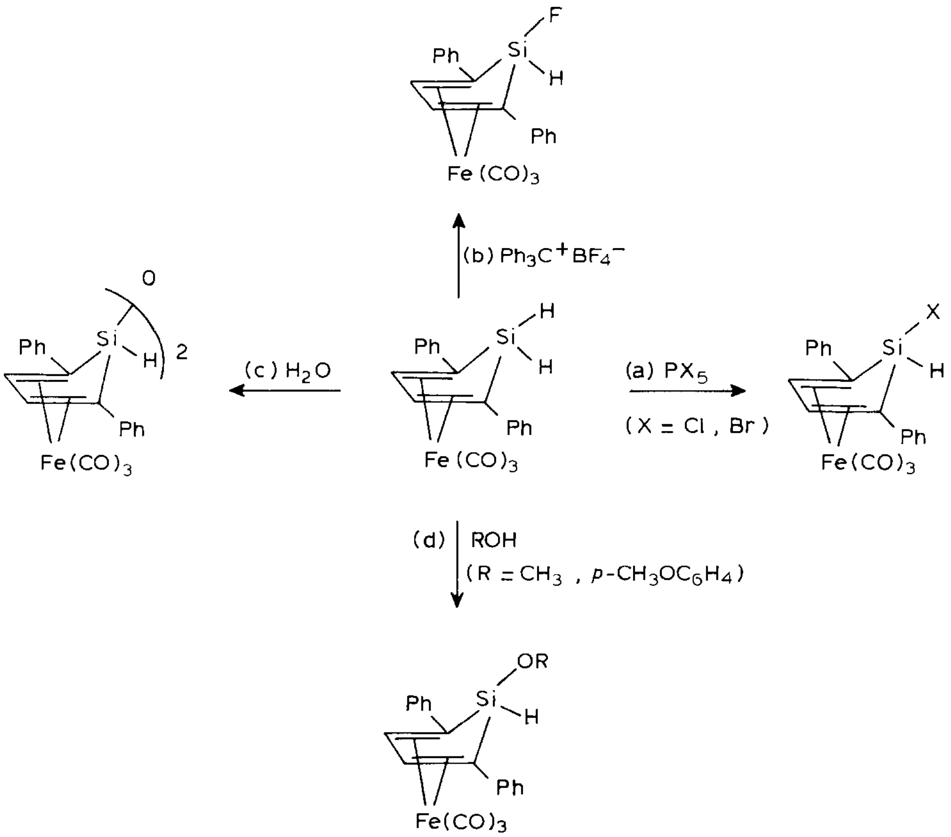
Treatment of 1,1-dimethoxy-2,5-diphenylsilacyclopentadiene [2] (**1**) with one equivalent of $Fe_2(CO)_9$ in toluene at 50°C gives a good yield (60%) of (η^4-1,1-dimethoxy-2,5-diphenylsilacyclopentadiene)tricarbonyliron (**2**) (Scheme 1). The related reaction between **1** and $Cr(COD)(CO)_4$ leads to the corresponding η^4-silacyclopentadiene derivative, **3**. The reduction of **2** and **3** with $(i\text{-}Bu)_2AlH$ provides the stable dihydro complexes **4** and **5**, respectively. **1** reacts with octacarbonyldicobalt to give a monosubstituted η^4-silacyclopentadiene complex, **6**. As observed previously [3], the monosubstituted cobalt complex **6** reacts with an excess of silole to give the corresponding disubstituted derivative **7**. Treatment of **7** with iodine in carbon tetrachloride [4] gives (η^4-1,1-dimethoxy-2,5-diphenylsilacyclopentadiene)iododicarbonylcobalt (**8**). Finally, reaction of **1** with $W(CO)_5(THF)$ proceeds similarly to give the (η^4-silole)$W(CO)_4$ complex **9**.

The lability of the *exo* substituent [5,6] and the displacement of both *exo* and *endo* substituents with retention of configuration at silicon have been reported [7]; the steric hindrance of the metallic moiety does not control the reactivity and the stereochemical outcome at silicon. The availability of this new silicon-disubstituted



SCHEME 1. (a) THF, r.t., 15 h, 50%; (b) hexane, r.t., 7 h, 77%; (c) hexane, 40 °C, 4 h, 82%; (d) CCl_4, r.t., 1 h, 80%; (e) Fe: toluene, 50 °C, 15 h, 60%; (f) Cr: hexane, 50 °C, 12 h, 55%; (g) hexane, r.t., 1 h, 70%.

(η^4-silole) derivatives allow us to make a direct comparison of the relative reactivities of *exo* and *endo* substituents both bonded to the same silicon atom. The data observed in the case of the (η^4-1,1-dihydrogeno-2,5-diphenylsilacyclopentadiene)-tricarbonyliron complex, **4**, are summarized in scheme 2.



SCHEME 2. (a) X = Cl: CCl_4, r.t., 1 h, 71%; X = Br: THF, −40 °C to r.t., 0.5 h, 82%; (b) CH_2Cl_2, r.t., 2 h, 82%; (c) acetone, 50 °C, 0.5 h, 89%; (d) R = OCH_3: hexane, r.t., 3 h, 84%; R = p-$CH_3OC_6H_4$: hexane, 40 °C, 3 h, 73%.

Whatever the nature of the reagent (PX_5, ROH, or BF_4^-), reactions lead selectively to the *exo* isomer in good yields (70–100%); the position of the hydrogen atom bonded to silicon, i.e., *endo* or *exo* with respect to the $Fe(CO)_3$ moiety, can be unequivocally assigned by ^1H NMR spectroscopy [8]. Cleavages of the Si–H bond are well-known to occur with retention of configuration at silicon [9]. Retention was also demonstrated in the case of the (η^4-1-hydrogeno-1-*endo*-methyl-2,3,4,5-tetraphenylsilacyclopentadiene)tricarbonyliron [5,6]. It is thus, evident that our results are clearly consistent with an enhanced reactivity of the *exo*-Si–H bond and its selective cleavage with retention.

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