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USE OF 1,2,3-SELENADIAZOLES IN THE SYNTHESIS OF 1,1'-BIS(DIPHENYLSELENOPHOSPHORYL)FERROCENE

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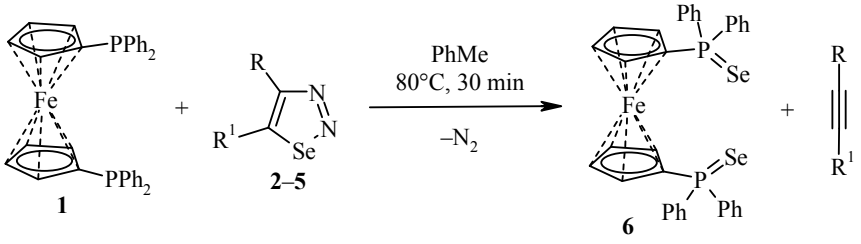
A method has been developed for obtaining 1,1'-bis(diphenylselenophosphoryl)ferrocene based on utilization of 1,2,3-selenadiazoles as the source of selenium. The molecular structure was confirmed by X-ray analysis.

Keywords: 1,1'-bis(diphenylphosphino)ferrocene, 1,1'-bis(diphenylselenophosphoryl)ferrocene, 1,2,3-selenadiazole, selenium.

1,2,3-Selenadiazole derivatives play an important role in solving many theoretical and practical problems of organic chemistry [1]. Their interesting property is the ability to eliminate molecules of nitrogen and selenium with the formation of acyclic derivatives and new heterocyclic systems [2]. In turn, the synthesis of 1,1'-bis(phosphino)ferrocene selanes is of interest, since these compounds act as promising complex-forming ligands with salts of copper [2], silver [3, 4], and gold [4]. Previously we described a reaction of 1,2,3-selenadiazoles with tributyl- and triphenylphosphines [5]. In the present work, a method is given for obtaining the 1,1'-bis(diphenylphosphino)ferrocene diselane, and its molecular structure has been investigated.

Substituted 1,2,3-selenadiazoles **2-5** react with 1,1'-bis(diphenylphosphino)ferrocene (dppf) (**1**) upon heating in toluene.



2 R = *i*-Pr, R^1 = H; **3** R = Ph, R^1 = H; **4** R = 2-thienyl; R^1 = H; **5** R = Me, R^1 = COOEt

According to the experimental data obtained, the nature of the initial 1,2,3-selenadiazoles **2-5** had practically no influence on the yield of 1,1'-bis(diphenylselenophosphoryl)ferrocene (**6**). The desired compound was formed in 93-98% yield. The derivative **6** was previously obtained in 95% yield by heating compound **1** with elemental selenium [6].

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An X-ray structural investigation was carried out on crystals of compound **6** grown in a mixture of ethyl acetate–petroleum ether. There are data in the literature on the crystal structure of a diselane **6** solvate with dichloromethane [6]. Results are given in the present work of the X-ray structural analysis of the pure derivative **6** crystal structure (Fig. 1). As in the case of the solvate with CH_2Cl_2 [6], the molecule of the obtained compound **6** is in a particular position (center of inversion), consequently numbering is given only for the atoms found in the independent part of the unit cell.

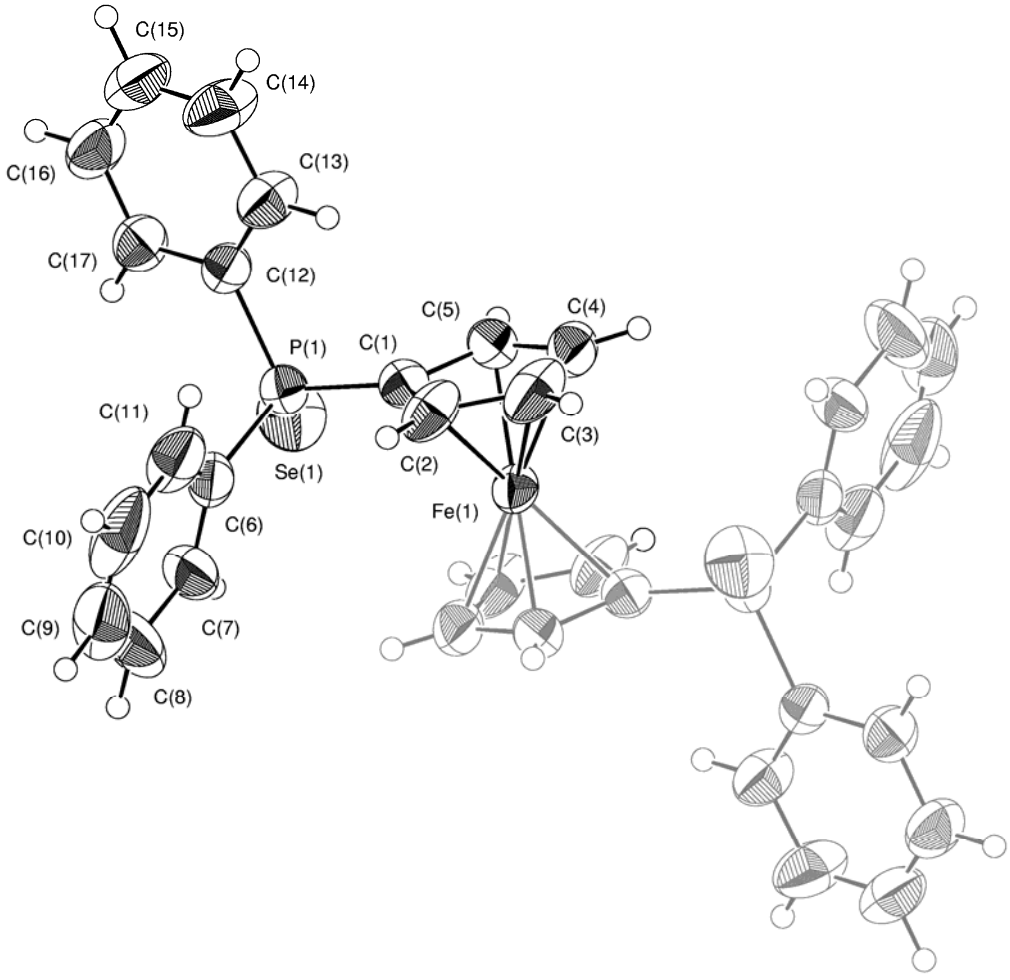

Fig. 1. Spatial model of the compound **6** molecule with atoms denoted by ellipsoids of thermal vibrations of 50% probability.

The ferrocene system has a characteristic symmetry D_{5d}; the values of the bond lengths, valence, and dihedral angles in the compound **6** molecule are close to those given in [6]. However, the crystal structure of the investigated compound **6** was significantly different from the structure described in [6]. A projection is shown in Fig. 2 of the crystal structure of compound **6** along the crystallographic direction [1 0 0]. A characteristic feature of this structure is the shortened intermolecular contacts Se···Se, the length of which is 3.491(1) Å, significantly lower than the sum of the van der Waals radii for Se at 3.80 Å [7-9]. As a result of these contacts the molecules are combined in chains stretched along the [0 0 1] direction. It should be noted that similar contacts also occur in the structure of the CH_2Cl_2 solvate, but in the latter case their length is equal to 3.528(1) Å [6]. According to the literature data of [7, 9] shortened intra- and intermolecular Se···Se contacts are fairly common.

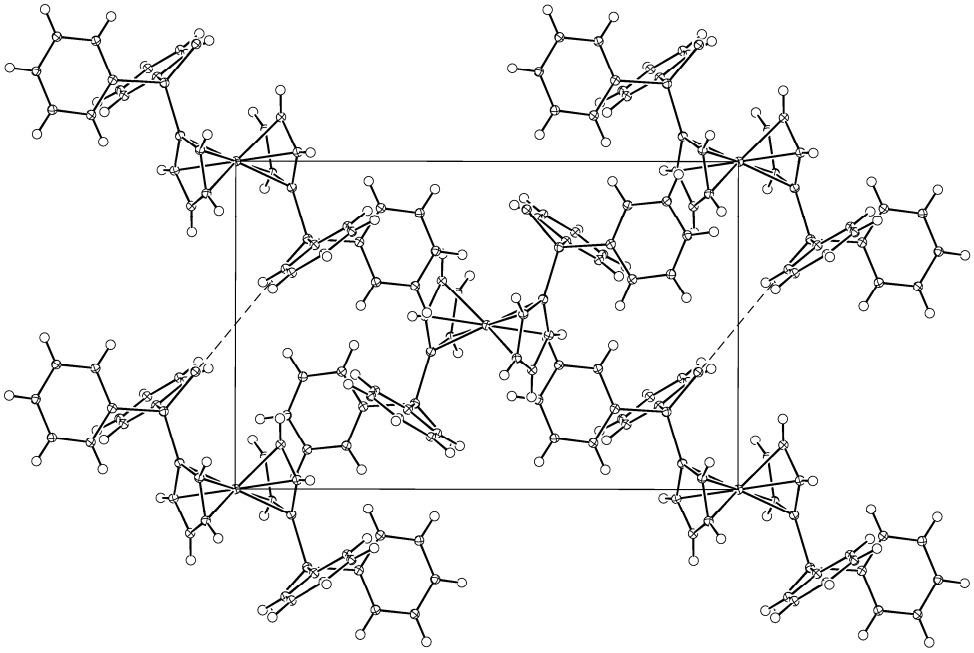

Fig. 2. Projection of the crystal structure of compound **6** along the crystallographic *a* axis.

We have thus developed a new method for the synthesis of 1,1'-bis(diphenylselenophosphoryl)-ferrocene, using 1,2,3-selenadiazoles. The molecular and crystal structure of the obtained compound has been investigated by X-ray analysis.

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury 400 instrument (400 and 100 MHz, respectively) in $CDCl_3$, internal standard was HMDS (δ 0.05 ppm). Monitoring of the reaction progress was performed by TLC on Merck Kieselgel plates (eluent CH_2Cl_2) with visualization in UV light.

1,1'-Bis(diphenylselenophosphoryl)ferrocene (6). A mixture of 1,2,3-selenadiazole **2-5** [10-13] (2.1 mmol) and 1,1'-bis(diphenylphosphino)ferrocene (**1**) (0.554 g, 1.0 mmol) was dissolved in toluene (10 ml) and heated to 80°C for 30 min. The solvent was then evaporated and the residue recrystallized from a mixture of EtOAc–petroleum ether. The data of ^{1}H and ^{13}C NMR spectra for 1,1'-bis(diphenylselenophosphoryl)-ferrocene (**6**) agreed with the literature data of [**6**].

X-Ray Structural Investigation of 1,1'-Bis(diphenylselenophosphoryl)ferrocene (6). Monocrystals of compound **6** obtained by crystallization from an EtOAc–petroleum mixture belonged to the monoclinic system. The parameters of the crystal lattice were: *a* 8.8821(4), *b* 16.1458(7), *c* 10.9639(5) Å; β 104.987(2)°; *V* 1518.8(1) Å^3; *F*(000) 712; μ 3.021 mm^{-1}; d_{calc} 1.557 g·cm^{-1}; *Z* 2; space group $P2_1/n$. The intensities of 3381 independent reflections were measured on a Bruker-Nonius KappaCCD automatic diffractometer (MoKα-radiation, λ 0.71073 Å, graphite monochromator) to $2\theta_{max}$ 55° at room temperature. The structure was solved on 2611 reflections with $I > 2\sigma(I)$ using the SIR97 set of programs [14]. Refinement was carried out by the least-squares method in a full-matrix anisotropic approximation with the aid of the SHELXL97 set of programs [15]. The final value of the probability factor *R* was 0.0687. Full crystallographic information has been deposited at the Cambridge Crystallographic Data Center (deposit CCDC 870663).

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REFERENCES

1. Y.-J. Wu and B. V. Yang, *Prog. Heterocycl. Chem*., **22**, 259 (2011).
2. P. G. Pilloni, B. Longato, and G. Bandoli, *Inorg. Chim. Acta*, **277**, 163 (1998).
3. G. Pilloni, B. Longato, and G. Bandoli, *Inorg. Chim. Acta*, **298**, 251 (2000).
4. S. Canales, O. Crespo, M. C. Gimeno, P. G. Jones, and A. Laguna, *J. Organomet. Chem*., **613**, 50 (2000).
5. P. Arsenyan, K. Oberte, K. Rubina, S. Belyakov, and E. Lukevics, *Khim. Geterotsikl. Soedin.*, 599 (2004). [*Chem. Heterocycl. Compd.*, **40**, 503 (2004).
6. G. Pilloni, B. Longato, G. Bandoli, and B. Corain, *J. Chem. Soc*., *Dalton Trans*., 819 (1997).
7. M. Mantina, A. C. Chamberlin, R. Valero, C. J. Cramer, and D. G. Truhlar, *J. Phys. Chem. A*, **113**, 5806 (2009).
8. R. S. Rowland and R. Taylor, *J. Phys. Chem*., **100**, 7384 (1996).
9. I. Vargas-Baca and T. Chivers, *Phosphorus*, *Sulfur Silicon Relat. Elem*., **164**, 207 (2000).
10. I. Lalezari, A. Shafiee, and M. Yalpani, *Angew. Chem*., *Int. Ed. Engl*., **9**, 464 (1970).
11. A. Caplin, *J. Chem. Soc*., *Perkin Trans. 1*, 30 (1974).
12. M. Yalpani, I. Lalezari, and A. Shafiee, *J. Org. Chem.*, **36**, 2836 (1971).
13. P. Arsenyan, K. Oberte, O. Pudova, and E. Lukevics, *Khim. Geterotsikl. Soedin*., 1627 (2002). [*Chem. Heterocycl. Compd.*, **38**, 1437 (2002)].
14. A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, and R. Spagna, *J. Appl. Crystallogr*., **32**, 115 (1999).
15. G. M. Sheldrick, *Acta Crystallogr*., *Sect. A: Found. Crystallogr*., **A64**, 112 (2008).