

CYCLIC NITRILOTRIETHYLENE TRIORGANOSILYL TITANATE(IV):
"MONO-", "DI-" AND "TRITITANATES"*

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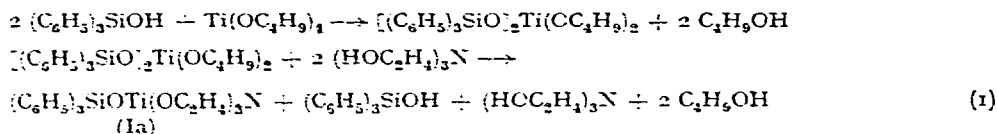
(Received September 20th, 1965)

The preparation of titanates containing triorganosilyl¹⁻³ or nitrilotriethylene⁵ groups has been reported. The present work describes three new classes of titanates containing both triorganosilyl and nitrilotriethylene groups: "monotitanates", $R_3SiOTi(OC_2H_4)_3N$ (I); a "dititanate", $[R_3SiOTi(OC_2H_4)_3N][ROTi(OC_2H_4)_3N]$ (II); and "trititanates", $[R_3SiOTi(OC_2H_4)_3N][N(C_2H_4O)_3TiOTi(OC_2H_4)_3N]$ (III).

The results of this study show that the course of reaction is dependent upon the steric requirements of the organic groups in $RR'R''Si-$ rather than the electrical nature of the organic groups concerned.

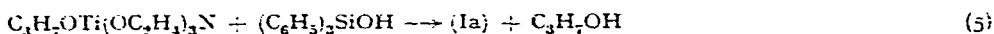
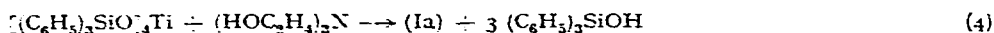
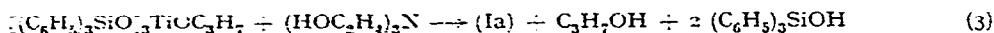
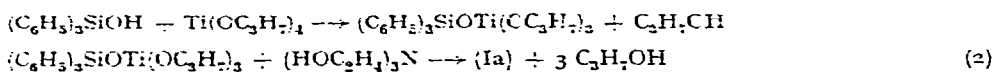
"MONOTITANATES"

A study of the monotitanates was undertaken when a nitrilotriethylene group was found to displace a triphenylsilyl and two butyl groups in bis(triphenylsilyl)dibutyl titanate to form cyclic nitrilotriethylene triphenylsilyl titanate(IV), (Ia).



Reports^{1,2} on the stability of Si-O-Ti linkages led several workers^{6,7} to attempt to prepare metal organic polymers of the type $[(R_3SiO)_2TiO]_n$, with some degree of success. The R groups were varied, and in the case of the triphenylsilyl homolog a molecular weight of 10,000 was reported⁷. The isolation of (Ia) may well be considered an indication that the Si-O-Ti bonds can be broken by triethanolamine which results in the formation of a chelated 5-coordinate titanium compound**.

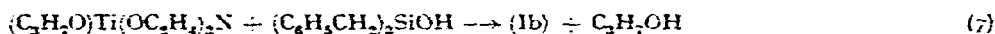
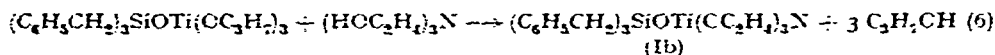
Other reactions found to produce (Ia) are:



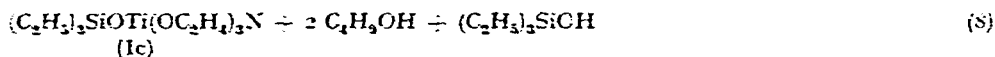
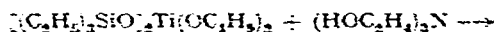
* Presented at the Second International Symposium on Organometallic Chemistry, Madison, Wis., September 1, 1965.

** X-ray studies of (Ia) and (Ib) by Dr. JAMES A. IBERS of Northwestern University are in progress.

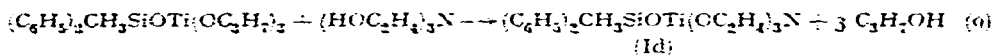
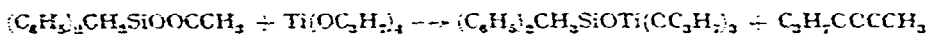
The ester interchange reactions in preparing (Ia) are applicable to the preparation of cyclic nitrilotriethylene tribenzylsilyl titanate(IV), (Ib).



Similarly, cyclic nitrilotriethylene triethylsilyl titanate (IV) (Ic), was isolated.

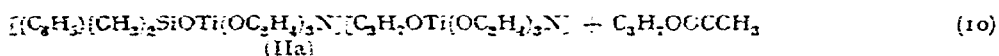
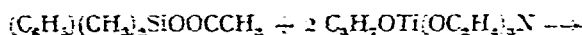


The cyclic nitrilotriethylene diphenylmethylsilyl titanate(IV), (Id), was also isolated; however, one reactant, diphenylmethylsilyl acetate, was varied from that used in the equations above.

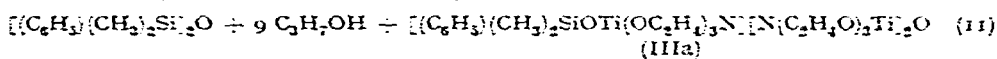
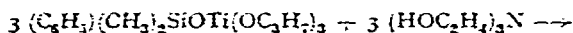


"DITITANATE" AND "TRITITANATE"

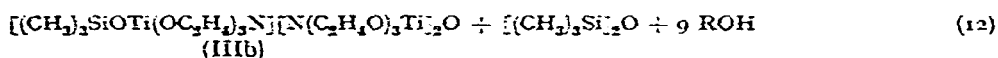
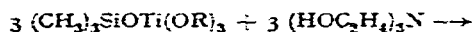
To complete the series, attempts were made to form the monotitanates of cyclic nitrilotriethylene phenyldimethylsilyl titanate(IV) and cyclic nitrilotriethylene trimethylsilyl titanate(IV). However, compounds of greater complexity were obtained in each case. The order of addition is important in the phenyldimethyl analogue. On addition of excess phenyldimethylsilyl acetate to cyclic nitrilotriethylene isopropyl titanate the dititanate, cyclic nitrilotriethylene phenyldimethylsilyl titanate(IV), (IIa), is formed.

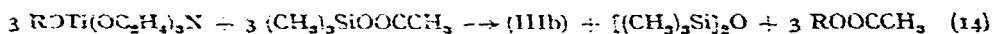
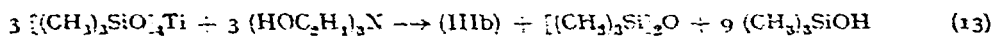


On reversing the order of addition of the reactants, the trititanate (IIIa) was obtained.



In the investigation of the trimethylsilyl analogue, only the trititanate was obtained, regardless of the order of addition.





The formation of (IIIb) is consistent with the formation of an unstable monotitanate intermediate which can rearrange to form a stable trititanate. The mechanism by which mono-, di- and trititanates are formed, has not been conclusively established.

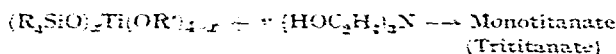
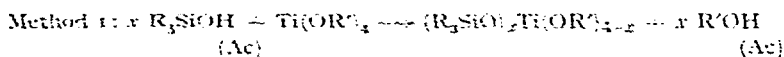
These results indicate that the R groups in the organosilane have a geometrical rather than electrical effect in determining whether mono-, di- or trititanates are obtained. Expansion of this series to include stannoxytitanium analogues is in progress.

EXPERIMENTAL

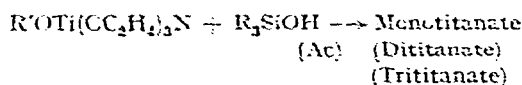
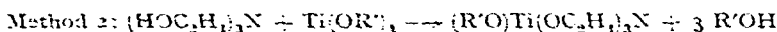
Trimethylchlorosilane and triphenylsilanol were obtained from Stauffer Chem. Co. and Union Carbide Corp.; triethylchlorosilane, diphenylchlorosilane and triethylsilane from Peninsular Chem. Research, Inc.; titanium alkoxides, from Dupont and Stauffer Chem. Co.; monohydroxyethyltrihydroxypropyl-ethylenediamine (Nalco L699) from Nalco Chem. Co. All other chemicals were obtained from Fisher Sci. Co. or Eastman Kodak. The compounds were maintained moisture free, after purification by recrystallization or distillation, and identified by their melting point or refractive index.

Analyses were obtained from The Glidden Co. laboratories, (Baltimore, Md.), Schwartzkopf Microanalytical Laboratories (N.Y.C.), and Galbraith Laboratories, Inc. (Knoxville, Tenn.). Molecular weights were obtained on a Mechrolab Vapor Pressure Osmometer Model 301A in toluene at 37°.

Two ester interchange methods are used in the preparation of this series of cyclic nitrilotriethylene triorganosilyl titanate(IV), mono-, di- and trititanates.



where $x = 1, 2$ or 4



Cyclic nitrilotriethylene triphenylsilyl titanate(IV), (Ia)

Method 1(a). Triphenylsilanol, m.p. 153–154.5° (lit.⁸ 155°), was prepared from triphenylchlorosilane, triethylamine, and water in toluene. The triphenylsilanol (27.64 g, 0.225 moles) was added as a dry powder to a refluxing solution of tetra-isopropyl titanate (28.42 g, 0.225 moles) in toluene (1200 ml). The isopropanol/toluene azeotrope was removed before triethanolamine (14.92 g, 0.225 moles) was added. A precipitate formed continuously as the isopropanol/toluene azeotrope was removed. The reaction product was cooled, filtered, washed with petroleum ether and dried,

yielding (79.5 g, 75%) white crystals of cyclic nitrilotriethylene triphenylsilyl titanate(IV), m.p. 268–270°. (Found: Si, 6.15, 6.16; Ti, 10.15, 10.22. $C_{24}H_{27}NO_4SiTi$ calcd.: Si, 5.98; Ti, 10.21%.)

Method 1(b). A solution of triphenylsilanol (5.53 g, 0.02 moles) in toluene (245 ml) was added to a refluxing solution of tetrabutyl titanate (3.40 g, 0.01 moles). After refluxing 30 minutes, the butanol-toluene azeotrope was removed. To this solution was added triethanolamine (2.98 g, 0.02 moles) and the azeotrope removed and the white crystalline solid (3 g, 72%) was isolated, m.p. 270–271°. (Found: Si, 6.07, 6.11; Ti, 10.58, 10.48. $C_{24}H_{27}NO_4SiTi$ calcd.: Si, 5.98; Ti, 10.21%.)

Method 1(c). Tetrakis(triphenylsiloxy)titanium¹ (2.30 g, 0.002 moles) was added to a beaker containing toluene (400 ml) and heated to reflux. Triethanolamine (0.60 g, 0.004 moles) was added by means of a hypodermic syringe. Most of the insoluble tetrakis(triphenylsiloxy)titanium reacted, forming a clear solution. The supernatant was decanted, cooled and filtered yielding cyclic nitrilotriethylene triphenylsilyl titanate(IV) (0.34 g, 36%) m.p. 266–268°. (Found: Si, 5.54, 5.70; Ti, 10.42, 10.50; mol. wt., 460. $C_{24}H_{27}NO_4SiTi$ calcd.: Si, 5.98; Ti, 10.21%; mol. wt., 469.)

Method 1(d). Every attempt at isolating tris(triphenylsiloxy)titanium isopropoxide by Method 1 led to the formation of tetrakis(triphenylsiloxy)titanium. This compound was obtained while reacting monohydroxyethyl trihydroxyisopropyl ethylenediamine (2.78 g, 0.01 moles) with tetraisopropyl titanate (5.88 g, 0.02 moles) and triphenylsilanol (11.05 g, 0.04 moles) in toluene (500 ml) and removing the isopropanol-toluene azeotrope with the intention of preparing $[(C_6H_5)_3SiO]_2Ti(OC_2H_4(OC_2H_5)NC_2H_4N(C_2H_5O)_2TiOSi(C_6H_5)_3)_2$. Instead, tris(triphenylsiloxy)titanium isopropoxide was isolated (7.51 g, 62%). (Found: C, 74.20; H, 5.45; Si, 8.95; Ti, 5.17, 5.02. $C_{27}H_{32}O_4Si_3Ti$ calcd.: C, 73.38; H, 5.62; Si, 9.03; Ti 5.13%.) To this compound (3.13 g, 0.0036 moles) in refluxing toluene (300 ml) was added triethanolamine (9.50 g, 0.0036 moles). After removal of the isopropanol-toluene azeotrope, the volume was reduced to 100 ml and allowed to stand for 16 h. A white crystalline solid was obtained (m.p. 268–270°).

Method 2. To a refluxing solution of triethanolamine (7.50 g, 0.05 moles) in toluene (400 ml) was added tetraisopropyl titanate (14.21 g, 0.05 moles) and the isopropanol-toluene azeotrope was removed. Triphenylsilanol (13.82 g, 0.05 moles) was added and the azeotrope was removed. On cooling, (Ia) was isolated (17 g, 73%), m.p. 267–270°. (Found: Si, 5.96; Ti, 10.42. $C_{24}H_{27}NO_4SiTi$ calcd.: Si, 5.98; Ti, 10.21%.)

The compound (Ia) is soluble in acetic anhydride, triethanolamine, and methanol; partially soluble in pyridine, dimethylformamide, ethanol and toluene; and insoluble in tetrahydrofuran, ethyl acetate, cellosolve, acetonitrile, dioxane, petroleum ether, ethyl ether, phenyl ether, isopropanol, acetone and water. Soxhlet extraction of (Ia) with ethanol destroyed the compound, while toluene was a slow (26 h) but excellent solvent. A dry acetone/chloroform solution proved to be an excellent medium for growing single crystals of (Ia).

Cyclic nitrilotriethylene tribenzylsilyl titanate(IV), (Ib)

Method 1. Tribenzylsilanol, m.p. 102–3° (lit.¹⁰ 104°) was prepared from tribenzylchlorosilane, pyridine and water in a benzene solution. A solution of tribenzylsilanol (31.85 g, 0.1 moles) in benzene (200 ml) was added to a refluxing solution of tetraisopropyl titanate (28.42 g, 0.1 mole) in benzene (400 ml). The azeotrope was

removed, triethanolamine (14.92 g, 0.1 mole) was added, and again the azeotrope was removed. On cooling, white crystals of (Ib) precipitated (29.3 g, 55%), m.p. 150–151°. (Found: Si, 5.18; Ti, 9.36; mol. wt., 509 (VPO in toluene), 495 (ebullioscopically in benzene); density 1.28 g/cc. $C_{27}H_{33}NO_4SiTi$ calcd.: Si, 5.49; Ti, 9.36; mol. wt., 511.) The m.p. remained unchanged after five months, but after 15 months the m.p. increased to 166–168°.

This synthesis was repeated yielding (Ib) (45.78 g, 90%) as a white crystalline substance whose m.p. was 168–169°. (Found: Si, 5.24, 5.37; Ti, 9.18; N, 2.68. $C_{27}H_{33}NO_4SiTi$ calcd.: Si, 5.49; Ti, 9.36; N, 2.74%.)

Method 2. Triethanolamine (29.83 g, 0.2 mole) was added to a refluxing solution of tetraisopropyl titanate (56.85 g, 0.2 mole) in cyclohexane (1200 ml) and the isopropanol/cyclohexane azeotrope removed. After cooling, tribenzylsilanol (63.7 g, 0.2 mole) was added as a powder, and the mixture was refluxed before removing the azeotrope. After filtration and washing with petroleum ether, (Ib) was isolated (79.1 g, 70%), m.p. 165–167°.

(Ib) is soluble in pyridine, dimethylformamide, acetic anhydride, chloroform, toluene, decalin (hot), methyl alcohol (hot), ethyl alcohol (hot), isopropanol (hot), triethanolamine (hot), and insoluble in cellosolve, dioxan, ethyl ether, *n*-hexane, petroleum ether and water.

Cyclic nitrilotriethylene triethylsilyl titanate(IV), (Ic)

Method 1(a). Triethylsilanol¹¹ was prepared from triethylsilane and potassium hydroxide, then neutralized with hydrochloric acid. Triethylsilanol (59.53 g, 0.45 mole) was added to a refluxing solution of tetraisopropyl titanate (127.91 g, 0.45 mole) and the azeotrope was removed. Triethanolamine (67.14 g, 0.45 mole) was added and the azeotrope and most of the solvent was removed. The white crystals were isolated by filtration, washed with petroleum ether and dried, m.p. 166–168°. Well defined crystals form in the filtrate on standing several days.

Method 1(b). Triethylsilanol (52.91 g, 0.04 mole) was added to tetrabutyl titanate (68.07 g, 0.02 mole) and the butanol was removed under vacuum. Toluene (300 ml) was added and the solution was refluxed. Triethanolamine (29.84 g, 0.2 mole) was added and the azeotrope was removed. The solvent was partially stripped and (Ic) was isolated by filtration, washed with petroleum ether and dried, m.p. 166–168°. (Found: C, 43.87, 44.11; H, 8.31, 8.52; Si, 9.22, 9.24; Ti, 15.68, 15.54; N, 4.66, 4.56. $C_{12}H_{24}NO_4SiTi$ calcd.: C, 44.30; H, 8.37; Si, 8.63; Ti, 14.72; N, 4.31%.)

Cyclic nitrilotriethylene diphenylmethylsilyl titanate(IV), (Id)

Method 1. Diphenylmethylsilyl acetate, n_D^{25} 1.5527 (lit.¹⁰ n_D^{20} , 1.5530), was prepared from diphenylmethylchlorosilane and sodium acetate in toluene. A solution of diphenylmethylsilyl acetate (7.71 g, 0.0301 mole) in toluene (160 ml) was added to tetraisopropyl titanate (8.55 g, 0.0301 mole) in toluene (120 ml), and the azeotrope removed. Triethanolamine (4.49 g, 0.0301 mole) was added to the solution and again the azeotrope was removed. Petroleum ether was added to the solution causing precipitation of (Id) as a white solid (10.5 g, 86%), m.p. 172–174°. (Found: Si, 6.68; Ti, 11.87; mol. wt., 395. $C_{19}H_{25}NO_4SiTi$ calcd.: Si, 6.89; Ti, 11.76%; mol. wt., 391.)

(Id) is soluble in decalin, dimethylformamide, acetic anhydride, ethylene glycol, tetrahydrofuran, phenyl ether, chloroform, toluene and benzene.

Cyclic nitrilotriethylene phenyldimethylsilyl titanate(IV) cyclic nitrilotriethylene isopropyl titanate(IV), (IIa)

Method 2. Cyclic nitrilotriethylene isopropyl titanate(IV) (12.15 g, 0.05 mole) was prepared in toluene (600 ml) and phenyldimethylsilyl acetate¹³ (9.71 g, 0.05 mole) in toluene (50 ml) was added and the azeotrope removed. On standing several days, a white solid, (IIa), precipitated. (IIa) was isolated by filtration, then washed with petroleum ether and dried (5.76 g, 39%). (Found: Si, 4.31; Ti, 16.01; N, 4.32. $C_{23}H_{42}N_3O_9SiTi_2$ calcd.: Si, 4.68; Ti, 15.95; N, 4.67%.)

The synthesis was repeated and (IIa) gave a m.p. 173–175°. (Found: Si, 4.54; Ti, 16.33; N, 4.66. $C_{23}H_{42}N_3O_9SiTi_2$ calcd.: Si, 4.68; Ti, 15.95; N, 4.67%.)

Cyclic nitrilotriethylene phenyldimethylsilyl titanate(IV) bis(nitrilotriethylene)titanate(IV), (IIIa)

Method 1. Phenyldimethylsilyl acetate¹³ (8.80 g, 0.0453 mole) was added to tetraisopropyltitanate (12.88 g, 0.0453 mole) in toluene (360 ml) and the azeotrope removed. Triethanolamine (6.76 g, 0.0453 mole) was added and the azeotrope again removed. The toluene was stripped until the first sign of precipitate, and the solution cooled, filtered and washed with cold toluene and hexane, yielding white crystals of (IIIa) (1.2 g, 11%), m.p. 196–197°. (Found: Si, 3.63; Ti, 19.33. $C_{26}H_{47}N_3O_{11}SiTi_2$ calcd.: Si, 3.75; Ti, 19.17%.)

Cyclic nitrilotriethylene trimethylsilyl titanate(IV) bis(nitrilotriethylene) titanate(IV), (IIIb)

Method 1(a). Trimethylsilyl acetate¹³ (6.60 g, 0.05 mole) in toluene (80 ml) was added to tetraisopropyl titanate (14.21 g, 0.05 mole) in toluene (250 ml) and the azeotrope removed. Triethanolamine (7.46 g, 0.05 mole) was added and the azeotrope removed. After removal of some toluene the solution was cooled, a white precipitate formed (8.68 g, 76%), m.p. 168.5–170°. (Found: Ti, 20.24; density 1.38 g/cc. $C_{21}H_{45}N_3O_{11}SiTi_2$ calcd.: Ti, 20.90%.)

Method 1(b). Trimethylsilanol⁹ (3.80 g, 0.04 mole) was added to tetraisopropyl titanate (11.37 g, 0.04 mole) and the azeotrope was removed. Triethanolamine (6.00 g, 0.04 mole) was added and the azeotrope removed. (IIIb) was isolated, m.p. 171–173°. (Found: Ti, 19.34; $C_{21}H_{45}N_3O_{11}SiTi_2$ calcd.: Ti, 20.90%.)

Method 1(c). Tetrakis(trimethylsiloxy)titanium (13.47 g, 0.033 mole) was reacted with tetraisopropyl titanate (28.42 g, 0.1 mole) in toluene (500 ml), then triethanolamine (20.00 g, 0.133 mole) was added and the azeotrope removed and (IIIb) isolated (11 g, 36%) m.p. 174–176°. Found: Si, 3.57; Ti, 20.21; N, 5.67. $C_{21}H_{45}N_3O_{11}SiTi_2$ calcd.: Si, 3.79; Ti, 20.90; N, 5.77%.)

Method 2. Cyclic nitrilotriethylene isopropyl titanate(IV) (12.15 g, 0.05 mole) was prepared in toluene (500 ml), and trimethylsilyl acetate (6.50 g, 0.05 moles) in toluene (50 ml) was added and the azeotrope was removed. A solid precipitated on standing overnight (5.40 g, 47%), m.p. 174°. (Found: Si 3.60; Ti, 19.54. $C_{21}H_{45}N_3O_{11}SiTi_2$ calcd.: Si 4.09; Ti, 20.90%.)

SUMMARY

Titanium organic compounds containing nitrilotriethylene and triorganosilyl

groups have been isolated. These include: "monotitanates", $R_3SiOTi(OC_2H_4)_3N$; a "dititanate", $[R_3SiOTi(OC_2H_4)_3N][ROTi(OC_2H_4)_3N]$; and "trititanates", $[R_3SiOTi(OC_2H_4)_3N][N(C_2H_4O)_3TiOTi(OC_2H_4)_3N]$. The results of this study show that the course of reaction is dependent upon the steric requirements of the organic groups in $RR'R''Si-$ rather than the electrical nature of the organic groups concerned.

REFERENCES

- 1 V. A. ZEITLER AND C. A. BROWN, *J. Am. Chem. Soc.*, 79 (1957) 4616.
- 2 W. D. ENGLISH AND L. H. SOMMER, *J. Am. Chem. Soc.*, 77 (1955) 170.
- 3 K. A. ANDRIANOV AND B. G. DULOVA, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, (1958) 644.
- 4 D. C. BRADLEY AND I. M. THOMAS, *Chem. Ind. (London)*, (1958) 1231.
- 5 C. M. SAMOUR (to The Kendall Co.), *U.S. Patent* 2,935,522 (May 3, 1960).
- 6 K. A. ANDRIANOV, A. A. ZHDANOV, N. A. KURASHEVA AND V. G. DULOVA, *Dokl. Akad. Nauk SSSR*, 112 (1957) 1050; *Chem. Abstr.*, 51 (1957) 14544d.
- 7 K. A. ANDRIANOV AND E. Z. ASNOVICH, *Vysokomol. Soed.*, 1 (1959) 743; *Chem. Abstr.*, 54 (1960) 16412h.
- 8 E. G. ROCHOW, *Introduction to the Chemistry of the Silicones*, Wiley, New York, 2nd edn., 1951, p. 182.
- 9 R. D. SAUER, *J. Am. Chem. Soc.*, 66 (1944) 1707.
- 10 W. H. DAUDI AND J. W. HYDE, *J. Am. Chem. Soc.*, 74 (1952) 387.
- 11 I. G. KHASKIN, *Zh. Obshch. Khim.*, 23 (1953) 32.

J. Organometal. Chem., 5 (1966) 413-419