Journal of Organometallic Chemistry, 187 (1980) 1—8

THE REACTION OF THE TRIMETHYLCHLOROSILANE/MAGNESIUM REAGENT WITH *gem*-DIBROMOCYCLOPROPANES

DIETMAR SEYFERTH * and DON P. DUNCAN

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139 (U.S.A.)

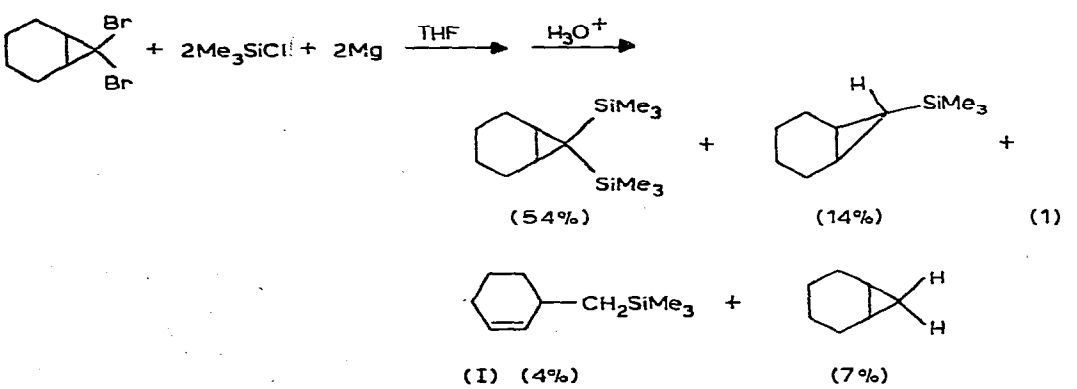
(Received August 28th, 1979)

Summary

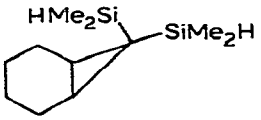
The reaction of the trimethylchlorosilane/magnesium reagent with *gem*-dibromocyclopropanes in tetrahydrofuran medium results in the formation of silylated cyclopropanes and/or silylated ring-opened products, depending on the substituents on the cyclopropane ring.

Introduction

During the course of a previous study we had investigated the silylation of 7,7-dibromonorcarane using the trimethylchlorosilane/magnesium reagent [1]. This reaction gave the expected 7,7-bis(trimethylsilyl)norcarane in 54% yield, but three other products were formed in lower yield (eq. 1). Two of these, 7-*anti*-trimethylsilylnorcarane and norcarane, could be rationalized in terms of the reduction processes, probably free radical in nature, which often accompany reactions of Grignard or Barbier systems with polyhalogenated compounds. However, a mechanism was not proposed for the formation of the ring-opened product, I.



In a later project we had need of an authentic sample of 7,7-bis(dimethylsilyl)norcarane II [2], and we proposed to prepare this compound by the chlorosilane/magnesium route. In view of the unexplained by-product formed in reaction 1, we thought that it would be of interest to expand this work to include the trimethylsilylation of a few other *gem*-dibromocyclopropanes.



(II)

Results and discussion

The trimethylchlorosilane/magnesium/*gem*-dibromocyclopropane reactions were carried out by adding the *gem*-dibromocyclopropane to an excess of the mixture of trimethylchlorosilane and magnesium turnings in tetrahydrofuran (THF) medium. Upon completion of the reaction, the reaction mixture was hydrolyzed. The results of these reactions are shown in Table 1. The methyl-substituted ethylenes stand out in that the major products derived from them were acyclic.

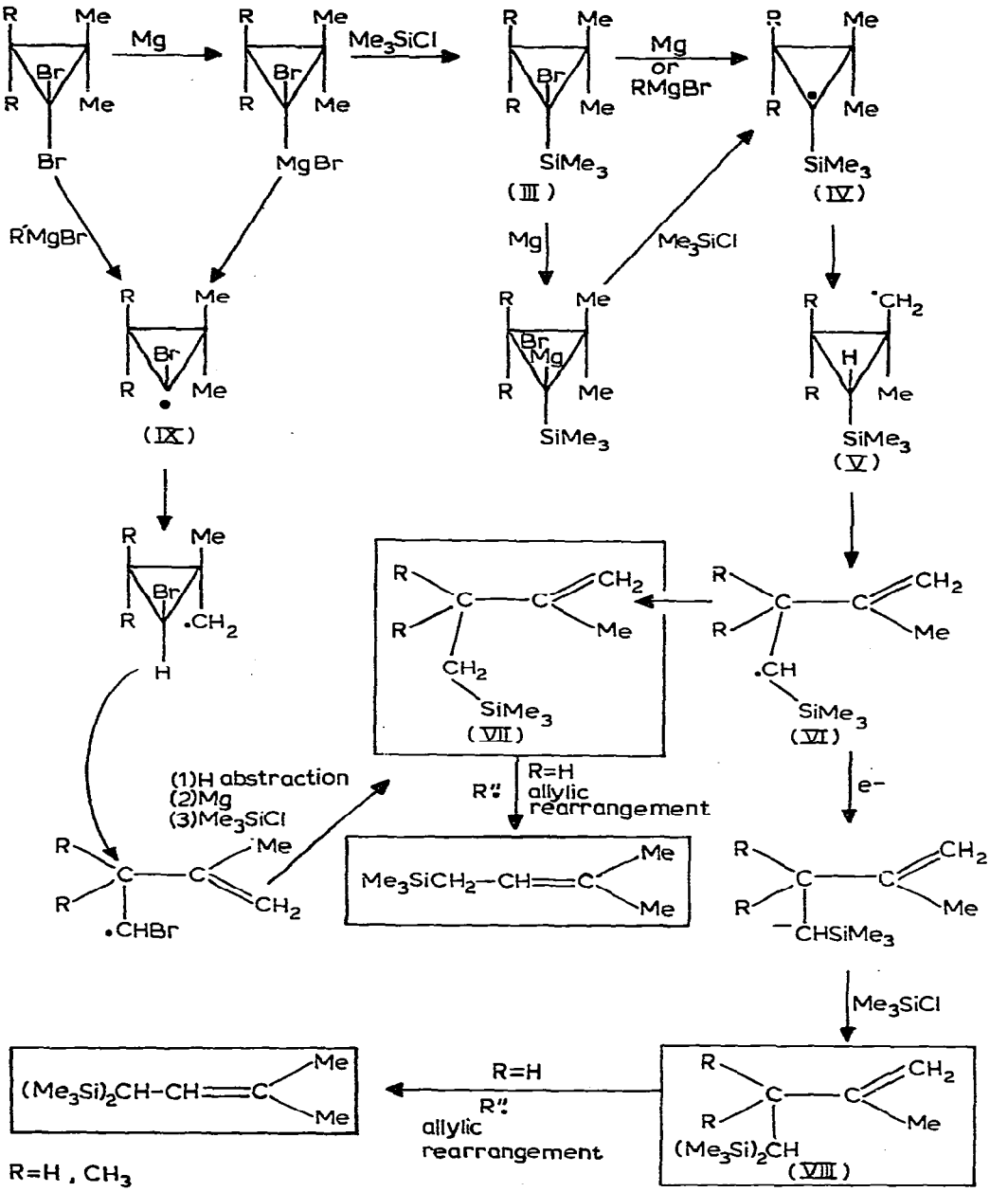
It seems reasonable to invoke radical intermediates in order to explain the formation of both ring-opened and reduced products. The cyclopropylcarbinyl-3-butenyl radical rearrangement is well known [3], and, considering the butenyl derivatives obtained as products in these reactions, it seems likely that this process is operative here.

Several mechanistic pathways are conceivable, as shown in Scheme 1. The disilylated products could be the result of further reactions of the initially formed *gem*-bromo(trimethylsilyl) derivative, III. Reaction of the rather hindered III with magnesium could generate a radical species, IV. Such a radical generation could be an induced process which requires the participation of trimethylchlorosilane as a co-reactant [3—5]. Such a mechanism has indeed been proposed by Dunoguès, Jousseaume and Calas [5] to account for the products observed in the reactions of acyclic *gem*-polychlorinated compounds with the trimethylchlorosilane/magnesium reagent in hexamethyl phosphoric triamide medium (eq. 2).

$$RMgX + Me_3SiCl \rightarrow R^{\bullet} + MgX^{+} + Me_3Si^{\bullet} + Cl^{-} \qquad (2)$$

Alternately, reaction of III with an organomagnesium compound in solution also could yield IV. It may be noted that radical intermediates have been postulated in the mono-reduction of *gem*-dibromocyclopropanes with CH_3MgBr in THF [6]. Once the radical IV has been formed, intra- or intermolecular hydrogen atom abstraction from a nearby CH_3 group could produce the cyclopropylcarbinyl radical V which rearranges to the more stable butenyl radical VI. As shown, hydrogen atom abstraction by VI gives the monosilylated vinylidene product, VII. Regeneration of a Grignard reagent from radical VI by recombination with Mg or $BrMg^{\bullet}$ and its subsequent reaction with Me_3SiCl (or combination of VI with silyl radicals generated in the "induced" mechanism) yields the disilylated vinylidene product, VIII. The monosilylated product also can be

SCHEME 1



obtained, using similar reasoning, from radical IX. The internal olefin products then result from radical-promoted allylic rearrangement to the more stable trisubstituted olefin. While such a reaction course is reasonable, it remains speculative and unproven.

In any case, as these few examples have demonstrated, the formation of a silylated product derived from cyclopropane ring opening is by no means

TABLE 1
REACTIONS OF *gem*-DIBROMOCYCLOPROPANES WITH THE TRIMETHYLCHLOROSILANE/MAGNESIUM REAGENT

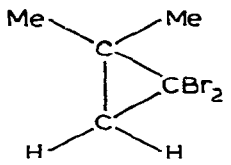
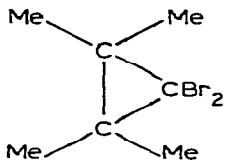
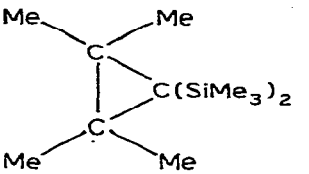
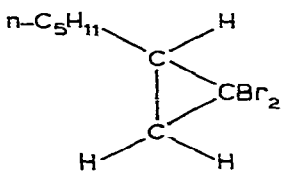
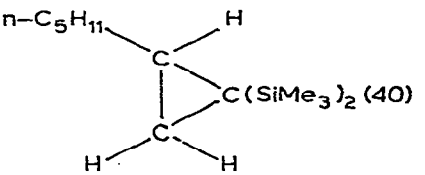
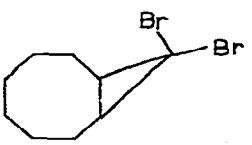
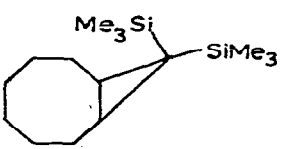
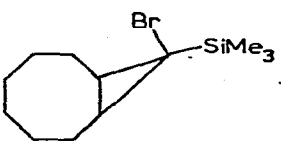
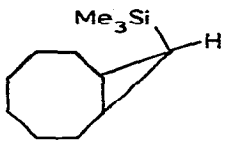
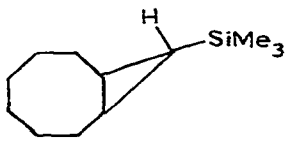
gem-Dibromocyclopropane	Products (% yield)
	$(Me_3Si)_2CHCH_2C(CH_3)=CH_2$ (58) $Me_3SiCH_2CH_2C(CH_3)=CH_2$ (20) $(Me_3Si)_2CHCH=CMe_2$ (12) $Me_3SiCH_2CH=CMe_2$ (4)
	$Me_3SiCH_2CMe_2C(CH_3)=CH_2$ (64)  (17) $(Me_3Si)_2CHCMe_2C(CH_3)=CH_2$ (5)
	 (40) + two minor, more volatile products (not identified)
	 (36)
	 (12)

TABLE 1 (continued)

gem-Dibromocyclopropanes	Products (% yield)
	 (6)
	 (5)

unique to the 7,7-dibromonorcarane system, and in some cases such ring-opened compounds are the only products formed in the silylation reaction. The main impetus for this brief study was provided by our need for a sample of 7,7-bis(dimethylsilyl)norcarane. This compound could be obtained in satisfactory yield by the reaction of the Me_2HSiCl/Mg reagent with 7,7-dibromonorcarane.

It would be of interest to examine a wider range of *gem*-dibromocyclopropanes in this reaction with the chlorosilane/magnesium reagent and to carry out experiments aimed at elucidation of the reaction mechanism. Such experiments, however, are beyond the scope of our present interests.

Experimental

General comments

Infrared spectra were recorded using a Perkin-Elmer Model 457A grating infrared spectrophotometer. Proton NMR spectra were obtained using a Varian T60, Perkin-Elmer R20 or Perkin Elmer R22 spectrometer. Samples were in carbon tetrachloride solution which contained chloroform as an internal standard. Chemical shifts are reported in δ units, ppm downfield from internal tetramethylsilane.

Gas-liquid chromatography (GLC) was used to analyze reaction products, determine purity, isolate samples for analysis and spectroscopy and to determine yields by the internal standard method.

Solvents were rigorously dried and all reactions were carried out under nitrogen in flame-dried glassware. The "standard apparatus" used in these experiments consisted of a three-necked, round-bottomed flask of appropriate size which was equipped with a mechanical stirrer, a pressure-equalizing addition funnel and a reflux condenser topped with a nitrogen inlet tube.

Trimethylchlorosilane was donated by Union Carbide Corp. The *gem*-dibromocyclopropanes were prepared by the bromoform/potassium tert-butoxide procedure [7].

Reactions of gem-dibromocyclopropanes with the trimethylchlorosilane/magnesium reagent

(a) 1,1-Dibromo-2,2-dimethylcyclopropane. The standard apparatus (300 ml flask) was purged with nitrogen, flame-dried and charged with 3.7 g (0.15 g atom) of magnesium turnings, 100 ml of THF and 17 ml (0.13 mol) of freshly distilled trimethylchlorosilane. The addition funnel was charged with 12.4 g (54 mmol) of 1,1-dibromo-2,2-dimethylcyclopropane in 10 ml of THF and this solution was added to the Me_3SiCl/Mg reagent, dropwise over a period of 1 h, with rapid stirring. A slight exotherm and precipitation of magnesium halide were noted. The mixture was stirred at room temperature for 4 h and then was hydrolyzed to the "dry end point" with saturated ammonium chloride solution. The mixture was filtered and the salts were washed with 50 ml of pentane. The residue was dissolved in 1 *N* hydrochloric acid and the resulting solution was extracted with pentane. The organic phases were combined, dried ($MgSO_4$), concentrated at reduced pressure to remove solvents, and the residue was trap-to-trap distilled (room temperature at 0.05 mmHg) into a receiver cooled to −78° C. The distillate was examined by gas-liquid chromatography (GLC) (10% DC-200 silicone oil, at 122° C). Three products were present. These were collected and identified:

i) The component of lowest GLC retention time was shown to be a mixture of two components by NMR analysis. The major compound was 3-methyl-3-buten-1-yltrimethylsilane, $Me_3SiCH_2CH_2C(CH_3)=CH_2$, X; the minor component was 3-methyl-2-buten-1-yltrimethylsilane, $Me_3SiCH_2CH=CMe_2$, XI. The mixture yield was 24%; the X/XI ratio was 82/18. Therefore, the yield of X was 20%, of XI, 4%. Characterization data were obtained for the mixture. (Anal. Found: C, 67.66; H, 12.77. $C_8H_{18}Si$ calcd.: C, 67.51; H, 12.75). n_D^{25} (mixture) 1.4206. NMR: δ −0.03 (s, Me_3Si of XI), 0.00 (s, Me_3Si of X), total integration 9H, 0.66 (t, *J* 8 Hz, $SiCH_2$ of XI), 0.67 (d, *J* 7 Hz, $SiCH_2$ of XI), total integration 2H, 1.55 (s, bd, CCH_3 of XI), 1.73 (s, bd, CCH_3 of X and XI) 1.98 (t, bd, *J* 8 Hz, CCH_2, X) and 4.63 ppm (m, bd, all =CH).

ii) 1,1-Bis(trimethylsilyl)-3-methyl-2-butene, $(Me_3Si)_2CHCH=CMe_2$, n_D^{25} 1.4513. (Anal. Found: C, 61.84; H, 12.31. $C_{11}H_{26}Si_2$ calcd.: C, 61.59; H, 12.22). NMR: δ 0.03 (s, 18H, Me_3Si), 1.16 (d, *J* 12 Hz, 1H, Si_2CH), 1.57 (s, 3H, CCH_3), 1.67 (s, 3H, CCH_3) and 5.01 (d, *J* 12 Hz, 1H, =CH). This product was obtained in 12% yield.

iii) 1,1-Bis(trimethylsilyl)-3-methyl-3-butene, $(Me_3Si)_2CHCH_2\underset{\displaystyle Me}{\overset{\displaystyle |}{C}}=CH_2$, n_D^{25} 1.4549, longest GLC retention time. (Anal. Found: C, 61.74; H, 12.19. $C_{11}H_{26}Si_2$ calcd.: C, 61.59; H, 12.22). NMR: δ 0.06 (s, 18H, Me_3Si), 0.10 (t, *J* 6 Hz, 1H, Si_2CH), 1.73 (s, bd, 3H, CCH_3), 2.19 (d, bd, *J* 6 Hz, $=CCH_2$), and 4.66 ppm (m, 2H, $=CH_2$). GLC analysis showed that this product was present in 58% yield.

(b) 1,1-Dibromo-2,2,3,3-tetramethylcyclopropane. The same procedure was used in the reaction of 12.8 g (46 mmol) of this dibromide with 3.7 g (0.15 g atom) of magnesium and 17 ml (0.13 mol) of Me_3SiCl in THF (120 ml total). The organic phase obtained upon work-up was concentrated and the residue was examined by GLC. One major product was present, in addition to two minor products of higher retention time. These were collected and characterized.

i) 2,2,3-Trimethyl-3-buten-1-yltrimethylsilane, $Me_3SiCH_2CMe_2C(CH_3)=CH_2$, n_D^{25} 1.4395, in 64% yield. (Anal. Found: C, 70.26; H, 12.93. $C_{10}H_{22}Si$ calcd.: C, 70.50; H, 13.02). NMR: δ 0.00 (s, 9H, Me_3Si), 0.85 (s, 2H, $SiCH_2$), 1.11 (s, 6H, Me_2C), 1.73 (s, 3H, $=CCH_3$) and 4.6 ppm (m, 2H, $=CH_2$).

ii) 2,3,3-Trimethyl-4,4-bis(trimethylsilyl)-1-butene, $(Me_3Si)_2CHCMe_2C(CH_3)=CH_2$, n_D^{25} 1.4511, in 5% yield. NMR: δ −0.02 and −0.01 (two s, total 18H, Me_3Si), 0.15 (s, 1H, Si_2CH), 1.12 (s, 6H, CMe_2), 1.75 (s, bd, 3H, $=CCH_3$) and 4.68 (m, 2H, $=CH_2$).

iii) 1,1-Bis(trimethylsilyl)-2,2,3,3-tetramethylcyclopropane, m.p. 110–112°C (GLC-collected sample), in 17% yield. (Anal. Found: C, 64.30; H, 12.26. $C_{13}H_{30}Si_2$ calcd.: C, 64.37; H, 12.47). NMR: δ 0.36 (s, 18H, Me_3Si) and 1.43 (s, 12H, Me_2C).

(c) 1,1-Dibromo-2-n-amylcyclopropane. The same procedure was used in the reaction of 9.6 g (36 mmol) of 1,1-dibromo-2-*n*-amylcyclopropane with 3.0 g (0.12 g atom) of magnesium and 12.3 g (94 mmol) of trimethylchlorosilane in THF (85 ml total). The organic phase obtained upon work-up was concentrated at reduced pressure and the residue was examined by GLC. One major product and two minor products (which were not isolated and characterized) were present. The major product was collected and identified as 1,1-bis(trimethylsilyl)-2-*n*-amylcyclopropane, n_D^{25} 1.4596. It was present in 40% yield. (Anal. Found: C, 65.71; H, 12.46. $C_{14}H_{32}Si_2$ calcd.: C, 65.54; H, 12.57). NMR: δ −0.01 (s, 9H, Me_3Si), 0.10 (s, 9H, Me_3Si), 0.30–1.40 ppm (m, bd, 14H, all other C–H).

(d) 9,9-Dibromobicyclo[6.1.0]nonane. The same procedure was used in the reaction of 14.1 g (50 mmol) of the dibromo compound with 3.7 g (0.15 g atom) of magnesium and 17 ml (0.13 mol) of trimethylchlorosilane in THF (110 ml total). The usual work-up gave an organic phase which was concentrated at reduced pressure to remove solvents. The residue was examined by GLC. Four products were collected and identified. In order of increasing GLC retention time, these were:

i) *anti*-9-Trimethylsilylbicyclo[6.1.0]nonane, n_D^{25} 1.4673; lit. [8] n_D^{25} 1.4670, in 5% yield. The IR and ^1H NMR spectra matched those reported [8].

ii) *syn*-9-Trimethylsilylbicyclo[6.1.0]nonane, n_D^{25} 1.4774; lit. [8] n_D^{25} 1.4778, in 6% yield. Spectral data matched those reported [8].

iii) *syn*-9-Bromo-anti-9-trimethylsilylbicyclo[6.1.0]nonane, n_D^{25} 1.5012. The IR and ^1H NMR spectra of this compound were in agreement with those reported previously [8].

iv) 9,9-Bis(trimethylsilyl)bicyclo[6.1.0]nonane, n_D^{25} 1.4830, in 36% yield. (Anal. Found: C, 67.06; H, 12.03. $C_{15}H_{32}Si_2$ calcd.; C, 67.08; H, 12.01). NMR: δ 0.00 (s, 9H, *syn*-Me_3Si), 0.19 (s, 9H, *anti*-Me_3Si) and 0.67–2.18 (m, bd, 14H, all other H). The *syn* and *anti*-Me_3Si assignments were based on similar assignments made in the case of the *syn*- and *anti*-7-trimethylsilylbicyclo[4.1.0] heptane isomers [9].

The preparation of 7,7-bis(dimethylsilyl)bicyclo[4.1.0]heptane, II

Essentially the same procedure as that described in the experiments above was used in the reaction of 58.4 g (0.23 mol) of 7,7-dibromonorcarane with 17.2 g (0.7 g atom) of magnesium turnings and 57 g (0.61 mol) of dimethylchlorosilane (Silar Laboratories) in THF (440 ml total). Standard work-up gave

an organic phase which was distilled to give 30.8 g (0.146 mol, 63%) of the title compound, b.p. 126—129°C at 23 mmHg, n_D^{25} 1.4881. (Anal. Found: C, 61.90; H, 11.42. $C_{11}H_{24}Si_2$ calcd.: C, 62.18; H, 11.39). NMR: δ 0.04 (d, *J* 4 Hz, 6H, *syn*-Me_2Si), 0.21 (d, *J* 4 Hz, 6H, *anti*-Me_2Si), 0.91—2.11 (m, bd, 10H, ring C—H), 3.59 (heptet, *J* 4 Hz, 1H, *syn*-SiH) and 4.12 ppm (heptet, *J* 4 Hz, 1H, *anti*-SiH).

Acknowledgment

The authors are grateful to the US Air Force Office of Scientific Research (NC)-ASFC (Grant AF-AFOSR-79-0007) for generous support of this work.

References

1 D. Seyferth and R.L. Lambert, Jr., J. Organometal. Chem., 88 (1975) 287.
2 D. Seyferth and D.P. Duncan, J. Organometal. Chem., 111 (1976) C21.
3 D.C. Nonhebel and J.C. Walton, Free Radical Chemistry, Cambridge University Press, Cambridge, 1974, pp. 480—481, 534—535.
4 W.A. Pryor, Free Radicals, McGraw-Hill, New York, 1966, pp. 116—124.
5 J. Dunogues, E. Jousseaume and R. Calas, J. Organometal. Chem., 71 (1974) 377.
6 D. Seyferth and B. Prokai, J. Org. Chem., 31 (1966) 1702.
7 P.S. Skell and A.Y. Garner, J. Amer. Chem. Soc., 78 (1956) 5430.
8 D. Seyferth, R.L. Lambert, Jr., and M. Massol, J. Organometal. Chem., 88 (1975) 255.
9 D. Seyferth, A.W. Dow, H. Menzel and T.C. Flood, J. Organometal. Chem., 44 (1972) 279.