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Synthesis and polymerization of 1-trimethylsiloxy- or 1-triphenylsiloxysilacyclobutanes

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Summary

Synthesis and polymerization behavior of 1-trimethylsiloxy- or 1-triphenylsiloxy-silacyclobutane derivatives were studied. These monomers gave polymers with reasonably high molecular weight by platinum catalyst like platinum 1,3-divinyl-1,1,3,3-tetramethyldisfloxane complex. Side-chain smectic, liquid crystalline polymer was obtained from 1-methyl-1-[3-{(4-cyanobiphenyl-4'-yl)oxy}propyl]dimethylsiloxysilacyclobutane.

In the polymerization by butyllithium or phenyllithium, monomers corresponding to the amounts of the initiator were consumed, but no polymers were formed. Apparently, elimination of the trimethylsiloxy or triphenylsiloxy group occurred in the nucleophilic attack of the initiator or propagating species on the silicon atom of the monomer.

Introduction

We reported new synthetic routes to functionalized disiloxane derivatives (1-3). The existence of disiloxane in the spacer or side chain is quite effective for polydiene, polystyrene or polyoxetane to exhibit liquid crystallinity(4-8). We also reported the synthesis of poly[(methylphenylsilylene)trimethylene] rich in isotacticity by polyaddition of optically active allylmethylphenylsilane in the presence of platinum catalyst(9). Combination of these results, namely siloxane in side chain and stereoregularity of the polycarbosilane main chain, is considered to lead to a development of new class of side-chain liquid crystalline polymers.

Control of molecular weight of the polymer is also very important to correlate such property of the polymer with the molecualr structure. Ring-opening polymerization of silacyclobutane will be a suitable method to control the molecular weight. Until now, there have been considerable number of reports on the polymerization of silacyclobutanes. However, there are only few reports on the controlled polymerization of the compounds. Matsumoto reported the living nature of the polymerization of 1,1-dimethyl- and 1,1-diethylsilacyclobutanes by butyllithium(10, 11). It is of great interest to study the ring-opening polymerization of optically active silacylobutane derivatives with mesogenic group connected on silicon atom through siloxane linkage to control the liquid crystalline behavior by controlling both molecular weight and stereoregularity of the polymer. As a preliminary experiment, we have studied the polymerizability of 1-trimethylsiloxy- or 1-triphenylsiloxysilacyclobutanes by platinum complex and butyl- or phenyllithium.

Experimental

General

300 MHz ^{1}H, 75.4 MHz ^{13}C-{^{1}H}NMR, ^{1}H-^{1}H COSY, and 79.5 MHz ^{29}Si NMR spectra were recorded on Varian NMR spectrometers model Gemini 2000, and UNITY INOVA 400, respectively. The chemical shifts were given in ppm relative to $CHCl_3$(7.26 ppm for ^{1}H, 77.0 ppm for ^{13}C) and tetramethylsilane(0.00 ppm for ^{29}Si) as internal standards in $CDCl_3$. IR spectra were measured on KBr disk sample on a JASCO VALOR-III spectrometer, and characteristic absorptions were given in cm^{-1}. Molecular weights of the polymers were estimated by a JASCO gel permeation chromatograph(GPC) model 980 at 40

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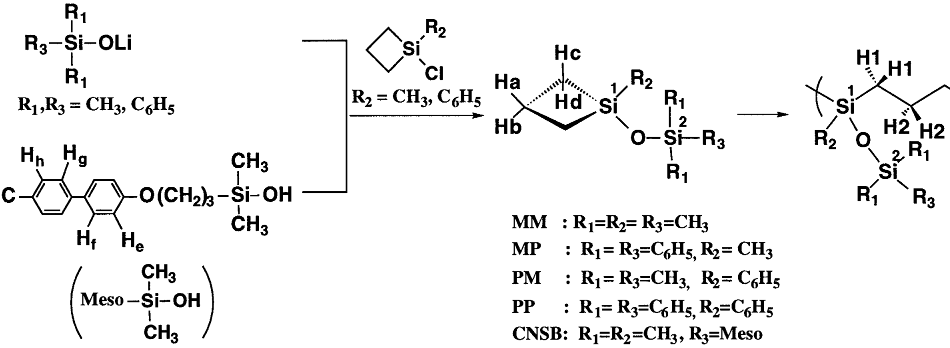
°C equipped with Shodex KF-800P(precolumn), KF-801 (exclusion molecular weight, polystyrene M_n = 1.5x10^3), and KF-804(exclusion molecular weight, polystyrene M_n=4.0x10^5) columns. Mass spectra(MS) were obtained on a SHIMADZU QP-5000 spectrometer. Optical polarization micrographs were taken on a Nikon optical polarization micrograph Model OPTIPHOTO-2 equipped with a Mettler FP82 hot stage.

Synthesis

1-Chloro-1-methylsilacyclobutane(61 %), 1,1-dichlorosilacyclobutane(69 %) and 1-chloro-1-phenylsilacyclobutane(40 %) were synthesized similarly to the reported methods(12, 13). Monomers were synthesized as shown in Scheme 1, and typical synthetic procedures are shown in the following. Indication of atoms is also shown in the scheme.



Scheme 1 . Synthetic routes to monomers and indication of atoms.

1-Methyl-1-trimethylsiloxysilacyclobutane(MM)

To lithium trimethylsilanolate(1) prepared from hexamethylcyclotrisiloxane (D_3)(2.30 g, 10.4 mmol) and methyllithium(1.03 M ether solution, 30.2 mL, 31.1 mmol) in ether(50 mL), 1-chloro-1-methylsilacyclobutane(3.75 g, 31.1 mmol) was added. After stirred for 1h at room temperature, phosphoric acid buffer solution(pH 6.86, 15 mL) was added, organic phase was separated, and the crude product was purified by distillation under reduced pressure(3.05 g, 56 %). Bp.80-83°C/95 mmHg.

^{1}H NMR δ 0.12(s, 9H, Si(CH_3)$_3$), 0.23(s, 3H, SiCH_3), 1.04-1.27(m, 4H, *H*c, *H*d), 1.43-1.62(m, 1H, *H*a or *H*b), 1.88-2.02(m, 1H, *H*a or *H*b). ^{29}Si NMR δ 9.62(Si^1), 5.19(Si^2). IR: 1254(Si-C), 1055 (Si-O-Si). MS (m/z): 175(M+H$^+$), 159(M$^+$-CH$_3$).

1-Methyl-1-triphenyisiloxysilacyclobutane(MP)

This compound was purified by column chromatography(hexane, Rf: 0.29, 37 %).

^{1}H NMR δ 0.27(s, 3H, SiCH_3), 1.13-1.19(m, 4H, *H*c, *H*d), 1.46-1.63(m, 1H, *H*a or *H*b), 1.81-1.92(m, 1H, *H*a or *H*b), 7.33-7.49(m, 9H, aromatic protons), 7.56-7.62(m, 6H, aromatic protons). ^{29}Si NMR δ8.28(Si$_1$), -19.98(Si^2). MS (m/z): 361 (M+H$^+$).

1-Phenyl-trimethylsiloxysilacyclobutane(PM)(66 % Bp.74-77°C/1.4 mmHg) and **1-phenyl-1-triphenylsiloxysilacyclobutane(PP)**(31 %, Mp.63-65 °C) also gave reasonable analysis data.

1-Methyl-1-[3-{(4-cyanobiphenyl-4'-yl)oxy}propyl]dimethylsiloxysilacyclobutane (CNSB)

1-Chloro-1-methylsilacyclobutane(0.44 g, 3.66 mmol) was condensed with [3-{(4-cyanobiphenyl-4'-yl)oxylpropyl]dimethylsilanol(4) in THF(10 mL) in the presence of triethylamine (0.37 g, 3.66 mmol) at room temperature. The crude compound was purified by column chromatography (hexane:dichloromethane =1 : 1, Rf: 0.35). Viscous liquid(0.40 g, 48 %).

^{1}H NMR δ 0.16(s, 6H, $\mathrm{Si^2C}H_3$), 0.24(s, 3H, $\mathrm{Si^1C}H_3$), 0.70(m, 2H, $\mathrm{Si^1C}H_2$), 1.14(m, 4H, H_c, H_d), 1.43-1.60(m, 1H, H_a or H_b), 1.76-2.00(m, 3H, $\mathrm{Si^2C}H^2\mathrm{C}H_2$, H_a or H_b), 4. 00(t, 2H, J = 6.6 Hz, $\mathrm{C}H_2\mathrm{O}$), 6.99(d with fine coupling, 2H, J = 9.0 Hz, H_e), 7.53(d with fine coupling, 2H, J = 9.0 Hz, H_f), 7.64, 7.69(two d with fine coupling, 2H each, J = 8.7 Hz, H_g, H_h).
IR: 2227(CN), 1251 (Si-C), 1050(Si-O-Si).

Polymerization by platinum complex

Polymerizations were carried out mainly with PtDVTMDS (platinum 1,3-divinyl-1,1,3,3-tetramethyldisiloxane)(14). Formed polymers were recovered by precipitation from THF into methanol and purified by reprecipitation from THF into methanol. The name of polymers are abbreviated by the combination of P and the abbreviation name of the monomer.

PMM

^{1}H NMR δ 0.01(s, 3H, $\mathrm{Si^1C}H_3$), 0.06(s, 9H, $\mathrm{Si^2C}H_3$), 0.56(m, 4H, H1), 1.37(q, 2H, J = 4.8 Hz, H2). ^{13}C NMR δ -1.43($\mathrm{Si^1}C\mathrm{H_3}$), 1.90($\mathrm{Si^2}C\mathrm{H_3}$), 17.05($\mathrm{CH_2}C\mathrm{H_2CH_2}$), 21.62 ($\mathrm{Si^1}C\mathrm{H_2}$). ^{29}Si NMR δ 6.43($\mathrm{Si^1}$, $\mathrm{Si^2}$). IR: 1253(Si-C), 1059(Si-O-Si).

PPM and **PPP** gave reasonable NMR and IR data.

PCNSB

The polymerization was carried out at 120°C for 12h. 0.013 g, 11 %.

^{1}H NMR δ 0.03(s, 3H, $\mathrm{Si^1C}H_3$), 0.07(s, 6H, $\mathrm{Si^2C}H_3$), 0.40-0.62(broad, 6H, H1, $\mathrm{Si^1C}H_2$), 1.24-1.41(broad with a small peak in the higher field, 2H, H2), 1.75-1.90(broad with a small peak in the lower field, 2H, $\mathrm{C}H_2\mathrm{CH_2O}$), 3.80-3.98(broad, 2H, $\mathrm{C}H_2\mathrm{O}$), 6.88-7.00(m, 2H, He), 7.40-7.68(m, 6H, Hf, Hg, Hh). IR: 2226(CN), 1060(Si-O-Si).

Model reaction of phenyllithium with MM

To a solution of phenyllithium(0.91 M ether-cyclohexane solution, 5.22 mL, 4.75 mmol) in THF(3.28 mL), MM(0.83 g, 4.75 mmol) was slowly added at -40°C. The reaction mixture was stirred for 1h at the temperature and quenched with ethanol and phosphoric acid buffer solution(pH 6.86, 15 mL). The organic materials were extracted, dissolved in THF, and poured into methanol to separate oligomers from the mixture(0.16 g, M_n=1060, M_n/M_w= 1.18). Two materials were obtained as separable major fraction by column chromatography(hexane) and were proved to be methylpropyldiphenylsilane(0.09 g, Rf: 0.53) and 1-methyldiphenylsilyl-3-(methylphenylpropylsilyl)propane(0.04 g, Rf: 0.33). The rest fraction(0.42 g) could not be separated.

1-Methyldiphenylsilyl-3-(methylphenylpropylsilyl)propane

^{1}H NMR δ 0.19(s, 3H, $\mathrm{PhSiC}H_3$), 0.50(s, 3H, $\mathrm{Ph_2SiC}H_3$), 0.70(m, 2H, $\mathrm{C}H_2\mathrm{CH_2CH_3}$), 0.85(m, 2H, $\mathrm{PhSiC}H_2$), 0.91 (t, 3H, J = 7.2 Hz, $\mathrm{CH_2C}H_3$), 1.13(m, 2H, $\mathrm{Ph_2SiC}H_2$), 1.28 (m, 2H, $\mathrm{SiCH_2C}H_2\mathrm{CH_2Si}$), 1.47(m, 2H, $\mathrm{CH_2}CH_2\mathrm{CH_3}$), 7.28-7.37(m, 9H, aromatic protons), 7.41-7.48(m, 6H, aromatic protons). MS (m/z): 402 ($\mathrm{M^+}$).

Attempted polymerization of MM by phenyllithium ([M]/[I] = 20)

To a solution of MM(0.83 g, 4.75 mmol) in THF(3.52 mL) was added phenyllithium (1.02 M ether-cyclohexane solution, 0.23 mL, 0.23 mmol) at -40°C. After stirred for 1h, ethanol(1.0 mL) was added to stop the reaction. **1-Ethoxy-1-propyl-1,3,3,3-tetramethyldisiloxane** was recovered by distillation (Bp. 113-115°C/130 mmHg, 0.83 g, 80 %).

^{1}H NMR δ 0.05(s, 3H, $\mathrm{SiC}H_3$), 0.10(s, 9H, $\mathrm{Si(C}H_3)_3$), 0.54(m, 2H, $\mathrm{SiC}H_2$), 0.96(t, 3H, J = 7.2 Hz, $\mathrm{CH_2CH_2C}H_3$), 1.20(t, 3H, J = 6.6 Hz, $\mathrm{OCH_2C}H_3$), 1.38(m, 2H, $\mathrm{CH_2C}H_2\mathrm{CH_3}$), 3.73(m, 3H, $\mathrm{OC}H_2$). ^{29}Si NMR δ -13.16($\mathrm{C_2H_5O}Si$), 7.26($Si\mathrm{(CH_3)_3}$). IR: 1256(Si-C), 1062(Si-O-Si). MS (m/z): 221 ($\mathrm{M{+}H^+}$), 205 ($\mathrm{M^+{-}CH_3}$), 177 ($\mathrm{M^+{-}C_3H_7}$).

Results and Discussion

Polymerization by platinum complex

The results of the polymerization are shown in Table 1.

Table 1. Polymerization of silacyclobutanes in bulk

Monomer	Cat/Initiator	Temp. (°C)	Time (h)	Yield (%)	M_n ($\times 10^{-4}$)[c]	M_w/M_n[c]
MM	PtDVTMDS[a]	80	18	63	1.31	4.98
	H_2PtCl_6[a]	80	0.8	–	–	–[d]
	PhLi[b]	-40	2	–	–	–[e]
MP	PtDVTMDS[a]	60	1	–	–	–[d]
PM	PtDVTMDS[a]	60	0.25	72	17.3	2.88
PP	PtDVTMDS[a]	80	0.5	52	1.89	20.9[f]
SCBN	H_2PtCl_6[a]	120	12	11	1.54	4.45

a) [M] / [Cat] = 10,000. b) In THF, [M]/[I]=20, [M]=1.0 M. c) Estimated by GPC, correlating to standard polystyrene in THF. d) Geled. e) No polymerization. f) There is some disorder in the polymer structure.

Polymerization by PtDVTMDS gave reasonable yield and molecular weight of the polymers. Mesogenic monomer also gave reasonably high molecular weight polymer. Monomers with triphenylsiloxy substituent tended to gel. Four kinds of signals were observed in ^{13}C NMR, and two kinds in ^{29}Si NMR of PPM. These facts indicate that the polymers were formed through regiospecific ring-opening of the monomers. This is also true for other polymers. In ^{13}C NMR of PPM, splitting of $SiCH_2$ assignable to diad tacticity is observed (Figure 1). The equal strength of signals at 20.42 and 20.48 ppm indicates that the polymer is atactic. Such splitting based on the tacticity will be helpful in elucidation of not only the stereoregularity of these polymers but also that of the polymers from optically active 1,1,2-trisubstituted monomers in the future.

PCNSB exhibited smectic phase by annealing at room temperature (Figure 2).

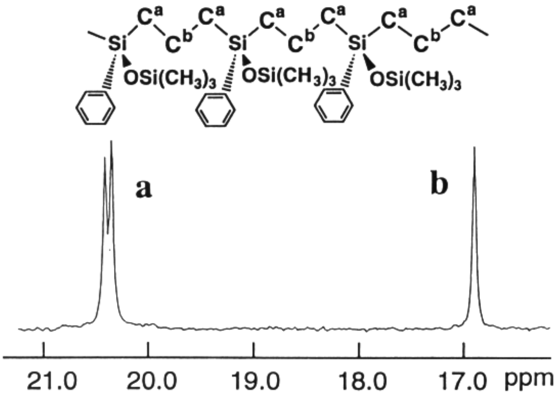


Figure 1. ^{13}C NMR spectrum of the main chain region of PPM (75 MHz, room temperature in $CDCl_3$).

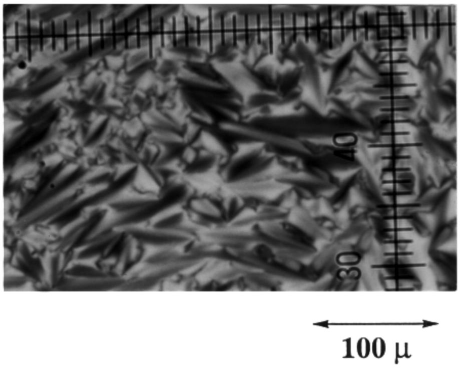
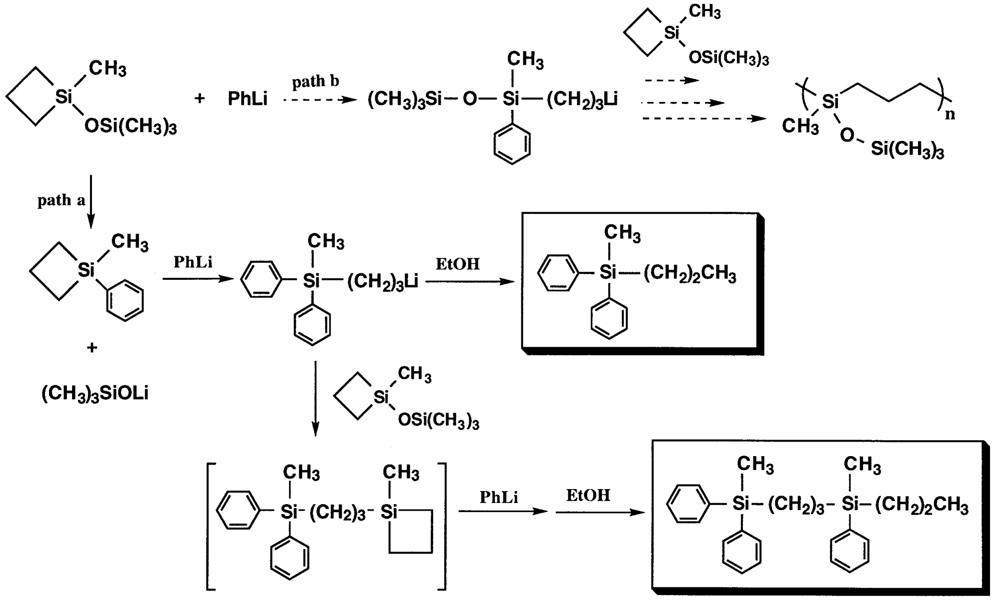


Figure 2. Optical polarization micrograph of PCNSB annealed at room temperature for 1 month.

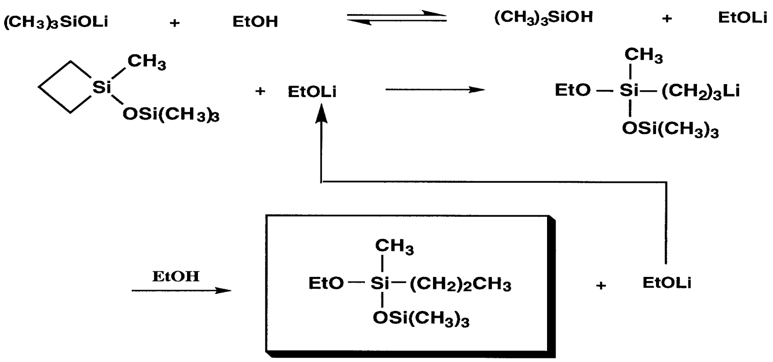
Polymerization by alkyllithium

Contrary to the polymerization by platinum complex, anionic polymerization by butyl- or phenyllithium did not give methanol insoluble polymer. It was shown that almost 95% of the monomer remained as unreacted checked by GLC before stopping the reaction with methanol. In order to clarify the reason why monomers only corresponding to the amounts of the initiator were consumed in the anionic polymerization, elementary reactions of phenyllithium. with MM(molar ratio, phenyllithium : MM=1 : 1) were studied(see model reaction in experimental section). Methylpropyldiphenylsilane and 1-methyidiphenylsilyl-3-(methylphenylpropyl-silyl)propane were isolated from the reaction system. This fact clearly indicates that the initial reaction of phenyllithium. with MM is a nucleophilic attack of phenyllithium on the silicon atom of the ring of the monomer. Since trimethylsiloxy anion is a better leaving group(path a) than the carbanion formed by the cleavage of the silacyclobutane ring(path b), elimination of trimethylsilanolate occurred after the nucleophilic attack of phenyllithium. Thus, 1-methyl-1-phenylsilacyclobutane was formed as an intermediate, which was further opened by phenyllithium to lead to methylpropyldiphenylsilane and 1-methyldiphenylsilyl-3-(methylphenylpropylsilyl)propane (dimer of 1-methyl-1-phenylsilacyclobutane). 1-Methyl-1-[3-(methyldiphenylsilyl)propyl]-silacyclobutane could not be isolated. Whole reaction scheme in the initial steps of the polymerization would be written as shown in Scheme 2.



Scheme 2. Reaction of MM with phenyllithium in the initial steps.

Here, comments must be made on the fate of the unreacted monomers in anionic polymerization by phenyl- or butyllithium ([M]/[I]=20) by quenching with ethanol. When the polymerization system was treated with ethanol, all the monomers disappeared after 30 min, instead, 1-ethoxy-1-propyl-1,3,3,3-tetramethyldisiloxane was recovered as ether soluble fraction. When MM was added to a solution of phenyllithium and ethanol(1:20), the obtained material was the same. This compound was considered to be formed by catalyzed ethanolysis of the monomer as shown in Scheme 3. When methanol was used, 1-methoxy-1-propyl-1,3,3,3-tetramethyldisiloxane was obtained(Bp. 90-95°C/105 mmHg).



Scheme 3. Fate of MM with with ethanol (EtOH) as quenching agent.

Conclusions

Trialkylsiloxy substituted silacyclobutane can be polymerized by platinum catalyst, but not by alkyllithium. The polymer with mesogenic group was found to be a new side-chain type liquid crystalline polymer.

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References

1. Kawakami Y, Aoki T, Hisada H, Yamamura Y, Yamashita Y (1985) *Polym Commun* ***2 6***: 133
2. Mori A, Hishida T, Soga Y, Kawakami Y (1995) *Chem Lett* 107
3. Mori A, Sato H, Mizuno K, Hiyama T, Shintani K, Kawakami Y (1996) *Chem Lett* 517
4. Kawakami Y, Toida K, Ito Y (1993) *Macromolecules* ***2 6***: 1177
5. Kawakami Y, Toida K (1995) *Macromolecules* ***2 8***: 816
6. Kawakami Y, Ichitani M, Kunisada H, Yuki Y (1996) *Polym J* ***2 8***: 513
7. Kawakami Y, Inoue H, Kishimoto N, Mori A (1996) *Polym Bull* ***3 6***: 653
8. Kawakami Y, Suzuki M, Kato Y (1996) *Polym J* ***2 8***: 845
9. Kawakami Y, Takeyama K, Komuro K, Ooi O (1998) *Macromolecules* ***3 1***:551
10. Matsumoto K, Yamaoka H (1995) *Macromolecules* ***2 8***: 7029
11. Matsumoto K, Shimazu H, Deguchi M, Yamaoka H (1997) *J Polym Sci Part A: Polym Chem* ***3 5***: 3207
12. Auner N, Grobe J (1980) *J Organomet Chem* ***188***: 25
13. Dubac J, Mazerolles P, Lesbre M, Joly M (1970) *J Organomet Chem* ***2 5***: 367
    See also: Nametkin N S, Babich E D, Karel’skii V N, Vdovin V M (1971) *Izv Akad Nauk SSSR Ser Khim* 748
    Nametkin N S, Babich E D, Karel’skii V N, Vdovin V M (1971) *Izv Akad Nauk SSSR Ser Khim* 1033
    Pozdnyakova M V, Babich E D, Nametkin N S, Vdovin V M (1974) *Zh Anal Khim* ***2 9***: 598
14. Chandra G, Lo P Y, Hitchcock P B, Lappert M F (1987) *Organometallics* ***6***: 191