Inorganica Chimica Acta, 45 (1980) L261–L262

Synthesis of Ionic Germylmercury Complexes of Praseodymium by Hydride Method

L. N. BOCHKAREV, M. N. BOCHKAREV, YU. F. RADKOV, G. S. KALININA and G. A. RAZUVAEV

Institute of Chemistry, U.S.S.R. Academy of Sciences, Gorky, U.S.S.R.

Received July 21, 1980

We have found [1] that $(C_6F_5)_3GeH$ easily reacts with $(t\text{-BuO})_3Ln$, $[(Me_3Si)_2N]_3Ln$ and $(i\text{-PrO})_2PrCl$ THF (Ln = Pr, Sm) to give ROH or $(Me_3Si)_2NH$ in high yield, but these reactions give a complex mixture of products and do not lead to the expected bimetallic organometallic derivatives of the lanthanides. Earlier we observed the formation of a similar mixture of products in the reactions of $(C_6F_5)_3GeH$ with NH_3, Et_3N, $(Me_3Si)_2NH$ and while attempting to prepare $(C_6F_5)_3GeLi$ [2]. In all these reactions F^- anions have been found among the products. The IR spectra of such products exhibit additional bands at 1250, 950, 580 and 440 cm^{-1} together with absorption bands characteristic of C_6F_5–Ge fragments. We consider that additional bands can be attributable to the disubstituted perfluorinated benzene rings, Ge–C_6F_4–Ge. On the basis of these data we suppose that in the initial steps of the above mentioned reactions highly reactive nucleophilic species – $(C_6F_5)_3Ge^-$ anions – are formed. These anions attack C_6F_5 substituents to afford a number of by-products.

While studying the other possible preparation routes of organolanthanides we have found that reactions of $[(C_6F_5)_3Ge]_2Hg$ with lanthanides [1] and thallium [3] lead to the formation of ionic complexes containing $(R_3Ge)_3Hg^-$ and $(R_3Ge)_4Hg^{2-}$ mercury anions. It is reasonable to suggest that the formation of these mercury anions is due to the addition of $(C_6F_5)_3Ge^-$ anions being formed at the initial steps of the reactions to the starting germylmercury $[(C_6F_5)_3Ge]_2Hg$ [1, 3]. An analogous process of addition of organosilicon anions Me_2PhSi^- to $(Me_2PhSi)_2Hg$ with formation of $(Me_2PhSi)_3Hg^-$ and $(Me_2PhSi)_4Hg^{2-}$ mercury anions has been described by Oliver and coworkers [4].

Based on these findings we have attempted to use $[(C_6F_5)_3Ge]_2Hg$ as a reagent suppressing side-processes of substitution of fluorine atoms in reactions of tris(pentafluorophenyl)germane with alkoxy- and amidoderivatives of praseodymium. The attempt was successful. The reactions of $(t\text{-BuO})PrCl_2\cdot THF$, $(t\text{-BuO})_3Pr$ and $[(Me_3Si)_2N]_3Pr$ with $(C_6F_5)_3GeH$ in the presence of bis[tris(pentafluorophenyl)germyl] mercury at 50–55 °C in 1,2-dimethoxyethane (DME) solution led to the formation of complexes which are given in Table I. Products of substitution of fluorine in C_6F_5-rings have not been found in this case.

Thus, the reactions being considered can be described by the following equations

$$(t\text{-BuO})PrCl_2 + (C_6F_5)_3GeH + [(C_6F_5)_3Ge]_2Hg \xrightarrow{DME} t\text{-BuOH} + \{[(C_6F_5)_3Ge]_3Hg\}PrCl_2\cdot 3DME$$

(I)

$$(t\text{-BuO})_3Pr + 3(C_6F_5)_3GeH + 2[(C_6F_5)_3Ge]_2Hg \xrightarrow{DME} 3\ t\text{-BuOH} + \{[(C_6F_5)_3Ge]_7Hg_2\}Pr\cdot 3DME$$

(II)

The reaction of $[(Me_3Si)_2N]_3Pr$ with $(C_6F_5)_3GeH$ gives the partially substituted product III under the same conditions.

The formation of complexes I–III in reactions of $(C_6F_5)_3GeH$ with alkoxy- and aminoderivatives of

TABLE I. Analytical Data for the Complexes of Praseodymium.

	Compound	Yield (%)	M.p. (°C)	Analytical Data: Found (calcd.) %				
				C	H	F	Hg	Pr
I	$\{[(C_6F_5)_3Ge]_3Hg\}PrCl_2\cdot 3DME$	78	184–188	32.51 (32.97)	1.20 (1.26)	35.30 (35.56)	8.14 (8.34)	5.83 (5.86)
II	$\{[(C_6F_5)_3Ge]_7Hg_2\}Pr\cdot 3DME$	68	200–205	34.24 (34.33)	1.26 (0.63)	40.76 (40.95)	8.29 (8.31)	2.45 (2.92)
III	$\{[(C_6F_5)_3Ge]_6Hg_2\}PrN(SiMe_3)_2\cdot 3DME$	82	178–182	33.32 (34.28)	1.36 (1.10)	38.05 (38.72)		3.31 (3.19)

praseodymium is the first example of synthesis of ionic polynuclear organometallic complexes by the hydride method. The compounds obtained are weakly-coloured solids, sensitive to traces of moisture, well soluble in THF, DME, acetone and insoluble in hexane and toluene.

Earlier we supposed that the germylmercury complex of praseodymium prepared by transmetallation reaction of $[(C_6F_5)_3Ge]_2Hg$ with praseodymium contains one molecule of the starting germylmercury [5]. As a result of additional investigations it has been shown that this complex contains not one but two molecules of germylmercury. Its composition is identical to that of complex II obtained by the hydride method.

The following ionic structures can be suggested for organogermanium complexes of praseodymium being obtained.

$$\text{(I)}\quad \{PrCl_2\cdot 3DME\}^{+} \qquad {}^{-}\{Hg[Ge(C_6F_5)_3]_3\}$$

$$\text{(II)}\quad \{Pr\cdot 3DME\}^{3+} \qquad \left\{\begin{array}{l} {}^{-}Hg[Ge(C_6F_5)_3]_3 \\ {}^{2-}Hg[Ge(C_6F_5)_3]_4 \end{array}\right\}$$

$$\text{(III)}\quad \{PrN(SiMe_3)_2\cdot 3DME\}^{2+}\left\{\begin{array}{l} {}^{-}Hg[Ge(C_6F_5)_3]_3 \\ {}^{-}Hg[Ge(C_6F_5)_3]_3 \end{array}\right\}$$

The ionic nature of the complexes is confirmed by conductivity measurement of complex II ($\lambda_\infty = 59.1$ ohm^{-1} cm^2 mol^{-1}) in THF solution and by reactions with HCl and $(C_6F_5)_3GeBr$. The chemical properties of the complexes will be considered in more detail in the next paper.

It should be noted that an analogous ionic structure was proposed for the silylmercury complex of magnesium [4].

Experimental

All reactions were carried out in evacuated sealed ampoules. The melting points were determined in evacuated sealed capillaries. GLC analyses of products were carried out on a Tsvet-129 chromatograph with a catarometer detector using a 50 × 0.4 cm column packed with OV-17 (7%) on Chromaton N-AW-DMCS and a 300 × 0.3 cm column packed with SE-30 (5%) on Inerton AW, with helium as the carrier gas. IR spectra were recorded on a double-beam Zeiss-Jena Model UR-20 spectrometer. Samples of the crystalline compounds were prepared *in vacuo* as Nujol mulls.

Synthesis of I

To a solution of 0.18 g (0.50 mmol) of (t-BuO)-$PrCl_2\cdot THF$ in 5 ml of DME was added a solution of 0.37 g (0.67 mmol) of $(C_6F_5)_3GeH$ and 0.87 g (0.65 mmol) of $[(C_6F_5)_3Ge]_2Hg$ in 10 ml of DME. The mixture was heated at 50 °C for 05. h. The solvent and volatile products were removed by recondensation *in vacuo*. The residue was washed with toluene several times and dried *in vacuo* to give 1.08 g (78.1%) of I as a pale green solid, m.p. 184–188 °C. In the IR spectrum of I these are absorption bands characteristic of C_6F_5 groups bonded to a germanium atom [6] and an absorption band at 860 cm^{-1} characteristic of coordinated DME. GLC analysis of volatile products revealed the presence of 0.037 g (100%) of t-BuOH. Complex II was prepared in a similar manner.

Synthesis of III

To a solution of 0.26 g (0.42 mmol) of $[(Me_3Si)_2N]_3Pr$ in 5 ml of DME was added a solution of 0.77 g (1.34 mmol) of $(C_6F_5)_3GeH$ and 1.12 g (0.83 mmol) of $[(C_6F_5)_3Ge]_2Hg$ in 10 ml of DME. The mixture was heated at 50 °C for 0.5 h. The solvent and volatile products were removed by recondensation *in vacuo*. The pale brown residue was washed with toluene several times and dried *in vacuo* to afford 1.52 g (82.3%) of III as a colourless solid, m.p. 179–182 °C. The IR spectrum of III exhibits absorption bands characteristic of C_6F_5–Ge fragments [6] and coordinated DME. In addition, in the IR spectrum there are absorption bands at 1255, 925 and 840 cm^{-1} characteristic of $(Me_3Si)_2N$ groupings [7]. GLC analysis of volatile products showed the presence of 0.063 g (33.1%) of $(Me_3Si)_2NH$.

References

1 G. A. Razuvaev, L. N. Bochkarev, G. S. Kalinina, E. A. Fedorova and M. N. Bochkarev, *Abstr. I. All-Union Conf. Organometal. Chem., Moscow*, U.S.S.R. (1979) 94.

2 M. N. Bochkarev, N. S. Vyazankin, L. N. Bochkarev and G. A. Razuvaev, *J. Organometal. Chem., 110* (1976) 149.

3 M. N. Bochkarev, N. I. Gur'ev, L. V. Pankratov and G. A. Razuvaev, *Inorg. Chim. Acta, 44* (1980) L59.

4 E. A. Sadurski, W. H. Ilsley, R. D. Thomas, M. D. Glick and J. P. Oliver, *J. Am. Chem. Soc., 100* (1978) 7761.

5 G. A. Razuvaev, L. N. Bochkarev, G. S. Kalinina and M. N. Bochkarev, *Inorg. Chim. Acta, 24* (1977) L40.

6 R. D. Chambers and T. Chivers, *Organometal. Chem. Rev., 1* (1966) 279.

7 H. Bürger, W. Sawodny and U. Wannagat, *J. Organometal. Chem., 3* (1965) 113.