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Preliminary communication

THE CHEMISTRY OF SILOLES. SYNTHESIS AND REACTIONS OF η^6-[1-METHYL-1-(TRIMETHYLSILYL)DIBENZOSILACYCLOPENTADIEN 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)diben silole 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-(methyldiphenylsilyl)-1-(trimethylsilyl)dibenzosilole.

Recently, we found that the reaction of 1-methyl-1-(trimethylsilyl)dibenzosilole with an excess of an alkyllithium in THF affords a transmetallation prod uct, 1,1-dialkyldibenzosilole in quantitative yield [1,2], while reaction of (methyldiphenylsilyl)lithium under similar conditions, gives a dibenzosilacyclo pentadienide anion in high yield [3]. In order to learn more about the chemic behavior of the dibenzosilole derivative, we have prepared η^6-[1-methyl-1-(trimethylsilyl)dibenzosilacyclopentadiene]chromium tricarbonyl and investigat 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 diglyn [6] was refluxed for 24 h, yellow crystals identified as η^6-[1-methyl-1-(trimethylsilyl)dibenzosilacyclopentadiene]chromium tricarbonyl (II) (m.p.

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*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.

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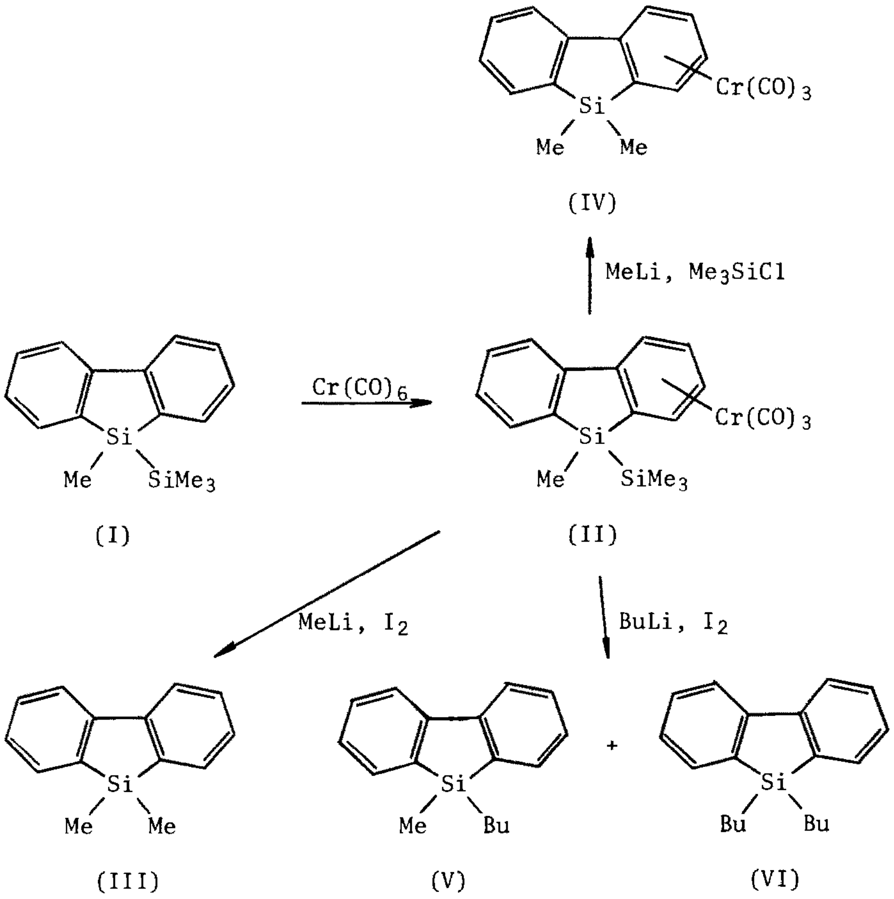
121—123°C, dec.) were obtained in 57% yield. The ^{1}H NMR spectroscopic analysis of II indicated it to be a mixture of *exo* and *endo* isomers in a ratio of 4/1 (^{1}H NMR δ (ppm) 0.10 (s, *exo*-Me_3Si), 0.33 (s, *endo*-Me_3Si), 0.44 (s, *endo*-MeSi 0.65 (s, *exo*-MeSi), 5.25—5.05 (1H, m, ring proton ($Cr(CO)_3$), 5.70—5.95 (3H, m, ring protons ($Cr(CO)_3$), 7.3—7.7 (4H, m, ring protons); M^+ (*m/e*) 404; IR ν(C≡O) 1970, 1886, 1865 cm^{-1}. Found: C, 56.21; H, 5.06. $C_{19}H_{20}O_3Si_2Cr$ calcd.: C, 56.41; H, 4.98%.

The reaction of compound II thus obtained with 1 equivalent of methyllithium in THF at −78°C, followed by iodine oxidation at room temperature, a forded 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 methyllithium. 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 oxid tion of IV (Scheme 1). The ^{1}H 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

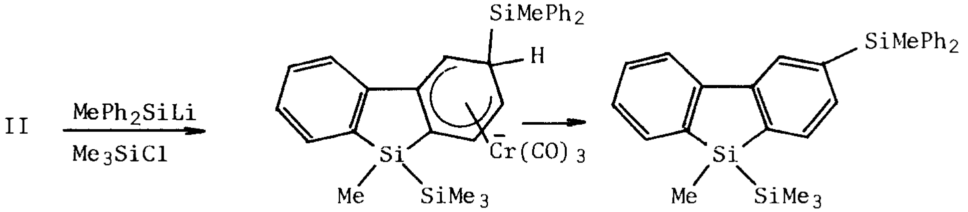


SCHEME 1

($Cr(CO)_3$), 7.25—7.60 (4H, m, ring protons), IR (ν(C≡O) 1950, 1890, 1860 cm^{-1}) and mass spectrum (exact mass, found: 346.0113 $C_{17}H_{14}O_3SiCr$ calcd.: 346.0117) for compound IV were consistent with the proposed structure. The formation of IV can best be understood in terms of transmetallation 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 transmetallation with butyllithium. Similar transmetallation 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 contras 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 o the silyl anion on the dibenzosilole ring. Thus, reaction of II with 1.6 equivalen of (methyldiphenylsilyl)lithium in THF followed by treatment with chlorotrimethylsilane gave 1-methyl-4-(methyldiphenylsilyl)-1-(trimethylsilyl)dibenzosilole (^1H NMR 0.09 (9H, s, Me_3Si), 0.46 (3H, s, MeSi), 0.86 (3H, s, MeSi), 7.0—7.8 (17H, m, ring protons); exact mass found: 464.1794 $C_{29}H_{32}Si_3$ 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 ^{13}C NMR and two-dimensional NMR spectra of the product VII.



SCHEME 2

(VII)

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References

1 M. Ishikawa, K. Nishimura, H. Sugisawa and M. Kumada, J. Organomet. Chem., 218 (1981) C21.
2 M. Ishikawa, T. Tabohashi, H. Sugisawa, K. Nishimura and M. Kumada, J. Organomet. Chem., 250 (1983) 109.
3 M. Ishikawa, T. Tabohashi, H. Ohashi, M. Kumada and J. Iyoda, Organometallics, 2 (1983) 351.
4 H. Sakurai, J. Hayashi and T. Kobayashi, J. Organomet. Chem., 110 (1976) 303.
5 P. Jutzi and A. Karl, J. Organomet. Chem., 214 (1981) 289.
6 A.M. Mance, N.D. Miro, C.H. Van Dyke, and N. Viswanathan, Inorg. Chem., 20 (1981) 635.
7 H. Gilman and R.D. Gorsich, J. Am. Chem. Soc., 80 (1958) 3243.
8 R.W. Coutant and A. Levy, J. Organomet. Chem., 10 (1967) 175.