

PREPARATION AND ^1H NMR STUDY OF SOLUBLE ALKOXY, ALKYL AND ARYLAMIDO DERIVATIVES OF SODIUM TETRAAMIDOALUMINATE

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Sodium tetraamidoaluminate reacts with alcohols and aromatic amines under formation of sodium alkoxyimidoaluminates or amido(arylamido)aluminates, respectively. The corresponding sodium amido(alkylamido)aluminates were prepared from sodium tetraamidoaluminate and sodium tetrakis(alkylamido)aluminates in 1,2-dimethoxyethane or pyridine solution. ^1H NMR spectra and in some cases also the cryoscopic molecular weights of the prepared compounds were measured.

Sodium tetraamidoaluminate, $\text{NaAl}(\text{NH}_2)_4$, *I* has been known since 1923 as a compound soluble in liquid ammonia only¹. Thanks to its recently solved direct synthesis², it will evidently find applications both in laboratory and industry³. *I* reacts with compounds having an active hydrogen in the molecule (alcohols, amines, ethyl malonate and even diphenylmethane) under evolution of ammonia^{4,5}. However, the amount of ammonia formed in the reaction of *I* with alcohols even at room temperature is greater than expected from stoichiometry. The explanation offered for this fact is that alkoxyamidoaluminates formed by partial alcoholysis are unstable at room temperature and yield alkoxyimido derivatives. This reaction has an analogy in the thermic stability of tetraamidoaluminates in solid state; *I* at temperatures above 70°C splits off ammonia and forms sodium diimidoaluminate⁶.

The products of partial hydrolysis of *I* are mostly well soluble in ethers and partially also in aromatic hydrocarbons. These soluble compounds contain in their molecules a NH or NH_2 group bonded to aluminum. Data on chemical shifts of such protons are very rare. The results of ^1H NMR measurements might therefore serve as a contribution to the understanding of bonding type and structure of these compounds. Table I summarizes chemical shifts of nitrogen-bonded protons in compounds giving good analyses for $\text{NaAlNH}(\text{OR})_2$ (*II*), measured in 1,2-dimethoxyethane solution. Besides the singlet evidently due to the NH proton of *II*, there is another broad singlet (line width > 15 Hz) in the spectrum. The later was ascribed to the protons of ammonia liberated by the reaction. In this case, the chemical shift of NH_3 protons depends on the nature of reacting alcohol ($\delta = 0.37 - 0.57$ ppm).

The signal is substantially broader than that of NH_3 dissolved in 1,2-dimethoxyethane ($\delta = 0.40$, line width 4 Hz). The products of alcoholysis of *I* are identical to those of 24 hours reaction of *I* with sodium tetraalkoxoaluminates $\text{NaAl}(\text{OR})_4$, (*III*).

The α - and β - CH_2 protons in the ^1H NMR spectra of compounds $\text{NaAlY}_2(\text{OCH}_2 \cdot \text{CH}_2\text{OCH}_3)_2$ (where $\text{Y} = \text{H}$ and $\text{OCH}_2\text{CH}_2\text{OCH}_3$, ref.⁷) in benzene solution appear as sharp triplets. Compound *II* with $\text{R} = \text{OCH}_2\text{CH}_2\text{OCH}_3$, prepared in benzene, exhibits broad unsplit singlets in the region of the α - and β - CH_2 protons, even if the nitrogen-bonded protons in this compound give rise to several signals (arranged in order of their decreasing intensity; $\delta = -0.58$ (s), -0.42 (s), 1.50 (t, $J = 6.5$ Hz), -1.52 (s); relative intensity ratio $c. 10 : 5 : 1 : 1$).

The products of reaction of *I* with water are insoluble in 1,2-dimethoxyethane. However, in pyridine solution the protons of ammonia formed in this reaction appear as a broad triplet at $\delta = 0.37$ ($J_{\text{N-H}} = 42$ Hz) with relative intensities $1 : 1 : 1$. This fact is explained by slowing the proton exchange caused by NH_3 acting as a solvating agent. An analogous triplet appears as a result of the interaction between *I* and NH_3 in 1,2-dimethoxyethane solution although in this case no tetraamidoaluminate was detected.

Primary and secondary aliphatic and aromatic amines ($\text{R}-\text{NH}_2$, *IV*) react with *I* similarly to alcohols. As found earlier^{4,5}, also in this reaction the amount of liberated ammonia is nearly stoichiometric although some sodium tetraamidoaluminate remains unresolved both in dimethoxyethane and pyridine. The solutions prepared in this way are in the case of aromatic and alkylaromatic amines colored. It can be inferred from the ^1H NMR spectrum that in reaction of aliphatic amines with *I* the

TABLE I

Chemical shifts of NH protons in ^1H NMR spectra of compounds prepared by the reaction of $\text{NaAl}(\text{NH}_2)_4$ (*I*) with alcohol ROH in the ratio $1 : 2$ in 1,2-dimethoxyethane (reaction time 1 h)

R	δNH^a	
$\text{CH}(\text{CH}_3)_2$	-0.89	-2.21 (0.05)
$\text{C}(\text{CH}_3)_3$	-1.03	$+0.12$ (0.15)
$\text{CH}_2\text{CH}_2\text{OCH}_3$	-0.97	-1.94 (0.2)
C_6H_5	-0.60	-1.30 (0.25)

^a All signals are singlets. Chemical shifts are given in ppm (δ -scale), negative values denote signals upfield from tetramethylsilane. The value in parentheses for the second signal indicates its relative intensity with respect to the signal of the prevailing component.

TABLE II

^1H NMR spectra of amines RNH_2 (*IV*), sodium tetrakis(alkylamido)aluminate $\text{NaAl}(\text{NHR})_4$ (*V*) and the products of reaction of sodium tetraamidoaluminate (*I*) with *IV* and *V* (*VI*), measured in pyridine and 1,2-dimethoxyethane

Compound ^{a,b}	-NH ₂	-NH-R	Others
<i>IVa</i> , Py	5.21 (s)	—	—
<i>Va</i> , Py	—	4.04 (s)	—
<i>IVa</i> + <i>Va</i> , 1 : 1, Py	5.10 (s)	4.03 (s)	—
<i>I</i> + <i>IVa</i> , 1 : 2, Py	-0.18 (s), -0.35 (s), +0.02 (s)	3.90 (s), 3.80 (s), 4.04 (s)	—
<i>I</i> + <i>IVa</i> , 1 : 4, Py	—	4.04 (s), 3.80 (s)	—
<i>I</i> + <i>Va</i> , 1 : 1, Py	-0.16 (s), -0.32 (s), +0.05 (s)	3.90 (s), 3.78 (s), 4.05 (s)	—
<i>I</i> + <i>Va</i> , 1 : 2, Py	-0.14 (s), +0.05 (s), -0.30 (s)	4.04 (s), 3.89 (s)	—
<i>I</i> + <i>Va</i> , 1 : 1, DME	-0.76 (s), -0.91 (s), -0.66 (s)	^c	—
<i>IVb</i> , Py	1.79 (s)	—	3.78 (s) ^d
<i>Vb</i> , Py	—	0.25 (t, <i>J</i> = 9)	4.45 (d, <i>J</i> = 9) ^d
<i>IVb</i> + <i>Vb</i> , 100 : 1 ^e , Py	1.79 (t, <i>J</i> = 7.5)	0.25 (t, <i>J</i> = 9) ^f	3.88 (t, <i>J</i> = 7.5) ^d
<i>Vb</i> , DME	—	-0.37 (t, <i>J</i> = 9)	4.12 (d, <i>J</i> = 8.5) ^d
<i>I</i> + <i>IVb</i> , 1 : 2, Py	+1.64 (bs), -0.40 (s)	—	3.85 (t, <i>J</i> = 7) ^d
<i>I</i> + <i>IVb</i> , 1 : 2, DME	+1.30 (bs), -1.05 (s)	—	^c
<i>I</i> + <i>Vb</i> , 1 : 1, Py	-0.44 (s), +1.76 (t, <i>J</i> = 7) ^f	0.17 (t, <i>J</i> = 8.5)	4.41 (d, <i>J</i> = 8.5) ^d
<i>I</i> + <i>Vb</i> , 1 : 1, DME	-1.04 (s), +1.39 (t, <i>J</i> = 7) ^f	-0.36 (t, <i>J</i> = 8.5)	3.82 (t, <i>J</i> = 7) ^{d,f}
<i>IVc</i> , Py	-1.33 (s)	—	4.10 (d, <i>J</i> = 8.5) ^d
<i>Vc</i> , Py	—	-0.36 (d, <i>J</i> = 9)	3.03 (sp) ^g
<i>Vc</i> , DME	—	-0.90 (d, <i>J</i> = 9)	2.9 ÷ 3.9 (m) ^g
<i>IVc</i> + <i>Vc</i> , 1 : 1, Py	^c	-0.35 (d, <i>J</i> = 9)	3.09 (sp) ^g
<i>IVc</i> + <i>Vc</i> , 1 : 1, DME	^c	—	3.3 ÷ 3.9 (m) ^g
<i>I</i> + <i>Vc</i> , Py	—	-0.91 (d, <i>J</i> = 9)	2.7 ÷ 3.5 (m) ^g
<i>I</i> + <i>Ic</i> , DME	-1.08 (s), -1.17 (s), -0.80 (d, <i>J</i> = 10)	—	^c
<i>IVd</i> , Py	1.87 (s)	—	—

<i>Vd</i> , Py	-0.12 ÷ -0.45 (m)	-	-
<i>Vd</i> , DME	-0.60 ÷ -0.80 (m)	-	-
<i>I</i> + <i>Vd</i> , Py	-0.31 (bs), -0.53 (bs)	-	-
<i>I</i> + <i>Vd</i> , DME	-0.75 (bs), -1.09 (bs)	-	-
<i>IVe</i> , Py	1.42 (s)	-	2.73 (s) ^d
<i>Ve</i> , Py	-0.18 (t, <i>J</i> = 8)	-	3.20 (t, <i>J</i> = 7) ^d
<i>Ve</i> , DME	-0.85 (t, <i>J</i> = 8.5)	-	2.75 (t, <i>J</i> = 8) ^d
<i>I</i> + <i>IVe</i> , DME	-1.11 (bs), -0.82 (bs)	-	2.61 (t, <i>J</i> = 7) ^d
<i>IVe</i> + <i>Ve</i> , DME	^c	-0.84 (t, <i>J</i> = 8.5)	2.76 (bs) ^d
<i>I</i> + <i>Ve</i> , Py	-0.49 (s), -0.19 (bs), -1.58 (bs)	-	2.68 (bs) ^d
<i>I</i> + <i>Ve</i> , DME	-1.04 (s), -0.79 (bs), -2.12 (s)	-	3.17 (bs) ^d
			2.62 (bs) ^d

^a Chemical shifts expressed in ppm (δ -scale). Negative sign denotes signals upfield from tetramethylsilane. Coupling constants are given in Hz; s singlet, t triplet, sp septet, m multiplet, bs broad singlet (line width 15 Hz). Signals are ordered according to their decreasing intensity. For index *a* R = C₆H₅, *b* R = CH₂C₆H₅, *c* R = CH(CH₃)₂, *d* R = cyclohexyl, *e* R = n-C₈H₁₇. ^b Py pyridine, DME 1,2-dimethoxyethane. ^c Signals overlapped by an intense solvent or R signal. ^d Signals of CH₂-NH protons. ^e δ and *J* are practically identical in the spectra for *IV*: *V* ratio 1 to 100. ^f Signal of low intensity. ^g Signals of CH-NH protons.

prevailing reaction course is the solvation of *I* by free amine besides the small percentage of substitution. The unstable solvate formed then splits off ammonia. Therefore, we prepared a series of tetrakis(alkylamido)aluminates ($\text{NaAl}(\text{NHR})_4$, *V*) from sodium tetrahydridoaluminate and corresponding amines *IV*. We studied using ^1H NMR both the products of the reaction $I + V$ and that of aminolysis of *I* (Table II, ref.⁸). It is known that the reaction of NaAlH_4 with certain amines (*e.g.*, isopropylamine) at the component ratio 1 : 1 leads to the polymeric alkylaminoalane⁹. Nevertheless, *Vc* prepared from NaAlH_4 and isopropylamine at the ratio 1 : 4 at room temperature in 1,2-dimethoxyethane does not contain (according to its ^1H NMR spectrum) any detectable amount of isopropylaminoalane¹⁰ (judged from the absence of Al—H signal and the presence of one methyl doublet only). The presence of other alkylaminoalanes in analogically prepared *V* is also improbable.

The product of reaction $I + V$ (*VI*) is well soluble in ethers and in pyridine. The reaction itself takes place even without solvent (mixing of both solid components in the case of *Va* ($\text{R} = \text{C}_6\text{H}_5$) produces violet colour and the reaction mixture is half-solid for some time) or in aromatic hydrocarbons in which *I* and *V* are insoluble. In pyridine or 1,2-dimethoxyethane, *VIa* remains dissolved up to 80% concentration.

Table II gives chemical shifts of *IV*, *V*, and of the products of their reaction with *I*, measured in 1,2-dimethoxyethane and pyridine. With tetraanilidoaluminate *Va*, only one signal of a R—NH—Al proton was observed (at $\delta = 4.04$ ppm, pyridine). Products of the reaction $I + IVa$ and $I + Va$, respectively, display in this region besides the above mentioned signal two overlapping singlets ($\delta = 3.90$ and 3.78 in pyridine); there are three singlets in the region of the expected Al— NH_2 proton resonances at $\delta = -0.16$, -0.32 , and $+0.05$ ppm. Similar properties, including the relative intensities of signals, exhibits also *VIa* in 1,2-dimethoxyethane.

It was found (by determination of the relative proportions of Na, Al, N_{total} and $\text{N}_{\text{bonded to aromatics}}$) that it is possible to prepare *VIa* by reaction of insoluble *I* and *Va* carried out in pyridine and dimethoxyethane. Maximal ratio $\text{Na} : \text{Al} : \text{N}_{\text{total}} : \text{N}_{\text{aniline}}$ is 1 : 1 : 4 : 2. Compound *VIa* splits off ammonia above 60°C; that is demonstrated in the ^1H NMR spectrum by a peak of the dissolved ammonia (in pyridine at 0.83 ppm, in 1,2-dimethoxyethane at 0.42 ppm), by the decrease in intensity of the peaks located upfield from tetramethylsilane and by an intensity enhancement of the 4.05 ppm peak in comparison with other peaks due to the $\text{NH—C}_6\text{H}_5$ protons resonating at higher field (3.90 and 3.78 ppm in pyridine). Chemical shifts of all protons remain practically the same.

Investigating the products of aminolysis of *I* by benzylamine *IVb* and that of reaction of sodium tetrakis(benzylamido)aluminate *Vb* with *I*, it was proved that in the former case the amine participates in solvation of *I* since there appears one signal of the Al— NH_2 protons upfield from tetramethylsilane. Protons of the NH_2 group belonging to benzylamine solvating *I* resonate at slightly higher field than those of benzylamine solvating *Vb*; the signal corresponding to the $\text{C}_6\text{H}_5\text{CH}_2\text{NHAl}$

protons (+0.25 ppm in pyridine, -0.37 ppm in dimethoxyethane) is entirely absent. As already mentioned above, ammonia (represented in the spectrum by the peak at 0.38 ppm in dimethoxyethane or at 0.81 in pyridine) is not split during the substitution reaction of benzylamine but as a result of the thermic instability of solvated *I* in solution. However, solid *I* is also solvated during the reaction, for the amount of benzylamine present in the solution does not correspond to the amount of benzylamine added. Whereas benzylamine itself displays two singlets for the NH₂ and CH₂ groups at room temperature, in the presence of *Vb* even at the ratio 100 : 1 the signals of both groups appear as triplets (coupling constant 7.5 Hz) with practically identical chemical shifts. Unlike to *VIa*, the compound *Vib* prepared by reaction of *I* and *Vb* has in the region of Al—NH₂ protons at negative δ -values one signal only (-0.44 ppm in pyridine, -1.04 ppm in 1,2-dimethoxyethane). A triplet analogous to that observed with *Vb* is observed in the region of Al—NH—R protons. Compound *Vib* is stable at room temperature. It decomposes slowly above 50°C and evolves both ammonia and benzylamine. The triplet corresponding to the solvating amine *Vb* (1.75 ppm in pyridine, 1.42 ppm in 1,2-dimethoxyethane, $J = 7$ Hz) is present in a very small extent in the spectrum of *Vib*. However, it dominates in the spectrum of the sample of *Vib* heated at 50°C for 10 h.

The reaction of *I* with other aliphatic amines (isopropylamine *IVc*, cyclohexylamine *IVd*, and n-octylamine *IVe*) leads to similar results as the reaction of *I* with benzylamine. With *IVe* is $\delta_{\text{NH}_2} = 2.62$ ppm for the solvating amine *Ve* and $\delta_{\text{NH}_2} = 2.76$ ppm when the amine solvates *I* or *VIe*, respectively (solvent: dimethoxyethane). Similar is also the course of reaction *I* + *V* with *Vb*—*Ve* but the reaction is slower for *Vc*—*Ve* and its products are less stable. Chemical shifts of singlets due to the Al—NH₂ protons differ for the individual R's: the doublet or triplet of the Al—NH—R protons of *V* is partially preserved in the case of *IVb* and *IV* only.

The molecular weights in dioxane solutions were determined cryoscopically for aniline and benzylamine derivatives *Va*, *VIa* and *Vb*, *Vib*, respectively. There are no differences in the number of peaks, their relative intensities and approximatively also in chemical shifts between the ¹H NMR spectra of *V* and *VI* measured in 1,2-dimethoxyethane and 1,4-dioxane. The molecular weight usually increases with concentration. The degree of association of *Va* is 1.13—1.75 in the concentration range 3—20%. Less soluble *Vb* is practically monomeric in the concentration range 2—7%. Assuming the summary formula NaAl(NH₂)₂(NHR)₂ for *VI*, degree of association of these compounds is greater than that of tetrakis(alkylamido)aluminates *V*: with *VIa* it is 1.54—2.28 (concentration range 3—21%), with *Vib* it is 1.82—2.22 (4—12%).

Since ¹H NMR indicates the presence of substantial amount of NaAl(NHR)₄ in the solution arising in the reaction between *I* and *V*, both ligands (NH₂ and NHR) therefore seem to be bonded to the same aluminum atom. The partial substitution of an alkylamido ligand for an amide one enhances the solubility and the association ability.

EXPERIMENTAL

All preparations of the above mentioned compounds and their reactions were carried out in the nitrogen atmosphere. The apparatus was dried by heating in the nitrogen stream. Sodium tetraamidoaluminate (*I*) was prepared by direct synthesis². For $\text{NaAl}(\text{NH}_2)_4$ (114.0) was calculated: 20.16% Na, 23.65% Al, 49.12% N; found: 20.90% Na, 22.83% Al, 48.14% N. The alcohols and amines were dried over a molecular sieve (Nalsit 4Å), calcium hydride and distilled before use. Sodium aluminum hydride was purified by crystallization from tetrahydrofuran. For NaAlH_4 (54.0) was calculated: 42.58% Na, 49.96% Al, 7.46% H^- ; found: 42.42% Na, 49.21% Al, 7.30% H^- .

¹H NMR spectra were measured on a Tesla BS-467 (60 MHz) spectrometer at 20°C and on a Varian XL-100 (100 MHz) spectrometer at 27°C, respectively. 7% solutions in 1,2-dimethoxyethane or pyridine containing tetramethylsilane as an internal standard were used. Molecular weights were determined cryoscopically by the procedure described earlier¹¹.

Reaction of Sodium Tetraamidoaluminate (*I*) with 2-Methoxyethanol

2-Methoxyethanol (1.32 g, 17.3 mmol) was injected during 5 minutes to the mixture of *I* (98.6%, 1 g, 8.6 mmol) and 1,2-dimethoxyethane (15 ml) contained in a 100 ml flask equipped by an Y-joint with rubber stopping and a reflux condenser, stirred by a magnetic stirrer and cooled to 0°C. The mixture was stirred one hour at room temperature and the ammonia formed was removed by a short evacuation. The solution exhibiting an element ratio $\text{Na} : \text{Al} : \text{N} = 1.01 : 1 : 1.03$ was diluted to 7% and used for the ¹H NMR spectra measurement. To check its thermic stability, the solution of $\text{NaAlNH}(\text{OCH}_2\text{CH}_2\text{OCH}_3)_2$ formed in the described reaction was heated to 80°C for 1 h. After this treatment was observed a negligible decrease of the NH_3 content of the solution only and the intensity of the peak of the aluminum-bonded imido group remained unchanged. The reaction of other alcohols and amines with *I* was performed in the same way. With the exception of aniline, substantial amount of solid substance remained unresolved in the reaction mixture from the aminolysis of *I*. The solution used for ¹H NMR measurements therefore had a markedly lower concentration.

Sodium Tetraanilidoaluminate (*Va*)

Aniline (about 4 g) was added to sodium aluminum hydride (98.5%, 2.66 g, 48.4 mmol) covered by ether (60 ml) in the nitrogen atmosphere. The reaction, accompanied by hydrogen evolution and heating to the boiling point, started after 5–10 minutes of stirring. Remaining aniline (total amount 18.05 g, 195.8 mmol) was added fast enough to keep the solution slowly boiling. The mixture was stirred 1 h under reflux, filtered and then allowed to stand 3 days at room temperature. After this time, the crystals of sodium tetraanilidoaluminate *Va* started to form. The solution was kept 48 h at 0°C, the crystals were filtered off under nitrogen and then dried at room temperature *in vacuo* (100 Pa). *Va* obtained in this way is insoluble in ether. For $\text{NaAl}(\text{NHC}_6\text{H}_5)_4$ (418.4) was calculated: 5.49% Na, 6.45% Al, 13.38% N; found: 5.33% Na, 6.15% Al, 12.95% N.

Sodium Tetrakis(benzylamido)aluminate (*Vb*)

Benzylamine (12.80 g, 119.1 mmol) was added to the stirred and cooled suspension of NaAlH_4 (1.65 g, 29.78 mmol) in 1,2-dimethoxyethane. The stirring was prolonged for 24 h at room temperature, the solid particles were filtered off and the solvent was evaporated at room tempera-

ture. The residue gave following elemental analysis: 4.89% Na, 5.52% Al, 11.49% N. For $\text{NaAl}(\text{NHCH}_2\text{C}_6\text{H}_5)_4$ (474.5) was calculated: 4.85% Na, 5.68% Al, 11.80% N. Similarly were prepared other sodium tetrakis(alkylamido)aluminates *Vc*–*Ve*. The reaction can be also performed in diethyl ether. However, the product *V* is insoluble in ether and precipitates already during the amonolysis of sodium aluminum hydride.

Reaction of Sodium Tetraamidoaluminate *I* with *Vb*

Vb (8.87 g, 18.16 mmol) dissolved in 1,2-dimethoxyethane (50 ml) was added to *I* (2.10 g, 18.16 mmol) in nitrogen atmosphere. The mixture was stirred 5 h at room temperature. Red solution containing only small amount of solid substances was obtained. Filtered solution exhibited element ratio Na : Al : N = 1.06 : 1 : 3.96. This solution was diluted to 7% and used for the ^1H NMR spectroscopy. Evaporation of this solution at room temperature yields red glassy substance. For $\text{NaAl}(\text{NH}_2)_2(\text{NHCH}_2\text{C}_6\text{H}_5)_2$ (294.1) was calculated: 7.82% Na, 9.17% Al, 19.04% N; found: 7.96% Na, 8.75% Al, 17.74% N. Similarly was performed the reaction of *I* with *Va*, *Vc*, *Vd*, and *Ve*. The products *Vlc* and *Vle* are colourless. The reaction mixture contained also the solid substance. *Vlb* and *Vla* were isolated in the solid state. For $\text{NaAl}(\text{NH}_2)_2 \cdot (\text{NHC}_6\text{H}_5)_2$ (266.3) was calculated: 8.63% Na, 10.13% Al, 21.03% N_{total} , 10.52% $\text{N}_{\text{aniline}}$; found: 8.92% Na, 9.85% Al, 19.25% N_{total} , 9.48% $\text{N}_{\text{aniline}}$.

REFERENCES

1. Bergstrom F. W.: J. Amer. Chem. Soc. *45*, 2788 (1923).
2. Čásenský B., Macháček J., Kříž O.: Czech. 201 494.
3. Čásenský B., Macháček J., Kříž O., Kubánek V.: Czech. 185 846.
4. Stehlík P., Kříž O., Stuchlík J., Čásenský B.: Chem. Prům. *30/55*, 298 (1980).
5. Kříž O., Stehlík P., Čásenský B.: Z. Chem. *20*, 219 (1980).
6. Brec R., Rouxel J.: C. R. Acad. Sci., Ser. C *264*, 512 (1967).
7. Kříž O., Fusek J., Trška P.: This Journal *43*, 3130 (1978).
8. Kříž O.: Chem. Ind. (London), 1981, 572.
9. Cucinella S., Dozzi G., Mazzei A., Salvatori T.: Organometal. Chem. *90*, 257 (1975).
10. Buseto C., Cesari M., Cucinella S., Salvatori T.: Organometal. Chem. *132*, 339 (1977).
11. Kříž O., Sochor P.: This Journal *41*, 193 (1976).

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