

THE ROLE OF BORON TRICHLORIDE IN THE SYNTHESIS OF PHENYLTRICHLOROSILANE FROM BENZENE AND TRICHLOROSILANE

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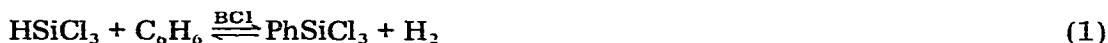
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Summary

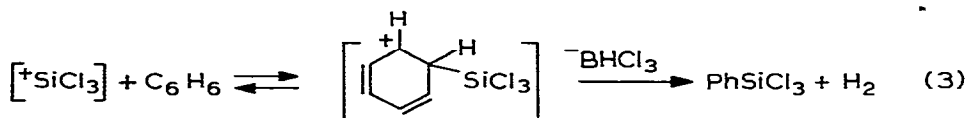
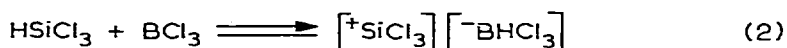
Benzene and trichlorosilane form phenyltrichlorosilane and hydrogen. Boron trichloride has long been used as the preferred catalyst for this process. The mechanism of catalysis is indicated as follows: $\text{BCl}_3 + x\text{HSiCl}_3 \rightarrow \text{H}_x\text{BCl}_{3-x} + x\text{SiCl}_4$; $\text{H}_x\text{BCl}_{3-x} + x\text{C}_6\text{H}_6 \rightarrow (\text{C}_6\text{H}_5)_x\text{BCl}_{3-x} + x\text{H}_2$; $(\text{C}_6\text{H}_5)_x\text{BCl}_{3-x} + x\text{HSiCl}_3 \rightarrow \text{H}_x\text{BCl}_{3-x} + x\text{C}_6\text{H}_5\text{SiCl}_3$.

Phenyltrichlorosilane can be prepared in the liquid phase from trichlorosilane and benzene at 300–350°C under autogenous pressure with 0.5 to 2.0% by weight of boron trichloride as a catalyst. Equilibrium is reached within three to six hours [1–3] (eq. 1). Under these conditions, redistribution reactions among



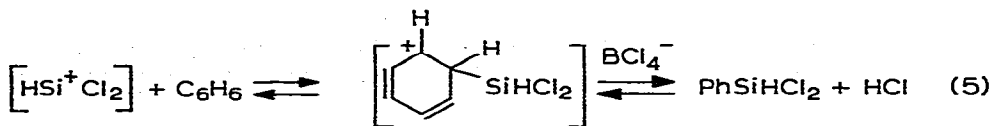
the phenyl, chloride, and hydride ligands to silicon also proceed to equilibrium to produce a mixture of dichlorosilane, trichlorosilane, tetrachlorosilane, benzene, phenyldichlorosilane and diphenyldichlorosilane [4,5]. Disubstituted benzene derivatives such as bis(trichlorosilyl)benzene are also formed.

This reaction was discovered by Barry of the Dow Corning Corporation who proposed [1], by analogy with the classical Friedel–Crafts condensation of alkyl halides with benzene, a mechanism in which a siliconium ion was formed by abstraction of a hydride ion from trichlorosilane by boron trichloride (eq. 2,3).



Mikheev et al. [6], with very limited evidence, proposed an unprecedented and

unlikely nucleophilic substitution of hydrogen on the aromatic ring. Ponomarev [7], having argued convincingly against a radical mechanism, proposed that boron trichloride abstracts a chloride ion from silicon, not hydride (eq. 4-6).



No direct chemical evidence was obtained for the proposed mechanism. The existence of a siliconium cation in the liquid phase is perhaps impossible due to the affinity of such species toward counteranions [8,9]. No proposal seems to explain why boron trichloride is a much better catalyst than other typical Friedel-Crafts catalysts such as aluminum chloride, ferric chloride, or zinc chloride [1].

Recently we studied the reaction of benzene with trichlorosilane in sealed glass tubes with 1 wt.% boron trichloride as catalyst. Figure 1 shows that at 330°C there was 2 h induction period during which little phenyltrichlorosilane formed. Diphenyldichlorosilane and all lower boiling materials were stripped from the mixture upon completion of the reaction to leave a residue which contained most of the boron. This residue was used instead of boron trichloride in a second series of experiments. Figure 1 shows no induction period in this case.

Benzene and trichlorosilane were heated with 28 wt.% boron trichloride for 2 h at 300°C. A voluminous bright yellow precipitate formed while the mixture

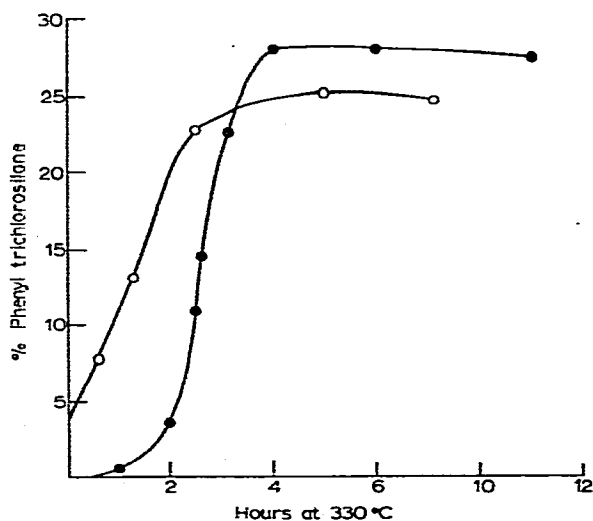


Fig. 1. Time dependence of reaction of 1/1 mol proportions benzene and trichlorosilane with 1 wt.% boron trichloride, ●; and 1.5/1 mol proportions benzene and trichlorosilane with 31% residue catalyst, ○.

was being cooled to room temperature. This redissolved upon reheating the sealed tube to 200°C. The tube was cooled, opened, with release of hydrogen, and the solids were isolated by filtration. The filtrate was mostly silicon tetrachloride, indicating that the boron trichloride, benzene, and the Si-H groups of the trichlorosilane had combined to form the yellow solid. The solid had an aromatic odor and burned with a smoky flame. It was a very effective catalyst for reaction of benzene with trichlorosilane, with no induction period. The solid was sublimed to give first a white solid (200°C, 2 torr) and then a smaller amount of deep yellow solid (250°C, 2 torr). The white solid melted over a range from 191 to 293°C and no close-melting fractions were obtained as crystals from heptane solution. Elemental analysis of the white solid corresponded to $C_{6.0}H_{5.3}B_{1.06}Si_{0.25}Cl_{0.10}O_{0.21}$. Approximately 40% of the boron had precipitated. The white solid was oxidized with hydrogen peroxide [10] in THF -78°C to produce mainly 1,2-dihydroxybenzene and a small amount of phenol. These products indicated a substantial amount of boron in the white solid was linked directly to *o*-phenylene radicals, and some to phenyl radicals. With the normal 0.5–2.0 wt.% BCl_3 in the reaction of benzene with trichlorosilane, the higher ratio of benzene to boron would probably increase the ratio of phenyl to phenylene linked boron substantially.

A tube containing benzene (23 wt.%), trichlorosilane (42 wt.%), and boron trichloride (35 wt.%), was heated for 6 h at 330°C and the liquid and solid contents were transferred to an NMR tube and sealed. The ^{11}B nucleus was observed at 70.6 MHz using a 51 K Gauss Fourier Transform NMR Spectrometer. Table 1 lists chemical shifts and relative areas of peaks in the spectrum at 16°C and 140°C, and the type of boron compounds believed to be responsible for each resonance. The major peak (E) was due to BCl_3 . The absence of peaks at positive shifts showed that neither tetracoordinate boron nor polyborohydrides were present.

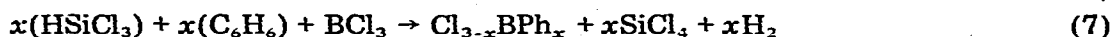
TABLE I
 ^{11}B NMR OF YELLOW SOLID

Peak	δ (ppm) ^a	Area 16°C	Area 140°C	Increase (%)	Closest related compound ^b
A	-45.7	5.2	7.0	35	
B	-44.8	5.6	6.5	16	$ClBPh_2$
C	-41.7	3.9	6.9	77	BPh_3
D	-37.9	27.9	34.0	22	Cl_2BPh
E	-29.1	55.4	55.4	0	BCl_3
F	-21.8		1.0		Cl_xBO_{3-x} 2
G	-14.5	2.5	4.9		Cl_xBO_{3-x} 2
H	-13.7		Tr		Cl_xBO_{3-x} 2
I	-12.4		1.1		Cl_xBO_{3-x} 2
J	-8.5		1.3		Cl_xBO_{3-x} 2

^a Relative to $B(OMe)_3$. ^b Literature value BCl_3 -29.2 [20]; Cl_2BPh -37.4 [21], -35.7 [20]; $ClBPh_2$ -43.6 [21]; BPh_3 -42.6 [20,21].

No obvious BH coupling was present. The yellow solid was almost entirely dissolved at 140°C. Peaks A, B, C, and D were larger at 140°C than at 16°C, probably due to yellow solid entering solution. These peaks had chemical shifts characteristic of phenylchloroboranes, ($\text{Ph}_x\text{BCl}_{3-x}$, peak area for $x = 1, 2$ or 3), but not matching exactly with those of previously reported individual compounds. This is ascribed to the presence of phenylene linkages. These could link some arylchloroborane moieties into oligomeric structures. No further identification was attempted. Relevant to the following discussion is the fact that boron-substituted aromatic compounds were formed.

The formation of arylchloroboranes and silicon tetrachloride from benzene, trichlorosilane and boron trichloride is consistent with equation 7. For simplicity,



the equation is written as if only phenylchloroboranes were formed. Two mechanisms were considered for eq. 7, shown respectively in eq. 9 and eq. 10, 11.



Equation 9 was tested by heating phenyltrichlorosilane with boron trichloride 4 h at 330°C in a sealed tube. No reaction occurred. Diphenyldichlorosilane* (Ph_2SiCl_2) and boron trichloride gave a mixture from which eighty percent of the phenyl groups were recovered as benzene, phenyltrichlorosilane or diphenyldichlorosilane. No evidence for any phenylboranes was obtained. Consequently, eq. 9 could not be important in the mechanism, and eq. 8, 9 were rejected.

There is some precedent for eq. 10, 11, however. Equation 10 represents reduction of boron trichloride by trichlorosilane. Such reductions have been well established with a variety of silicon hydrides near room temperature**, but not with trichlorosilane. We found that boron trichloride with an excess of trichlorosilane at 330°C gave 3 mol of tetrachlorosilane per mol of boron trichloride in agreement with eq. 10. Equation 11 represents boration of benzene. Such a reaction was reported by Hurd [17] who observed that benzene and diborane in 12 h at 100°C gave hydrogen and a yellow solution which precipitated a soft yellow solid. This was a mixture of phenylboranes, including triphenylborane***.

Benzene and trichlorosilane heated with a catalytic amount of triphenylborane reacted completely to phenyltrichlorosilane within 2 h, indicating high catalytic activity. It thus appeared that phenylboranes play an important role in

* Diphenyldichlorosilane in redistribution reactions of this type would be more likely to transfer phenyl groups than phenyltrichlorosilane [5].

** Silanes known to be reactive at 30 or less °C: disilane (Si_2H_6) [11,12], methylsilane (MeSiH_3) [13,16], dimethylsilane (Me_2SiH_2) [14,15], dimethylchlorosilane (Me_2SiHCl) [14,15], trimethylsilane (Me_3SiH) [15], methylchlorosilane (MeClSiH_2) [15], but not silane (SiH_4) [11,15], methyl-dichlorosilane (MeHSiCl_2) [14], or trichlorosilane (HSiCl_3) [15]. SiH_4 becomes reactive in a sealed tube in the liquid phase at 150°C [16]. Higher temperatures have apparently never been investigated.

*** Triphenylborane has also been isolated in 45% yield on heating tetraethylborane in excess benzene for 5 h at 180°C [18].

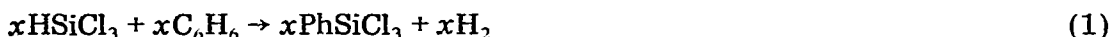
TABLE 2
REACTION OF TRIPHENYLBORANE WITH TRICHLOROSILANE AT 315°C

Reactants (mmol)	Time (min)	Product (mol %)			Conversion of BPh ₃ (%)
		HSiCl ₃	SiCl ₄	PhSiCl ₃	
HSiCl ₃ (4.7) BPh ₃ (1.28)	1.5	61	2	35	43
HSiCl ₃ (5.0) BPh ₃ (1.20)	4	59	1	40	55
HSiCl ₃ (5.0) BPh ₃ (1.01)	21	48	9	42	69
HSiCl ₃ (5.0) BPh ₃ (0.94)	270	34	22	44	78
HSiCl ₃ (4.6) BPhCl ₂ (4.85)	20	49	44	6	6
SiCl ₄ (5.0) BPh ₃ (1.13)	20	0	100	0	0

the catalysis, and this was now investigated in more detail.

Triphenylborane did not react with silicon tetrachloride at 315°C. However, triphenylborane reacted rapidly with trichlorosilane at 315°C to give phenyltrichlorosilane and presumably diborane (eq. 12, $x = 3$). Product distribution as a function of time is shown in Table 2*. Short heating times formed almost no redistribution products. Phenylidichloroborane reacted more slowly with trichlorosilane.

The rates of reaction in eq. 12 and 11 are rapid enough to account for the rate of phenyltrichlorosilane formation when a benzene/trichlorosilane mixture and 1% BCl₃ is heated. Thus the synthesis may proceed by transfer of phenyl from boron to silicon followed by regeneration of phenyl borane.



The reduction of boron trichloride (eq. 10) is slow, accounting for the induction period.

Dichlorosilane reacts without a significant induction period. Methylidichlorosilane reacts at a lower temperature than trichlorosilane. The increased reducing power of the silanes towards trichloroborane probably accounts for these observations.

Experimental

Gas-liquid chromatographic (GLC) separations were made on a Varian Aerograph A-710 chromatograph using 3/16" × 10' stainless steel columns packed with 16²/₃% OV-210 silicone gum on 100–120 mesh Chromosorb P (acid washed, DMCS treated). Column temperature after injection was raised from 50 to 270°C at 10°C per minute. Integration was by a Varian on-line computer. Response factors were obtained by injection of pure compounds. Mass spectra were obtained

* The limited triphenylborane conversion of 78% indicated either that an equilibrium was present or that the BPh₃ reactant had become slightly oxidized or hydrolyzed in handling. Small amounts of tetrachlorosilane are formed after long periods of heating.

with an AEI MS-30 mass spectrometer. Reagent grade benzene was distilled from sodium potassium alloy before use. Trichlorosilane was obtained from the Dow Corning Corporation and distilled before use. Boron trichloride was from Matheson Gas Co. Triphenylborane and phenyldichloroborane were purchased from Ventron Co. (Alfa Products). All operations were carried out under an atmosphere of nitrogen, or in a vacuum.

Time dependence of reaction. Experiments were conducted in 2.2 cm³ 8 mm × 200 mm sections of Corning No. 234082 special wall pyrex tubing. A stock solution was prepared by mixing benzene (27.6, 353 mmol), trichlorosilane (48.5 g, 358 mmol) and boron trichloride (Matheson) (0.76 g, 6.5 mmol). A series of tubes, sealed at one end, were each filled with 0.561 g of stock solution. The lower portion of each tube was cooled in dry ice, and the open end was sealed under nitrogen. The tubes were placed in steel protective jackets and heated at 330°C for various times while being turned end-over-end in an oven. A considerable release of hydrogen occurred, identified by mass spectrometry, when the tubes were opened. Toluene (0.5 ml) was added to each tube as an internal standard and analyses were effected by gas chromatography. Results are found in Fig. 1. The product distribution at 6 h was 28% PhSiCl₃, 18.7% C₆H₆, 17.0% HSiCl₃, 15.4% SiCl₄, 3.0% PhHSiCl₂, 1.9% Ph₂SiCl₂, and 16% other volatile compounds and residue of low volatility.

The product from a reaction which had been carried out in an autoclave was distilled to 275°C, 20 torr. The residue contained 90% of the boron charged. A new stock solution was prepared under nitrogen containing 31 wt.% of this residue in a 1/1.5 mol ratio trichlorosilane/benzene solution. Sealed tubes were prepared and heated as before.

High boron trichloride loading. Boron trichloride (2.15 g, 18.3 mmol), benzene (4.18 g, 53.5 mmol), and trichlorosilane (7.17 g, 52.9 mmol) were sealed in a 35 cm³ heavy wall glass ampule. The ampule was placed in a steel autoclave partially filled with toluene. The autoclave was heated 16 h at 250°C. The internal pressure within the ampule was partially compensated by the external pressure of the toluene, preventing breakage of the glass. The autoclave was cooled, and the ampule opened under nitrogen, to release the residual gasses. Liquids were evaporated at 120°C, 2 torr. The yellow solid remaining was washed with hexane that had been dried over sodium potassium alloy, and sublimed at 250°C, 2 torr to give 0.5 g yellow solid and a small amount of residue. The yellow solid was resublimed slowly to give first a white solid at about 200°C and then as the temperature was raised towards 250°C a smaller amount of deep yellow solid. The white solid initially melted in the range of 191–293°C, but remelting occurred between 181–190°C. Crystallization of a portion of the white solid from heptane was unsuccessful. The white solid was submitted for elemental analysis (C, 63.27; H, 4.70; B, 10.08; Cl, 12.38; Si, 6.20%). The white solid (0.137 g) was dissolved in tetrahydrofuran (0.69 ml) and cooled to -78°C. Aqueous hydrogen peroxide (0.34 ml 30% solution) in tetrahydrofuran was added slowly. Rapid strongly exothermic reaction occurred to produce a colorless solution upon warming to 25°C. The solution was silylated [19] with trimethylchlorosilane (4 ml) and hexamethyldisilazane (4 ml). The resulting mixture was centrifuged, the clear liquid decanted from the ammonium chloride, and excess silanes evaporated. Gas-liquid chromatography on both SE-30 and OV-210 liquid phase

columns revealed 56% of the product to be a compound with retention time identical with 1,2-bis(trimethylsiloxy)benzene, which had been synthesized independently from catechol. The 1,3 and 1,4 isomers had different retention times and were not present in the mixture. The presence of the 1,2 isomer was confirmed by GLC/mass spectrometry: m/e (%), 43(1.5), 45(7.9), 59(1.0), 73(100.0), 74(8.2), 75(4.5), 136(1.0), 151(1.8), 239(1.7), 254(11.5, M^+), 255(2.6, $M + 1^+$); exact mass determination 254.1194 (calcd for $\text{Si}_2\text{C}_{12}\text{H}_{22}\text{O}_2$, 254.1158). A small amount of trimethylsiloxybenzene was also present. No other aromatic compounds could be detected.

A sample of the original yellow solid with hydrogen peroxide oxidized to give an almost identical distribution of products.

Boron nuclear magnetic resonance. Benzene (0.2 g, 2.51 mmol), HSiCl_3 (0.35 g, 2.55 mmol) and BCl_3 (0.30 g, 2.58 mmol) were heated together 6 h at 330°C in a sealed tube. The tube was cooled, opened, and the liquid and solid contents transferred with rigorous exclusion of moisture and oxygen to a medium wall NMR tube. The ^{11}B nucleus was observed at 70.6 MHz using a Varian HR-220 51.7 K Gauss NMR spectrometer equipped with a Fourier Transform Data Acquisition Computer. Table 2 lists spectral results at 16 and 140°C .

Experiments with triphenylborane and mechanistic studies. A 1/1 mol ratio HSiCl_3 benzene solution during 2 h at 330°C with 5 wt.% triphenylborane (BPh_3) formed 25% PhSiCl_3 and 2.3% Ph_2SiCl_2 .

Ph_2SiCl_2 (0.6 g, 2.4 mmol) and BCl_3 (0.267 g, 2.3 mmol) during 4 h at 330°C in a sealed tube formed no solid other than a few black colored specks. GLC analysis showed that the volatile products were 3% benzene, 13% PhSiCl_3 , and 43% Ph_2SiCl_2 (percentages based on total weight of reagents). 80% of the C_6H_6 units charged were recovered as part of the three products. No reaction occurred when the experiment was repeated substituting PhSiCl_3 for Ph_2SiCl_2 .

HSiCl_3 (0.55 g, 4.1 mmol) and BCl_3 (0.12 g, 1.02 mmol) were heated in a sealed tube 4 h at 330°C to give 59.4% conversion of HSiCl_3 to SiCl_4 , and recovery of 17% HSiCl_3 , by GLC analysis of the products. Boron-containing products apparently did not elute from the GLC column.

A series of experiments in which triphenylborane and trichlorosilane were heated at 315°C in sealed tubes for various periods of time are described in Table 2. The silane products, SiCl_4 and PhSiCl_3 , and recovered HSiCl_3 were analyzed by GLC. Boron compounds did not elute from the GLC column. The rate of reaction was compared to that found for the PhSiCl_3 synthesis (Fig. 1), in which equilibrium was reached after 4 h at 330°C with 1% BCl_3 , with 35% conversion of HSiCl_3 to phenylsilane. From Table 1 a minimum of 7% of the boron was present as BPh_3 . Thus a maximum of 0.0035 mol BPh_3 was present for each mol of HSiCl_3 converted. Thus the boron to silicon exchange of 3 phenyl groups must have occurred once every $240 \times 0.0035 = 2.52$ minutes. This is approximately the rate actually observed with $\text{BPh}_3/\text{HSiCl}_3$ (Table 2, 43% BPh_3 conversion in 1.5 minutes at only 315°C). Since BPh_2Cl and BPhCl_2 also react with HSiCl_3 , the rate comparison has probably been made conservatively.

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References

- 1 A.J. Barry, J.W. Gilkey and D.E. Hook; *Ind. Eng. Chem.*, 51 (1959) 131.
- 2 A.J. Barry, J.W. Gilkey and D.E. Hook, *Advan. Chem. Ser.*, 23 (1959) 246.
- 3 A.J. Barry, U.S. Patent 2 499 561, 1950; *Chem. Abstr.*, 44 (1950) 5907.
- 4 V.N. Penskii, V.V. Ponomarev, K.A. Andrianov and S.A. Golubtsov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1971) 1898.
- 5 D.R. Weyenberg, L.G. Mahone and W.H. Atwell, *Anal. N.Y. Acad. Sci.*, 159 (1969) 38.
- 6 E.P. Mikheev, A.L. Klebanskii, G.N. Mal'nova and K.K. Popkov, *Plast. Massy*, No. 1 (1961) 19; E.P. Mikheev, G.N. Mal'nova *ibid.* No. 2 (1961) 31.
- 7 V.V. Ponomarev, S.A. Golubtsov, K.A. Andrianov and V.N. Penskii, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1971) 508.
- 8 A.G. MacDiarmid, *Intra-Sci. Chem. Reports*, 7 (1973) 83.
- 9 R.J.P. Corriu and M. Henner, *J. Organometal. Chem.*, 74 (1974) 1.
- 10 H.G. Kuivila, *J. Amer. Chem. Soc.*, 76 (1954) 870
- 11 C.H. VanDyke and A.G. MacDiarmid, *J. Inorg. Nucl. Chem.*, 25 (1963) 1503.
- 12 R. Schaeffer and L. Ross, *J. Amer. Chem. Soc.*, 81 (1969) 3486.
- 13 A.J. Vanderwiel and M.A. Ring, *Inorg. Nucl. Chem. Lett.*, 8 (1972) 421.
- 14 H. Jenkner, German Patent 1 161 542, 1964.
- 15 J.A. Conner, R.N. Haszeldine and G.J. Leigh, *Abstr. Papers, Intern. Organosilicon Symp., Prague, 1965*, p. 109.
- 16 L.J. Edwards, R.K. Pearson, U.S. Patent 3 007 768, 1957; *Chem. Abstr.*, 56 (1962) 11236d.
- 17 D.T. Hurd, *J. Amer. Chem. Soc.*, 70 (1948) 2053.
- 18 R. Köster, K. Reinert and K.H. Müller, *Angew. Chem.*, 72 (1960) 78.
- 19 S.H. Langer, *Chem. Ind. (London)*, (1958) 1664.
- 20 J.W. Emsley, J. Feeney and L.H. Sutcliffe, *High Resolution Magnetic Resonance Spectroscopy*, Vol. 2, Pergamon, London, p. 970-979.
- 21 H. Nöth and H. Vahrenkamp, *Chem. Ber.*, 99 (1966) 1049.