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Preliminary communication

GERMANIUM(II) PSEUDOHALIDES: $Ge(CN)_2$, $Ge(NCO)_2$ AND $Ge(NCS)_2$; SYNTHESES AND REACTIVITIES

MARIO ONYSZCHUK, ANNIE CASTEL, PIERRE RIVIERE, and JACQUES SATGE *
Laboratoire de Chimie des Organominéraux, U.A. du C.N.R.S. No. 477, Université Paul Sabatier, 118 route de Narbonne, 31062 Toulouse Cédex (France)

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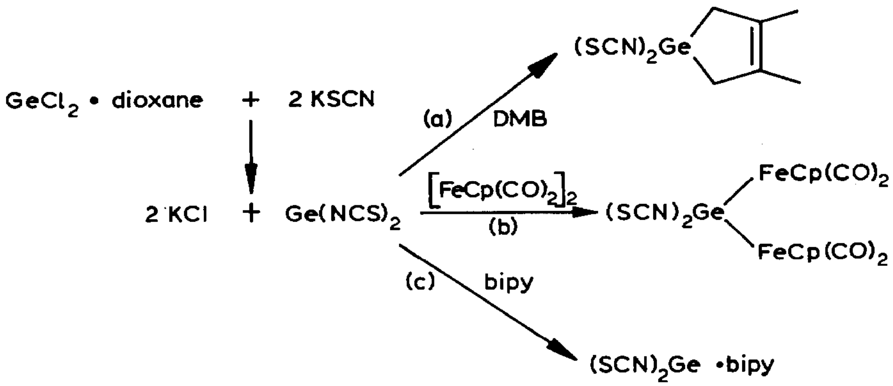
Summary

The hitherto unknown germanium(II) pseudohalides: $Ge(CN)_2$, $Ge(NCO)_2$ and $Ge(NCS)_2$, have been prepared by reactions of germanium(II) halides with corresponding silver or potassium salts; they are stable in tetrahydrofuran or acetone solution in which they are extremely sensitive to moisture, and they undergo cycloaddition, insertion, and Lewis acid–base reactions characteristic of highly reactive germylenes. Infrared spectra indicate that in tetrahydrofuran solution $Ge(CN)_2$ is the normal cyanide, whereas $Ge(NCO)_2$ and $Ge(NCS)_2$ are the isocyanate and isothiocyanate, respectively.

Among the great variety of known germanium(II) compounds [1], the pseudohalides, GeY_2 where $Y = CN$, NCO, NCS, NCSe and N_3, have not yet been reported. We are exploring their preparation and have so far obtained three of them, in which $Y = CN$, NCO and NCS, as highly reactive germylenes stable in tetrahydrofuran or acetone solution. Comparison of their reactivities with those of germanium(II) halides [2,3] and amides [4] was of particular interest to us as part of our continuing studies of germylenes [5].

Germanium(II) cyanide was obtained by the reaction of germanium(II) iodide with silver or mercuric cyanide, as well as by the exchange reaction between germanium(II) fluoride and trimethylcyanosilane; the highest yield (80%) resulted from the reaction with silver cyanide in refluxing tetrahydrofuran. Although stable in tetrahydrofuran or acetone and very sensitive to moisture, $Ge(CN)_2$ formed an intractable viscous liquid when the solvent was removed, probably owing to oligomerisation. The infrared spectrum of its tetrahydrofuran solution is dominated by a strong and sharp $\nu(CN)$ band at 2090 cm^{-1} assigned to the normal isomer [6,7].

The reaction of germanium(II) iodide with silver cyanate in refluxing tetrahydrofuran gave $Ge(NCO)_2$ quantitatively but, like $Ge(CN)_2$, this formed a very viscous liquid upon removal of the solvent, and it was not possible to isolate stoichiometric



SCHEME 1.

solvates. Infrared absorption bands at 2230 cm^{-1} (ν_{as}(NCO), strong and sharp) and 1448 cm^{-1} (ν_{s}(NCO), medium and broad) confirm that in tetrahydrofuran Ge(NCO)$_2$ is present only in the isocyanate form [6,7].

All attempts to prepare Ge(NCS)$_2$ by reaction of germanium(II) iodide with silver thiocyanate were unsuccessful. However, the compound was formed almost quantitatively in the reaction of GeCl$_2$ · dioxane with potassium thiocyanate in refluxing acetone. Unfortunately Ge(NCS)$_2$ also forms an intractable viscous film when solvent is pumped off, no doubt due to extensive oligomerisation. The presence in the infrared spectrum of its tetrahydrofuran solution of a strong and broad band at 2030 cm^{-1} strongly suggests that the compound is the isothiocyanate rather than the normal thiocyanate [6,7].

Surprisingly, the reaction of GeCl$_2$ · dioxane with potassium selenocyanate did not afford Ge(NCSe)$_2$, but instead gave GeSe$_2$ in a rapid, exothermic, and quantitative reaction represented by:

$$GeCl_2 \cdot C_4H_8O_2 + 2KSeCN \rightarrow GeSe_2 + 2KCl + (CN)_2 + C_4H_8O_2$$

The three germanium(II) pseudohalides were characterized by: (a) cycloaddition with 2,3-dimethylbuta-1,3-diene or 3,5-di-t-butylorthoquinone; (b) insertion reactions with [FeCp(CO)$_2$]$_2$ or dimethyldisulphide; and (c) Lewis acid–base complexation with 1,5-diazabicyclo[5.4.0]undec-5-ene or α,α'-bipyridine, all of which are typical of highly reactive germylenes [8–10]. Reaction products were identified by microanalysis, mass spectrometry, and infrared and ^{1}H NMR spectroscopy. For example (Scheme 1), the reaction of Ge(NCS)$_2$ in tetrahydrofuran solution with: (a), 2,3-dimethylbuta-1,3-diene gave the expected cyclopentene. Yield: 78%. M.p. 85–90 °C. IR (THF soln, KBr cells): 2000 s cm^{-1}. ^{1}H NMR (C_6D_6): δ 1.23s (CH$_3$, CH$_2$) ppm. Analysis: Found: C, 35.59; H, 3.74; N, 10.18; S, 2.31. $C_8H_{10}N_2S_2Ge$ calcd.: C, 35.50; H, 3.69; N, 10.34; S, 2.36%; (b) [FeCp(CO)$_2$]$_2$ gave the 1/1 insertion product. Yield: 49%. M.p. 210 °C (dec.). IR (Nujol): 2050s, 2070s cm^{-1}. ^{1}H NMR (CD$_3$COCD$_3$): δ 5.30s (C$_5$H$_5$) ppm. MS: $m/e = 544$ $(M)^+$; 516 $(M-\text{CO})^+$; 488 $(M-2\text{CO})^+$. Analysis: Found: C, 35.21; H, 1.91; N, 5.07; S, 10.71. $C_{16}H_{10}N_2S_2O_4Fe_2Ge$ calcd.: C, 35.42; H, 1.84; N, 5.16; S, 11.80%; and (c) α,α'-bipyridine gave the 1/1 adduct. Yield: 92%. M.p. 162–165 °C. (dec.). IR (Nujol): 2020m, 2070m cm^{-1}. ^{1}H NMR (CD$_3$COCD$_3$ + DMSO-d_6): δ7.43d,d; 7.97d,d;

8.57d,d (α,α'-bipy). Analysis: Found: C, 40.76; H, 2.27; N, 16.02. $C_{12}H_8N_4S_2Ge$ calcd.: C, 41.81; H, 2.27; N, 16.25%.

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