

Preliminary communication

THE CHEMISTRY OF SILOLES. SYNTHESIS AND REACTIONS OF η^6 -[1-METHYL-1-(TRIMETHYLSILYL)DIBENZOSILACYCLOPENTADIENE]CHROMIUM TRICARBONYL*

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Summary

η^6 -[1-Methyl-1-(trimethylsilyl)dibenzosilacyclopentadiene]chromium tricarbonyl (II) was prepared by the reaction of 1-methyl-1-(trimethylsilyl)dibenzosilole with chromium hexacarbonyl. The reaction of II with methyllithium in THF gave η^6 -(1,1-dimethyldibenzosilacyclopentadiene)chromium tricarbonyl. Similar reaction of II with butyllithium, followed by oxidation, gave 1-butyl-1-methyldibenzosilole and 1,1-dibutyldibenzosilole, while reaction with (methyl-diphenylsilyl)lithium under similar conditions afforded 1-methyl-4-(methyl-diphenylsilyl)-1-(trimethylsilyl)dibenzosilole.

Recently, we found that the reaction of 1-methyl-1-(trimethylsilyl)dibenzosilole with an excess of an alkylolithium in THF affords a transmetalation product, 1,1-dialkyldibenzosilole in quantitative yield [1,2], while reaction of (methyl-diphenylsilyl)lithium under similar conditions, gives a dibenzosilacyclopentadienide anion in high yield [3]. In order to learn more about the chemical behavior of the dibenzosilole derivative, we have prepared η^6 -[1-methyl-1-(trimethylsilyl)dibenzosilacyclopentadiene]chromium tricarbonyl and investigated its chemical behavior toward organolithium reagents**.

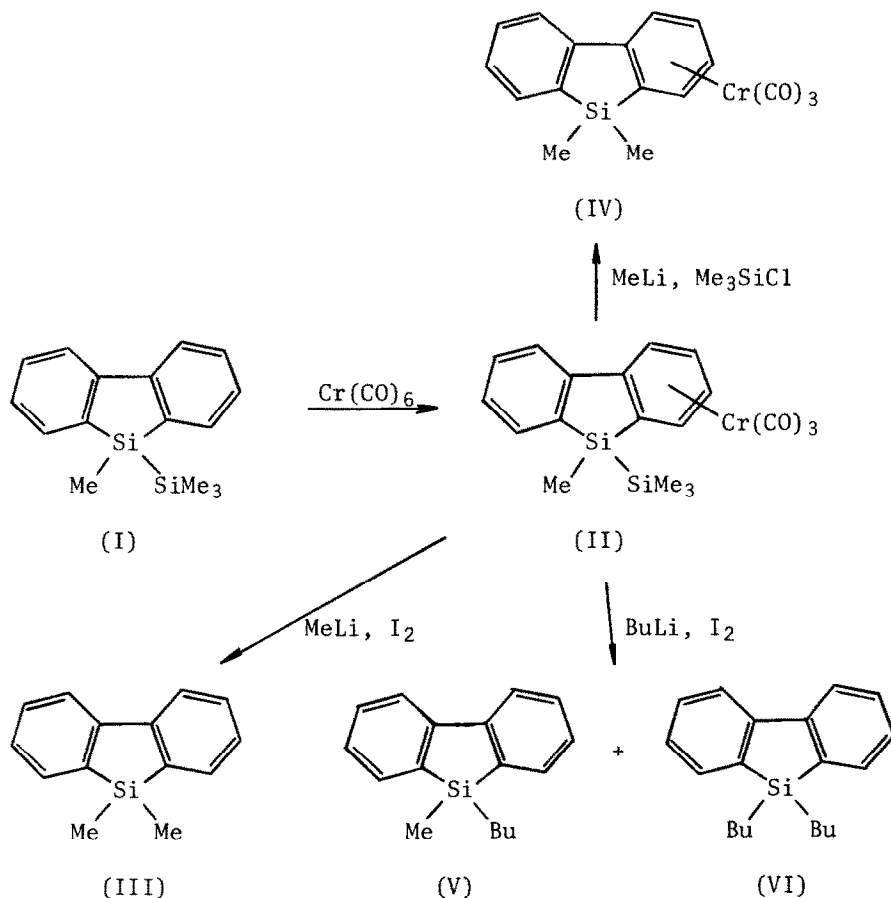
When a solution of 1-methyl-1-(trimethylsilyl)dibenzosilole (I) (16.4 mmol) and chromium hexacarbonyl (4.9 mmol) in a 1/2 mixture of glyme and diglyme [6] was refluxed for 24 h, yellow crystals identified as η^6 -[1-methyl-1-(trimethylsilyl)dibenzosilacyclopentadiene]chromium tricarbonyl (II) (m.p.

*Dedicated to Professor Makoto Kumada.

**Transition metal complexes of 2,5-diphenyl- and 2,3,4,5-tetraphenyl-silole have been reported, see refs. 4 and 5.

121–123°C, dec.) were obtained in 57% yield. The ^1H NMR spectroscopic analysis of II indicated it to be a mixture of *exo* and *endo* isomers in a ratio of 4/1 (^1H NMR δ (ppm) 0.10 (s, *exo*-Me₃Si), 0.33 (s, *endo*-Me₃Si), 0.44 (s, *endo*-MeSi), 0.65 (s, *exo*-MeSi), 5.25–5.05 (1H, m, ring proton (Cr(CO)₃), 5.70–5.95 (3H, m, ring protons (Cr(CO)₃), 7.3–7.7 (4H, m, ring protons); M^+ (m/e) 404; IR $\nu(\text{C}\equiv\text{O})$ 1970, 1886, 1865 cm^{-1} . Found: C, 56.21; H, 5.06. C₁₉H₂₀O₃Si₂Cr calcd.: C, 56.41; H, 4.98%.

The reaction of compound II thus obtained with 1 equivalent of methyl-lithium in THF at -78°C , followed by iodine oxidation at room temperature, afforded 1,1-dimethyldibenzosilole (III) (52% yield), whose spectral data agreed with those of an authentic sample [7,8]. In an effort to isolate a chromium tricarbonyl complex of III, we added chlorotrimethylsilane to the mixture produced by the reaction of II with methyl-lithium. As expected, η^6 -(1,1-dimethyldibenzosilacyclopentadiene)chromium tricarbonyl (IV) (m.p. 141–144°C, dec. was obtained (in 22% yield), indicating that compound III is produced by oxidation of IV (Scheme 1). The ^1H NMR (0.46 (3H, s, MeSi), 0.63 (3H, s, MeSi), 5.05–5.20 (1H, m, ring proton (Cr(CO)₃), 5.80–5.90 (3H, m, ring protons

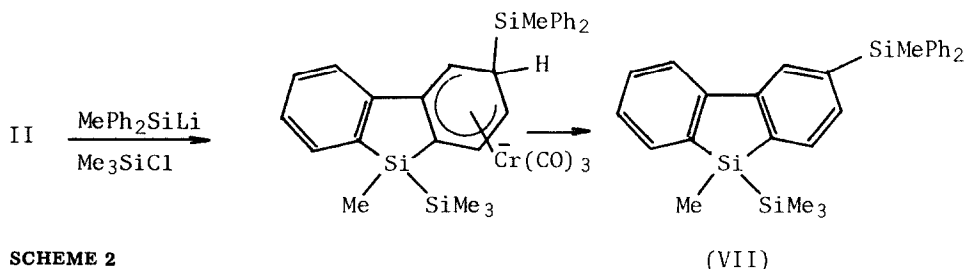


SCHEME 1

(Cr(CO)₃), 7.25–7.60 (4H, m, ring protons), IR ($\nu(\text{C}\equiv\text{O})$) 1950, 1890, 1860 cm⁻¹) and mass spectrum (exact mass, found: 346.0113 C₁₇H₁₄O₃SiCr calcd.: 346.0117) for compound IV were consistent with the proposed structure. The formation of IV can best be understood in terms of transmetalation between II and methyllithium.

Analogously, the reaction of II with 1.5 equivalent of butyllithium, followed by oxidation gave 1-butyl-1-methyldibenzosilole (V) and 1,1-dibutyldibenzosilole (VI) in 36 and 18% yield, respectively. All spectral data obtained for V and VI were identical with those of an authentic sample [2]. The formation of VI in this reaction clearly indicates that a methyl group on the silicon atom of the chromium complex also undergoes transmetalation with butyllithium. Similar transmetalation has been observed in the reaction of 1,1-disubstituted dibenzosiloles with organolithium compounds [2].

We next investigated the reaction of II with a silyllithium reagent. In contrast to the reaction of the 1-methyl-1-(trimethylsilyl)dibenzosilole with (methyldiphenylsilyl)lithium, in which a stable dibenzosilacyclopentadienide anion was formed [3], compound II afforded a product arising from nucleophilic attack of the silyl anion on the dibenzosilole ring. Thus, reaction of II with 1.6 equivalent of (methyldiphenylsilyl)lithium in THF followed by treatment with chlorotrimethylsilane gave 1-methyl-4-(methyldiphenylsilyl)-1-(trimethylsilyl)dibenzosilole (¹H NMR 0.09 (9H, s, Me₃Si), 0.46 (3H, s, MeSi), 0.86 (3H, s, MeSi), 7.0–7.8 (17H, m, ring protons); exact mass found: 464.1794 C₂₉H₃₂Si₃ calcd.: 464.1811 in 16% yield (Scheme 2); 51% of the starting II was recovered unchanged. The location of a methyldiphenylsilyl group on the aromatic ring was confirmed by the ¹³C NMR and two-dimensional NMR spectra of the product VII.



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