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Alkali Metal Thioselenophosphinates, $M[SeSPR_2]$: One-Pot Multicomponent Synthesis, DFT Study, and Synthetic Application

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Diverse alkali metal thioselenophosphinates, $M[SeSPR_2]$ (M = Li, Na, K, Rb, and Cs; R = alkyl, aryl, aralkyl, and hetaralkyl), have been synthesized in 78–94 % yields by means of a one-pot multicomponent reaction between secondary phosphanes, sulfur, selenium, and alkali metal hydroxides under mild conditions (room temperature, –50 °C, 0.5 h, EtOH). The molecular and electronic structure of the $[SeSPPh_2]^-$ anion and its coordination behavior towards Li^+, Na^+, and K^+ cations have been investigated at the B3LYP level of theory. The alkylation of the alkali metal thioselenophosphinates with various organic halides proceeds regiosecifically at the selenium center to form Se–organyl thioselenophosphinates, $R_2P(S)SeR'$ (R′ = Me, Et, Bn, allyl, propargyl), in 78–96 % yields. By the action of molecular iodine, the alkali metal thioselenophosphinates instantly (room temperature, ca. 1 s, 1,4-dioxane) undergo selective Se–Se oxidative coupling to afford the corresponding diselenides, $R_2P(S)SeSe(S)PR_2$, in 81–92 % yields. The alkali metal thioselenophosphinates are readily converted into the corresponding ammonium derivatives. Square-planar Ni^{II} complexes, $Ni[SeSPR_2]_2$ (R = Ph, CH_2CH_2Ph), have been prepared in 68–81 % yield by the treatment of sodium thioselenophosphinates, $Na[SeSPR_2]$, with $NiBr_2$ at room temperature ($EtOH/CH_2Cl_2$, 10 min).

Introduction

The alkali metal dithiophosphinates, $M[S_2PR_2]$, represent one of the most studied classes of chalcogeno-phosphorus organic compounds.[1] They are widely used as extraction[2] and flotation[3] reagents, versatile ligands in coordination chemistry,[4] and intermediates for the synthesis of lubricant oil additives,[5] agrochemicals,[6] vulcanization accelerators,[7] antitumor and antimicrobial agents,[8] as well as single-source precursors (SSPs) of remarkable nanomaterials.[9] The selenium analogues, the diselenophosphinates, $M[Se_2PR_2]$, are less studied,[10] although in recent years they have gained special attention on account of their applications as ligands for the design of SSPs to advanced nanomaterials[11] and building blocks for organic and inorganic syntheses.[12]

In sharp contrast, the mixed alkali metal thioselenophosphinates, $M[SeSPR_2]$, have been virtually ignored, mainly owing to the lack of expedient methods for their synthesis. At the same time, such salts are of special interest because the adjacent sulfur and selenium atoms should impart to these compounds beneficial features of both dithiophosphinates and diselenophosphinates. Moreover, one might expect that the thioselenophosphinates would possess new, unpredictably useful proprieties.

In addition, alkali metal thioselenophosphinates are convenient starting compounds for the preparation of both S and Se derivatives of thioselenophosphinic acids[13] as well as numerous novel and useful metal complexes,[14] some of which are already applied as single-source precursors for the fabrication of desired nanomaterials. For instance, silver(I) thioselenophosphinate, $[Ag(SeSPiPr_2)]_4$, is employed for the deposition of Ag_2Se films by means of aerosol-assisted and low-pressure chemical vapor deposition methods.[11f] More recently, O'Brien et al. have been reported the use of lead(II) thioselenophosphinate, $Pb[SeSPPh_2]_2$, for the preparation of PbSe micro- and nanocrystals.[15]

A conventional approach to the synthesis of the alkali metal thioselenophosphinates is conducted on the basis of the reaction of monochlorophosphanes R_2PCl with elemental sulfur or selenium to form $R_2P(X)Cl$ (X = S or Se) fol-

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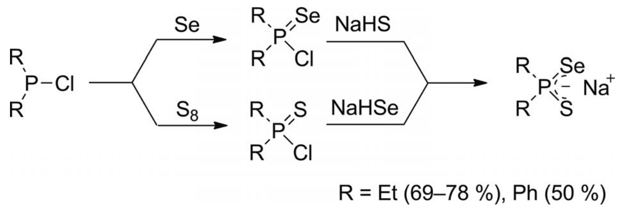
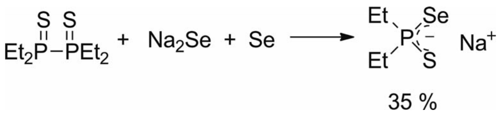
lowed by treatment with NaSeH or NaSH, respectively, to give sodium salt, Na[SeSPR$_2$] (R = Et, Ph) in 50–78 % total yield[14d,16] (Scheme 1).



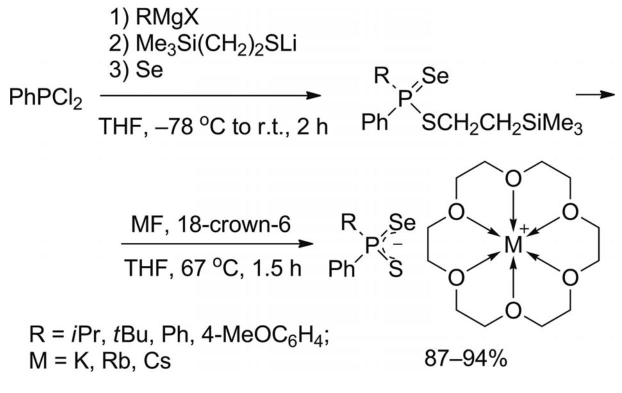
Scheme 1. A conventional syntheses of sodium thioselenophosphinates.

The preparation of sodium diethylthioselenophosphinate, Na[SeSPEt$_2$]·2H$_2$O, in low yield (35 %) by the reaction of tetraethyldiphosphane disulfide, Et$_2$P(S)P(S)Et$_2$, with sodium selenide and elemental selenium (Scheme 2) has also been reported.[16]



Scheme 2. An alternative route to sodium thioselenophosphinate.

Murai et al. have published[13] the original approach to alkali metal thioselenophosphinates, which involves several synthetic steps that utilize phenyldichlorophosphane, Grignard and organolithium reagents, elemental selenium, alkali metal fluorides, 18-crown-6 ether, as well as 2-(trimethylsilyl)ethanethiol (Scheme 3). Notably, this method allows one to obtain the K, Rb, and Cs thioselenophosphinates only as complexes with 18-crown-6 ether.[13]



Scheme 3. Synthesis of alkali metal thioselenophosphinates.

Clearly, the above reactions suffer from unsatisfactory atom economy. Therefore, it is highly desirable to invent a more straightforward approach for the synthesis of alkali metal thioselenophosphinates.

Recently,[17] we briefly disclosed the synthesis of alkylammonium thioselenophosphinates from secondary phosphanes, sulfur, selenium, and amines.

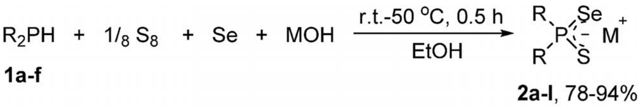
The present work is aimed at unfolding this promising approach further, and extending its scope in particular. To that end, we have implemented for the first time the multicomponent reaction between secondary phosphanes, elemental sulfur and selenium, and alkali metal hydroxides, which has in fact proven to be a novel general and efficient synthesis of alkali metal thioselenophosphinates. Furthermore, preliminary results on application of the synthesized salts and their study by DFT calculations are also reported.

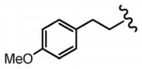
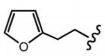
Results and Discussion

Synthesis of Alkali Metal Thioselenophosphinates

Our experiments have shown that secondary phosphanes **1a–f** react with elemental sulfur (S$_8$), elemental selenium, and alkali metal hydroxides in a 1:0.125:1:1 molar ratio (room temp., –50 °C, 0.5 h, EtOH) to selectively afford alkali metal thioselenophosphinates **2a–l** in 78–94 % yields (Table 1).

Table 1. One-pot synthesis of alkali metal thioselenophosphinates **2a–l**.



Entry	Phosphane	R	M	Product	Yield[a] (%)
1	**1a**	Cy	Na	**2a**	91
2	**1b**	(CH$_2$)$_2$Ph	Li	**2b**	92
3	**1b**	(CH$_2$)$_2$Ph	Na	**2c**	85
4	**1b**	(CH$_2$)$_2$Ph	K	**2d**	76
5	**1b**	(CH$_2$)$_2$Ph	Cs	**2e**	79
6	**1c**	CH$_2$CH(Me)Ph	K	**2f**	92
7	**1c**	CH$_2$CH(Me)Ph	Cs	**2g**	89
8	**1d**		K	**2h**	94
9	**1e**		Rb	**2i**	78
10	**1f**	Ph	Na	**2j**	88
11	**1f**	Ph	K	**2k**	82
12	**1f**	Ph	Cs	**2l**	91

[a] All yields refer to isolated products.

As seen in Table 1, this multicomponent reaction has proved to be a very general route for a wide array of Li, Na, K, Rd, and Cs thioselenophosphinates. Indeed, a variety of secondary phosphanes have been involved in this reaction, in which alkyl, aralkyl, hetaralkyl, and aryl substituents appear to be suitable.

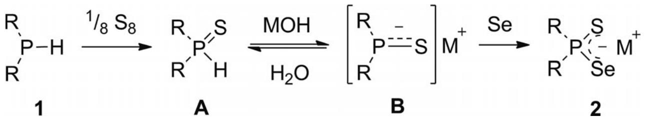
It is worth noting that the multicomponent reaction proceeds with 100 % atom economy except for the elimination of water. Moreover, a nontoxic "green" solvent[18] (95 %

aqueous ethanol) has been used in the synthesis. As mentioned above, conventional syntheses of thioselenophosphinates require toxic (especially dry) solvents (e.g., THF, 1,4-dioxane, or benzene).[13,16]

The synthesized thioselenophosphinates **2a–l** are microcrystalline powders, stable in air for several days. These compounds are highly soluble in water and in polar organic solvents (e.g., DMSO, EtOH, $CHCl_3$, 1,4-dioxane). Unfortunately, attempts to obtain single crystals of alkali metal salts **2a–l** were unsuccessful.

The structures of compounds **2a–l** have been proved by multinuclear NMR (^{1}H, ^{13}C, ^{31}P, and ^{77}Se) and IR spectroscopy. The ^{31}P NMR spectra of thioselenophosphinates **2a–l** show a sharp singlet in the range of δ = 43.98–73.84 ppm, flanked by one typical pair of ^{77}Se satellites ($^1J_{P,Se}$ = 550–645 Hz). The ^{77}Se NMR spectra display a doublet ($^1J_{P,Se}$ = 550–645 Hz) in the range of δ = –86 to 4 ppm. The values of ^{31}P,^{77}Se coupling constants are between the coupling constant values for phosphorus–selenium single (200–600 Hz) and double bonds (800–1200 Hz), thus corresponding to a phosphorus–selenium bond order of approximately 1.5. The ^{1}H and ^{13}C NMR spectra of **2a–l** reveal the presence of corresponding organic groups at the phosphorus atoms. In the solid-state IR spectra of **2a–l**, strong bands at 560–630 cm^{-1} correspond to stretching vibrations of the P–S bonds. Stretching vibrations of the P–Se bond are observed in the region of 450–525 cm^{-1}.

The tentative pathway of thioselenophosphinate formation in this multicomponent reaction includes the following steps: (i) oxidation of phosphanes **1** with elemental sulfur to give secondary phosphane sulfides **A**; (ii) deprotonation of the latter by the metal hydroxides, MOH, to generate the *P,S*-ambident thiophosphinite **B**; and (iii) oxidation of anions **B** with elemental selenium to afford thiselenophosphinate **2** (Scheme 4).



Scheme 4. The possible mechanism of the multicomponent reaction between secondary phosphanes, sulfur, selenium, and alkali metal hydroxides.

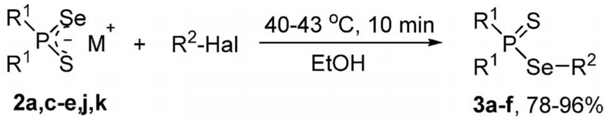
Reactivity of Alkali Metal Thioselenophosphinates

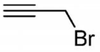
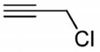
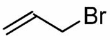
To elucidate the reactivity of alkali metal thioselenophosphinates and to demonstrate their applicability to the synthesis of more complex chalcogeno-phosphorus organic compounds, we have investigated some reactions that involve thioselenophosphinates **2a–e,j,k**, namely, (i) alkylation with organic halides, (ii) oxidation by molecular iodine, and (iii) counterion exchange.

Synthesis of Thioselenophosphinic *Se*-Esters

The data on the thioselenophosphinic esters are very limited: only about ten examples of these compounds have been reported.[13,16,19] However, such esters are promising precursors for creating advanced nanomaterials and agrochemicals from metal chalcogenides. To obtain the new representatives of thioselenophosphinic esters, salts **2a,c–e,j,k** were introduced into the reaction with various organic halides. Experiments have shown, that in all the cases, alkylation takes place chemoselectively at the selenium center of the ambident $[SeSPR_2]^-$ anion with the formation of the corresponding *Se*-esters **3a–f** in 78–96% yield (Table 2). This result is in good agreement with the data of Murai et al.[13b] on the reaction of tetraalkylammonium salts, $[Bu_4N][SeSPPh_2]$ and $[Me_4N][SeSP(tBu)Ph]$, with MeI or allyl bromide.

Table 2. Chemoselective reaction of thioselenophosphinates with organic halides.



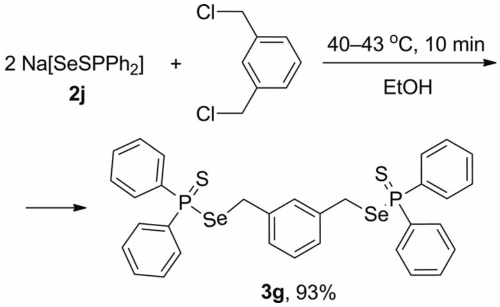
Entry	Salt	R^1	M	R^{2}Hal	Product	Yield[a] (%)
1	**2a**	Cy	Na	MeI	**3a**	96
2	**2c**	$(CH_2)_2Ph$	Na	EtI	**3b**	90
3	**2e**	$(CH_2)_2Ph$	Cs	EtI	**3b**	82
4	**2c**	$(CH_2)_2Ph$	Na	 Br	**3c**	92
5	**2d**	$(CH_2)_2Ph$	K	 Cl	**3c**	88
6	**2j**	Ph	Na	MeI	**3d**	95
7	**2j**	Ph	Na	BnCl	**3e**	87
8	**2k**	Ph	K	 Br	**3f**	78

[a] All yields refer to isolated products.

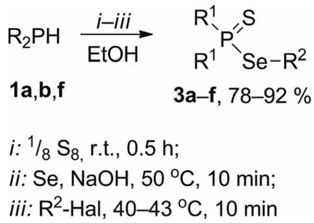
The synthesis of thioselenophosphinic bis-ester **3g** in high yield (93%) by the treatment of salt **2j** with 1,3-bis(chloromethyl)benzene at a 2:1 molar ratio under the same conditions has additionally demonstrated the generality of this reaction (Scheme 5).

Moreover, the thioselenophosphinic *Se*-esters **3a–f** can be successfully synthesized with the same yield in a one-pot procedure by means of the multicomponent reaction between secondary phosphanes **1a,b,f**, sulfur, selenium, MOH, and R^2-Hal (Hal = halide) (Scheme 6).

The structure of thioselenophosphinic esters **3a–g** clearly follows from their ^{31}P and ^{77}Se NMR spectra. In particular, the ^{31}P NMR spectrum of **3a–g** shows a sharp singlet at δ = 53–87 ppm flanked by one set of ^{77}Se satellites ($^1J_{P,Se}$ = 344–365 Hz), whereas the ^{77}Se NMR spectrum contains a doublet at δ = 239–362 ppm with a characteristic one-bond ^{31}P,^{77}Se coupling of 344–365 Hz. The presence of the P=S



Scheme 5. Synthesis of thioselenophosphinic bis-esters **3g**.



Scheme 6. One-pot synthesis of thioselenophosphinic esters **3a**–**f**.

bond in esters **3a**–**g** is supported by the appearance of a strong band in the region 612–646 cm^{-1} in the IR spectra.

DFT calculations of the two model isomers, $Ph_2P(S)SeMe$ and $Ph_2P(Se)SMe$, have confirmed that the *Se*-esters are more stable than the *S*-esters; the difference in Gibbs free energies calculated at the B3LYP/6-31+G(d,p) level is 4.5 kcal mol^{-1}.

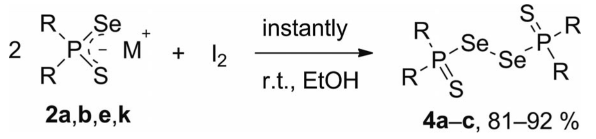
Synthesis of Bis(diorganothiophosphanyl)diselenides

The oxidative dimerization of thioselenophosphinate anions by the action of the appropriate oxidant is a promising route to the corresponding disufides, diselenides, or mixed species (i.e., thioselenides). These compounds are supposed to be prospective intermediates for the direct synthesis of thioselenophosphinic diesters by means of the addition to alkenes and alkynes.

We have found that the treatment of thioselenophosphinates **2a**,**b**,**e**,**k** with elemental iodine in a 2:1 molar ratio gives diselenides **4a**–**c** chemoselectively in 81–92% yields (Table 3). The reaction instantly proceeds in 1,4-dioxane at room temperature to avoid the formation of the expected disulfides, $(R_2P{=}Se)_2S_2$, or thioselenides, $R_2P(Se)S{-}Se(S)PR_2$ (^{31}P NMR spectroscopy).

To understand the chemo- and regioselectivity of the oxidative coupling of thioselenophosphinate anions, DFT computations were performed. We suggest that such a coupling is triggered by the one-electron oxidation of $[R_2PSeS]^-$ anions with iodine to afford the corresponding free radicals, $[R_2PSeS]^{\cdot}$, which are the key precursors of the reaction products. Apparently, the structure of the latter strongly depends on localization of the unpaired electron in intermediate $[R_2PSeS]^{\cdot}$ radicals. Our calculation [UB3LYP/6-311+G(d,p)] of the model $[Me_2PSeS]^{\cdot}$ free radical shows that approximately 60% of the spin density is localized on the Se atom, and approximately 40% of the spin density is distributed over the S atom (Figure 1). Therefore, $[R_2PSeS]^{\cdot}$ radicals should act as Se-centered ones. Indeed, the experimentally observable products are diselenides **3a**–**c**. Moreover, calculations [B3LYP/6-31+G(d,p)] of three alternative products of dimerization of $[Me_2PSeS]^{\cdot}$ radicals [i.e., $(Me_2P{=}S)_2Se$, $Me_2P(Se)S{-}Se(S)PMe_2$, and $(Me_2P{=}Se)_2S$] have confirmed that the diselenide is more stable than the disulfide and thioselenide by 17.8 and 7.9 kcal mol^{-1}, respectively.

Table 3. Chemoselective reaction of thioselenophosphinates with elemental iodine.



Entry	Salt	R^1	M	Product	Yield[a] [%]
1	**2a**	Cy	Na	**4a**	85
2	**2b**	$(CH_2)_2Ph$	Li	**4b**	82
3	**2e**	$(CH_2)_2Ph$	Cs	**4b**	92
4	**2k**	Ph	K	**4c**	81

[a] All yields refer to isolated products.

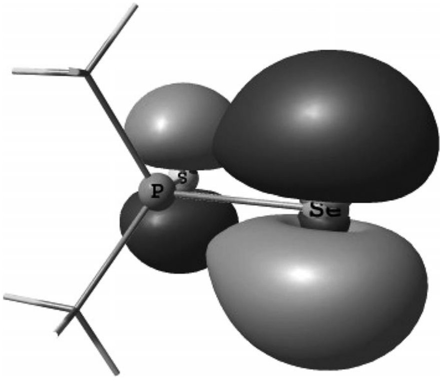


Figure 1. Electron-density plot for the singly occupied molecular orbital (SOMO) of $[Me_2PSeS]^{\cdot}$ free radical calculated at the UB3-LYP/6-31+G(d,p) level.

It should be emphasized that compounds **4a**–**c** are representatives of a rare family of bis(diorganothiophosphanyl)-diselenides, $(R_2P{=}S)_2Se_2$. Currently, only two representatives of these diselenides have been prepared, namely, $[Ph(tBu)P{=}S]_2Se_2$[20] and $(Et_2P{=}S)_2Se_2$.[16,21]

Diselenides **4a**,**b** are air- and moisture-stable red-orange crystals, which are highly soluble in most organic solvents. These compounds have been characterized in solution and the solid state by multinuclear NMR spectra and X-ray crystallography.

Diselenide **4a** crystallizes in the triclinic $P\bar{1}$ space group, whereas diselenide **4b** crystallizes in the monoclinic *C*2/*c* space group with a solvating benzene molecule per unit. Their crystallographic data are listed in Table 4. The structure of **4a** is formed by two crystallographically independent $(Cy_2P{=}S)_2Se_2$ molecules, one of which is shown in Figure 2. The molecular structure of diselenide **4b** is presented on Figure 3. As expected, the P atoms in diselenides **4a**,**b**

Table 4. Data collection and refinement parameters for **2m**, **4a**,**b**, and **5a**,**b**.

	2m	**4a**	**4b**	**5a**	**5b**
Empirical formula	$C_{32}H_{44}N_2P_2S_2Se_2$	$C_{48}H_{88}P_4S_4Se_4$	$C_{38}H_{42}P_2S_2Se_2$	$C_{24}H_{20}NiP_2S_2Se_2$	$C_{32}H_{36}NiP_2S_2Se_2$
Formula mass [g mol^{-1}]	740.67	1233.14	782.70	651.09	763.30
Space group	$P\bar{1}$	$P\bar{1}$	$C2/c$	$C2/c$	$P\bar{1}$
a [Å]	9.6873(7)	12.3414(14)	35.555(10)	10.5564(3)	9.2442(5)
b [Å]	13.8550(11)	12.8348(13)	6.0157(14)	15.1155(5)	10.2796(6)
c [Å]	15.1765(12)	20.750(2)	37.465(10)	16.2080(4)	10.2934(6)
α [°]	114.657(2)	75.470(4)	90.00	90.00	102.506(2)
β [°]	99.788(3)	73.031(4)	113.280(17)	106.413(1)	108.251(2)
γ [°]	91.719(2)	68.788(4)	90.00	90.00	109.609(2)
V [Å^3]	1812.7(2)	2891.6(5)	7361(3)	2480.85(12)	816.55(8)
Z	4	4	8	4	1
$D_{calcd.}$ [g cm^{-3}]	1.357	1.416	1.413	1.743	1.552
μ [mm^{-1}]	2.266	2.823	2.235	4.025	3.070
T [K]	200	240	200	200	200
Reflections collected	48935	93610	22800	26271	27110
Independent reflections	7175 (R_{int} = 0.0532)	12584 (R_{int} = 0.0447)	7805 (R_{int} = 0.0372)	4212 (R_{int} = 0.0441)	4854 (R_{int} = 0.0392)
R_1, wR_2 [$I > 2\sigma(I)$]	0.0471, 0.1289	0.0261, 0.0699	0.0595, 0.1599	0.0287, 0.0712	0.0311, 0.0859
R_1, wR_2 (all data)	0.0699, 0.1463	0.0393, 0.0924	0.0906, 0.1845	0.0416, 0.0761	0.0446, 0.0913
Goodness of fit	1.093	1.182	1.065	1.078	1.127
Largest diff. peak and hole [e Å^{-3}]	1.18 and 0.59	0.53 and –0.61	1.99 and –1.07	0.42 and –0.36	0.46 and –0.34

adopt a slightly distorted tetrahedral geometry. The P–S bond lengths in **4a**,**b** lie in the range of 1.943–1.960 Å, which is comparable to 1.940(2) Å in $[Ph(tBu)P{=}S]_2Se_2$.[20] The average Se–Se distances (2.335 Å) fall close to the values found in similar diselenido compounds.[20–22] The P–Se bond lengths range 2.252–2.309 Å, which are comparable to those observed in compounds that bear the P^V–Se single bonds.[20–23] Both molecules of **4a** have similar structural motifs and display *sin–anti* configuration of the S–P–Se–Se–P–S unit with Se–Se–P–S torsion angles of 22.03(4) and 175.34(3)° for one molecule and –18.98(4) and –170.98(3)° for the other molecule. In contrast, the S–P–Se–Se–P–S chain in diselenide **4b** adopts an *anti–anti* configuration with Se–Se–P–S torsion angles of –167.65(9) and 177.87(8)°. The P–Se–Se–P torsion angles in the both diselenides have an *anti* configuration with values of –129.17(2) and 130.36(3)° for **4a** and 146.36(7)° for **4b**.

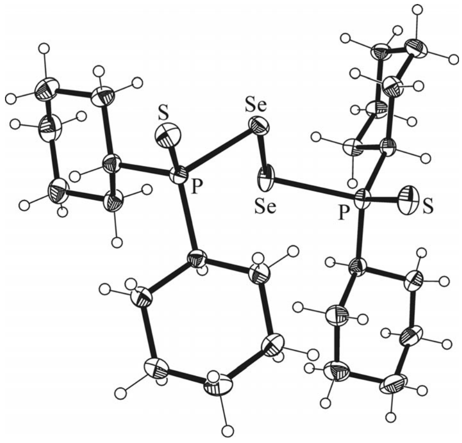


Figure 2. Perspective view of diselenide **4a** (30 % thermal ellipsoid). Selected bond lengths [Å] and angles [°]: Se–Se 2.3346(4); P–Se 2.2544(7)–2.3092(7); P–S 1.9430(9)–1.9599(9); S–P–Se 104.49(3)–116.37(4); P–Se–Se 99.761(19)–102.80(2).

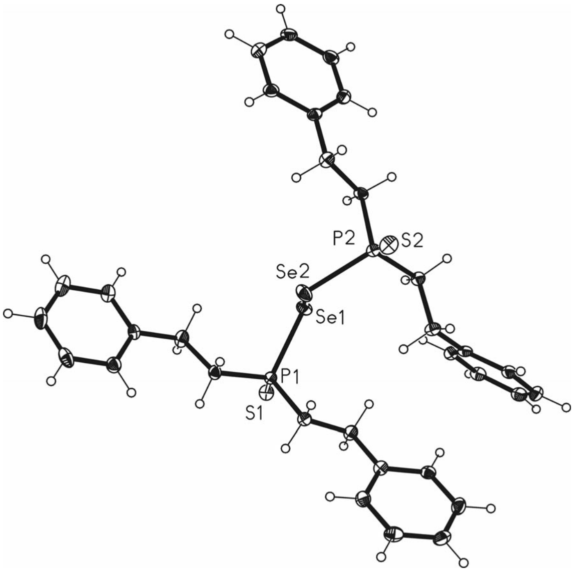
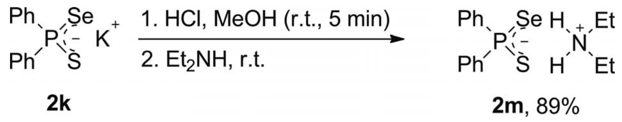


Figure 3. Perspective view of diselenide **4b** (30 % thermal ellipsoid) with benzene solvate molecule omitted for clarity. Selected bond lengths [Å] and angles [°]: Se1–Se2 2.3867(11), Se1–P1 2.2524(18), Se2–P2 2.2569(17), P1–S1 1.956(2), P2–S2 1.946(2), P1–Se1–Se2 98.70(5), P2–Se2–Se1 102.36(5), S1–P1–Se1 105.76(8), S2–P2–Se2 106.65(8).

Synthesis of Alkylammonium Thioselenophosphinates

In the example of the conversion of $K[SeSPPh_2]$ (**2k**) to $Et_2NH_2[SeSPPh_2]$ (**2m**), it has been shown that alkali metal thioselenophosphinates can be successfully used for preparation of the corresponding alkylammonium salts. Thus, acidification of salt **2k** with a solution of HCl in methanol (room temp., 5 min, MeOH) followed by treatment with diethylamine furnishes the corresponding ammonium salt **2m** in 89 % isolated yield (Scheme 7).



Scheme 7. Synthesis of *N*,*N*-diethylammonium thioselenophosphinate **2m**.

According to X-ray analysis, thioselenophosphinate **2m** crystallizes in the triclinic space group $P\bar{1}$. The selected crystallographic data for **2m** are presented in Table 4. The structure of **2m** is formed by two sets of crystallographically independent $[SeSPPh_2]^-$ and $[Et_2NH_2]^+$ ions. The geometry of the phosphorus atom in the $[SeSPPh_2]^-$ anion is a distorted tetrahedron (Figure 4). The S and Se atoms in both independent anions are disordered over two positions with Se/S:S′/Se′ occupancy ratios of 0.66:0.34 and 0.74:0.26. It is worth noting that such disordering of chalcogen atoms is quite typical for salts of thioselenophosphinic acids.[13,15,17]

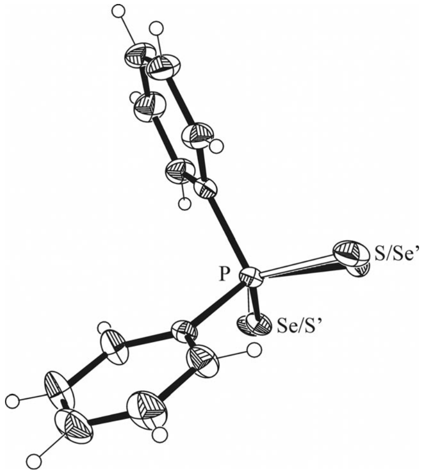


Figure 4. Perspective view of the $[Ph_2PSeS]^-$ anion (shows one of two independent anions) in salt **2m** (30% thermal ellipsoid). The S and Se atoms are disordered over two positions.

One-dimensional infinite chains of molecules **2m** along the *a* axis are formed in the crystal through intermolecular hydrogen bond N–H···S with parameters detailed in Table 5 and Figure 5. Notably, the normal S···H and Se···H contacts are 2.92 and 3.10 Å.[24] In addition to the hydrogen bond, the C–H···π interaction of the hydrogen atoms of the C4–H, C7–H, and C24–H bonds with phenyl rings are observed; the atom-to-plane distances are 2.91, 2.89, and 2.92 Å.

Table 5. Hydrogen-bonding parameters [Å and] for compound **2m** (Ch = S, Se).

N–H···Ch	N–H [Å]	H···Ch [Å]	N···Ch [Å]	N–H···Ch angle [°]
N1–H···S1	0.92	2.73	3.476(7)	139
N1–H···Se1	0.92	2.87	3.633(4)	141
N1–H···S2	0.92	2.37	3.289(5)	172
N2–H···S1	0.92	2.48	3.383(7)	167
N2–H···Se2	0.92	2.73	3.539(4)	147
N2–H···S2	0.92	2.66	3.341(5)	131

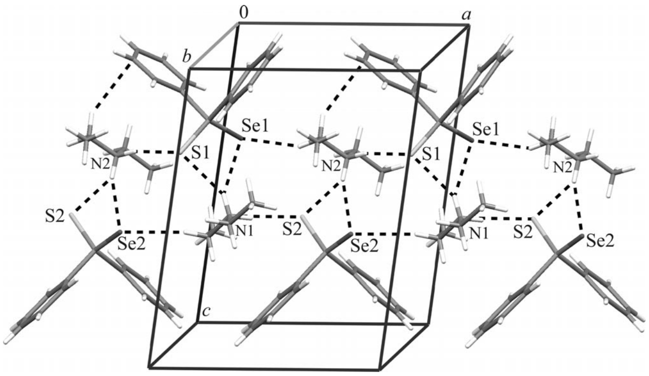
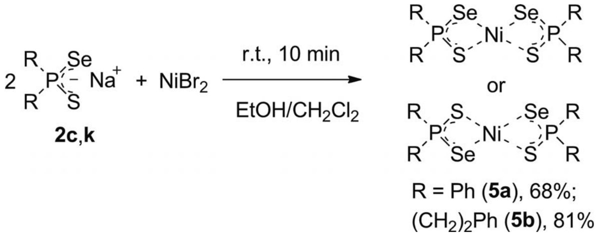


Figure 5. Fragment of the 1D infinite chains in the crystal of compound **2m**.

Synthesis of Ni^{II} Thioselenophosphinate Complexes

Currently, the investigation of reactions of thioselenophosphinates **2a–l** with heavy-metal ions is underway, and some preliminary results on the preparation and characterization of $Ni[SeSePR_2]_2$ complexes are reported herein. It should be emphasized that there are no structurally characterized examples of nickel thioselenophosphinates. However, examples of dithiophosphinato,[2a] diselenophosphinato,[11c,11e] and diselenophosphonato[25] Ni^{II} complexes are known.

We have found that reaction of sodium salt **2c** or **2k** with $NiBr_2$ in a 2:1 molar ratio proceeds under mild conditions (room temp., $EtOH/CH_2Cl_2$, 10 min) to give Ni^{II} thioselenophosphinates **5a**,**b** in high yields (Scheme 8).



Scheme 8. Synthesis of Ni^{II} thioselenophosphinates.

Complexes **5a**,**b** were isolated as dark green crystals, which are soluble in dichloromethane and chloroform. The molecular structures of Ni^{II} thioselenophosphinates have been established by single-crystal X-ray diffraction (Figures 6 and 7). The selected crystallographic data are given in Table 4. The selenium and sulfur atoms in the Ni^{II} thioselenophosphinates are disordered over two positions in an Se/S:Se′/S′ ratio of 0.662:0.338(1) (for **5a**) and 0.565:0.435(1) (for **5b**) with the retention of the *cis* arrangement of selenium atoms. In each complex, the nickel atom is located on the crystallographic inversion center and is coordinated by four chalcogen atoms of thioselenophosphinate ligands in a square-planar geometry. Therefore, both $[SeSPR_2]$ groups act as S,Se-bidentate ligands. For **5a**, the $Ni(SePS)_2$ metallobicycle formed is nonplanar: the maximum and minimum deviations from the mean plane constituted by P1, S1, Se1, and Ni1 are 0.200 and 0.102 Å, respectively. Meanwhile, the corresponding values for **5b** are 0.029 and 0.005 Å [i.e., the Ni(SePS)$_2$ unit in this compound is almost planar]. As expected, the P atoms in **5a**,**b** adopt a slightly distorted tetrahedral geometry. The C–P bond lengths lie in the range 1.801–1.817 Å, which are comparable to the corresponding values in similar Ni^{II} complexes.[11c,11e]

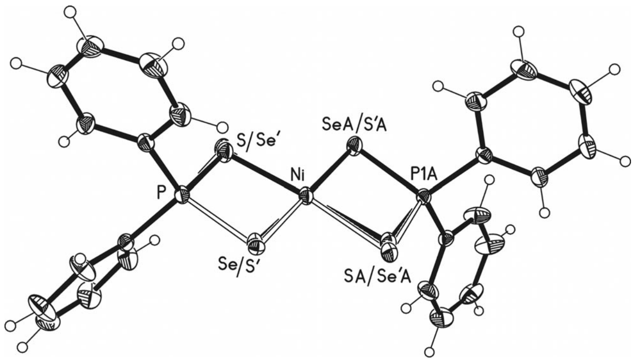


Figure 6. Perspective view of complex **5a** (30% thermal ellipsoid). The S and Se atoms are disordered over two positions with Se/S:S′/Se′ occupancy ratio of 0.662:0.338(1).

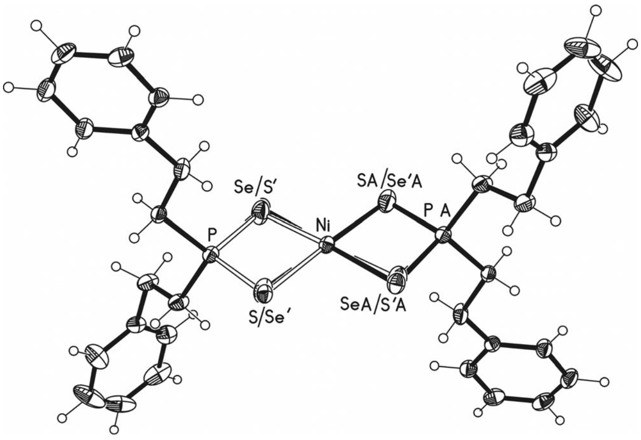


Figure 7. Perspective view of complex **5b** (30% thermal ellipsoid). The S and Se atoms are disordered over two positions with Se/S:S′/Se′ occupancy ratio of 0.565:0.435(1).

The solid-state IR spectra of Ni^{II} thioselenophosphinates show bands at 563, 537 (for **5a**) and 589, 568, 552 cm^{-1} (for **5b**), which are assigned to the P–S stretching vibration. The P–Se bond-stretching vibrations occur at 503, 475, 420 (for **5a**) and 501, 468, 458, 430 cm^{-1} (for **5b**).

To investigate the *cis*/*trans* isomerism of Ni^{II} thioselenophosphinates, DFT gas-phase calculations [B3LYP/6-311++G(df,p)] of model isomers of Ni(SeSPMe$_2$)$_2$ have been performed. The *trans*-Ni(SeSPMe$_2$)$_2$ turned out to be more stable than the *cis* isomer by 0.2 kcal mol^{-1} (Figure S1 in the Supporting Information).

The synthesized Ni^{II} complexes are highly prospective SSPs to nickel chalcogenide and/or phosphide nanoparticles that possess many remarkable properties.

DFT Study of Alkali Metal Thioselenophosphinates

Before this work, data on the structural chemistry of alkali metal thioselenophosphinates were scarce, if any. In particular, X-ray investigations and quantum-chemical models of these compounds have not been reported. Therefore, molecular and electronic structures as well as coordinating capability of [SeSPR$_2$]$^-$ anions toward alkali metal cations remain unexplored.

To address this challenge, we have performed DFT investigations of Li, Na, and K diphenylthioselenophosphinates, M[SeSPPh$_2$] and M$_2$[SeSPPh$_2$]$_2$, at the B3LYP [6-31+G(d,p), 6-311++G(d,p), and 6-311++G(3df,3pd)] level of theory in the Gaussian 09 package.[26]

Our calculations have revealed that the phosphorus atom in the [SeSPPh$_2$]$^-$ anion adopts a distorted tetrahedral environment (see the bond-angle values in Figure 8). The P–Se and P–S bond lengths are intermediate between the corresponding single and double bonds. Indeed, in the optimized geometry [B3LYP/6-31+G(d,p)] of Se–methyl thioselenophosphinate, Ph$_2$P(S)SeMe, P=S and P–Se distances are 1.971 and 2.277 Å; whereas in the isomeric ester, Ph$_2$P(Se)-SMe, P–S and P=Se bonds lengths are 2.116 and 2.146 Å, respectively (Figure S2 in the Supporting Information).

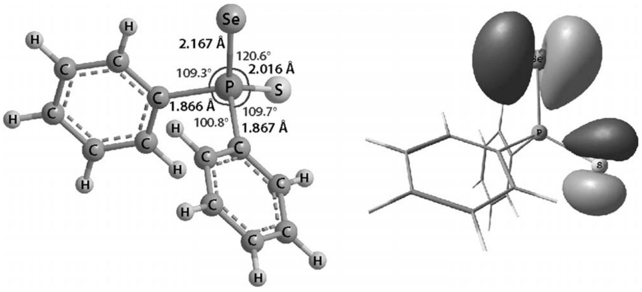


Figure 8. B3LYP/6-31+G(d,p) optimized geometry of [SeSPPh$_2$]$^-$ anion and view of its HOMO.

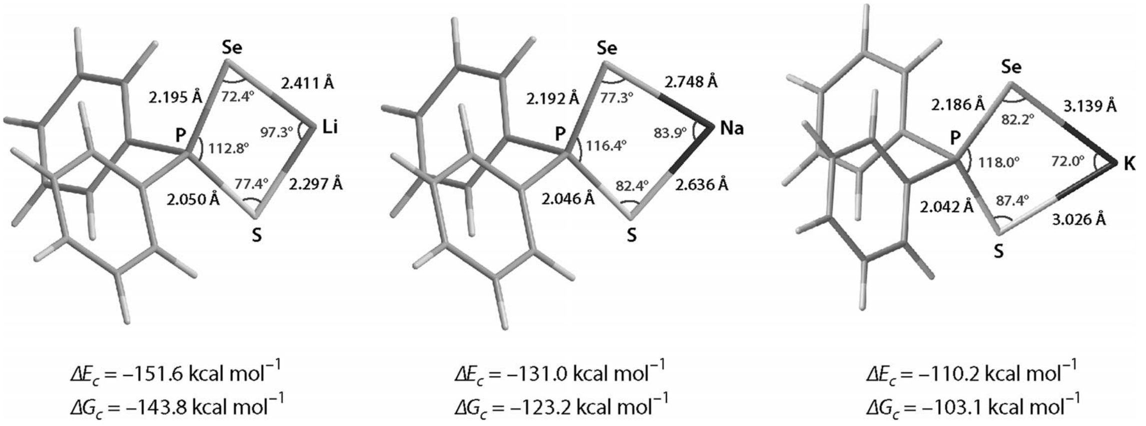
The influence of the basis-set size on the geometrical parameters of the [SeSPPh$_2$]$^-$ anion is insignificant. For instance, the differences in bond lengths and bond angles are less than 0.02 Å and 1.1°, respectively (see Table S1 in the Supporting Information). Therefore, the further DFT study was carried out at the B3LYP/6-31+G(d,p) level of theory.

Atomic charges have been calculated using natural bonding orbital (NBO) analysis[27] for the HF/6-31+G(d,p) wave function. As expected, the negative charge of the [SeSPPh$_2$]$^-$ anion is distributed between sulfur and selenium atoms. The absolute charge value on the sulfur atom (–0.750) is a little bit larger than on the selenium atom (–0.709). On the contrary, according to data from Murai et al.,[13b] the Mulliken charges [HF/6-31+G(d)] on the chalcogen atoms in the simplest [SeSPH$_2$]$^-$ anions are –0.670 for S and –0.831 for Se. Note that the NBO charges in the [SeSPH$_2$]$^-$ anion additionally calculated by us show that the S atom is more negative (–0.802) than the Se atom (–0.767). The inconsistency between NBO and Mulliken charges is due to the known problems of atom-charge evaluation.[28] Nevertheless, literature data indicate that the NBO analysis is preferable to the Mulliken calculations.[28,29] Shapes of the HOMO in $[SeSPPh_2]^-$ (Figure 8) and $[SeSPH_2]^-$[13b] anions are in good compliance, which testifies to a greater localization of the HOMO on the Se atom. According to the hard and soft (Lewis) acids and bases (HSAB) theory,[30] the results obtained demonstrate that the Se atom in the thioselenophosphinate anion is a relatively softer nucleophilic site than the S atom towards electrophiles. Indeed, protonation and acylation of thioselenophosphinates proceed on the sulfur atom (charge control), whereas alkylation occurs on the selenium atom (orbital control), which corresponds to the literature[13b] and our data (see above).

On the potential energy surface (PES) of interaction of the $[SeSPPh_2]^-$ anion with Li^+, Na^+, and K^+ cations, the minima are found to correspond to $M[SeSPPh_2]$ complexes (Figure 9). The alkali metal cation in the structure of $M[SeSPPh_2]$ interacts simultaneously with S and Se atoms of the $[SeSPPh_2]^-$ anion, thus forming the almost planar four-membered MSPSe cycle. When increasing the size of the metal cation, the SPSe bite angle increases from 112.8 to 118.0°, whereas the M–S and M–Se bond lengths decrease. At the same time, the P–S and P–Se bond lengths change insignificantly (Figure 9).

The absolute values of the formation energies, ΔE_c, of $M[SeSPPh_2]$ complexes in the gas phase (with zero-point vibrational energy contributions) are over 110 kcal mol^{-1} (Figure 9). Notably, $Li[SeSPPh_2]$ is the most stable, whereas $K[SeSPPh_2]$ is the least stable.

It is worth noting that the interaction of alkali metal cations with the thioselenophosphinate anion might result in the formation of not only monomers $M[SeSPPh_2]$, but also dimers $M_2[SeSPPh_2]_2$. This is supported by the examples of $Li_2(SeSPPh_2)_2$ and $K_2(SeSPPh_2)_2$ (Figure 10), which also correspond to minima on the PES. The structure of the dimers $M_2[SeSPPh_2]_2$ depends substantially on the cation M^+ size. Indeed, if for $K_2(SeSPPh_2)_2$ the coordination contacts KSe (K′Se′) and KSe′ (K′Se) are observed (Figure 10), in the case of $Li_2(SeSPPh_2)_2$ only LiSe and Li′Se′ appear (LiSe′ and Li′Se distances are more than 4.1 Å). Upon going from $M[SeSPPh_2]$ to $M_2[SeSPPh_2]_2$ the P–S and P–Se bond lengths remain almost unchanged, whereas the SPSe angle value decreases by approximately 3°. The most significant differences are observed for the M–S and M–Se bond lengths: they are substantially higher in dimers $M_2[SeSPPh_2]_2$ than in $M[SeSPPh_2]$ (see Figures 9 and 10).

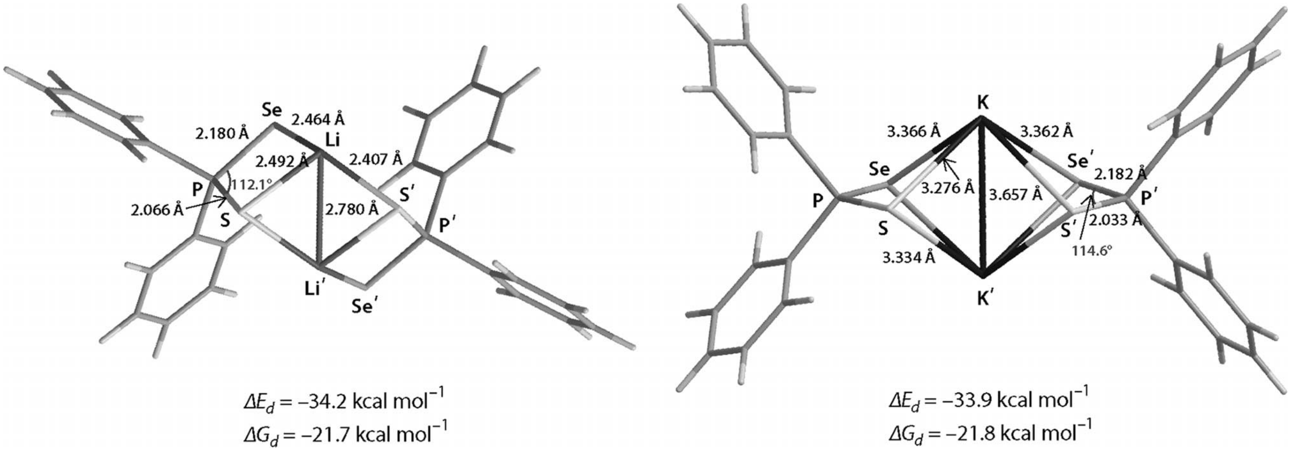


$\Delta E_c = -151.6$ kcal mol^{-1}
$\Delta G_c = -143.8$ kcal mol^{-1}

$\Delta E_c = -131.0$ kcal mol^{-1}
$\Delta G_c = -123.2$ kcal mol^{-1}

$\Delta E_c = -110.2$ kcal mol^{-1}
$\Delta G_c = -103.1$ kcal mol^{-1}

Figure 9. B3LYP/6-31+G(d,p)-optimized geometries of $M[SeSPPh_2]$ complexes in the gas phase and corresponding complexation energies, $\Delta E_c = E(M[SeSPPh_2]) - \{E([SeSPPh_2]^-) + E(M^+)\}$.



$\Delta E_d = -34.2$ kcal mol^{-1}
$\Delta G_d = -21.7$ kcal mol^{-1}

$\Delta E_d = -33.9$ kcal mol^{-1}
$\Delta G_d = -21.8$ kcal mol^{-1}

Figure 10. B3LYP/6-31+G(d,p)-optimized geometries of $M_2[SeSPPh_2]_2$ complexes in the gas phase and corresponding dimerization energies, $E_d = E(M_2[SeSPPh_2]_2) - 2E(M[SeSPPh_2])$.

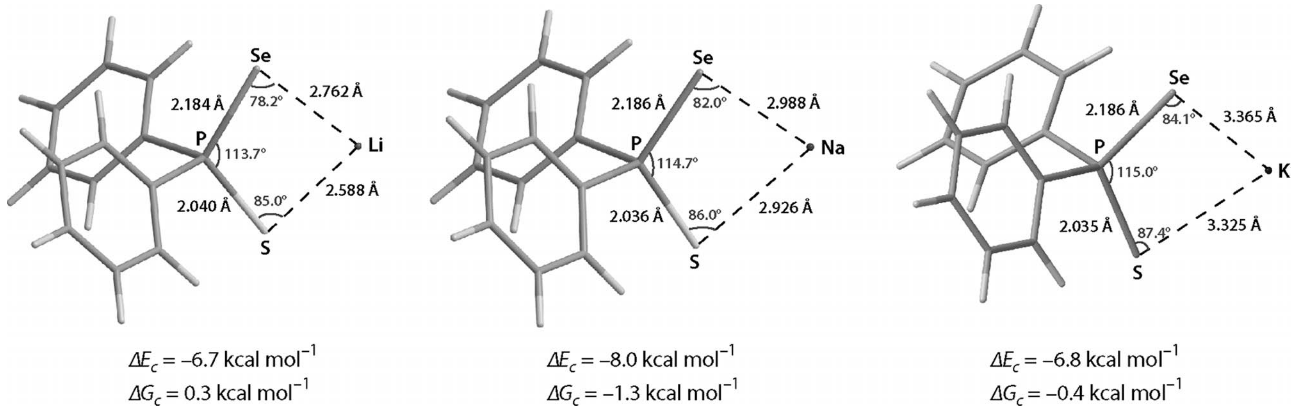


Figure 11. B3LYP/6-31+G(d,p)-optimized geometries of M[SeSPPh$_2$] complexes in a water solution and the corresponding complexation energies.

As expected,[31] in the highly polar solution [ε = 78.35; conductor-like polarizable continuum model (C-PCM)],[32] the interaction of cationic and anionic units of M[SeSPPh$_2$] and M$_2$[SeSPPh$_2$]$_2$ salts is insignificant (see ΔE_c values in Figure 11, and E_d in Figure 12). In this case, the structural parameters of the anionic part of M[SeSPPh$_2$] and M$_2$[SeSPPh$_2$]$_2$ are close to those of the free [SeSPPh$_2$]$^-$ anion (see, for example, the data in Figures 8 and 11). Moreover, according to the positive values of complexation free energy for Li[SeSPPh$_2$] and K$_2$[SeSPPh$_2$]$_2$ under the standard conditions in the highly polar solution (ε = 78.35; C-PCM model), these complexes are dissociated (see ΔG_c in Figure 11 and ΔG_d in Figure 12). Meanwhile, Na[SeSPPh$_2$] and K[SeSPPh$_2$] complexes are in equilibrium with their ions.

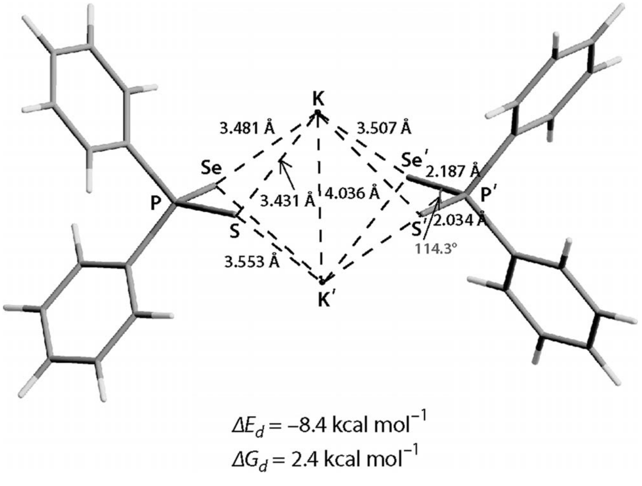


Figure 12. B3LYP/6-31+G(d,p)-optimized geometry of the K$_2$[SeSPPh$_2$]$_2$ complex in a water solution and the corresponding dimerization energy.

If one were to take into account the effect of not only polar but also donor–acceptor properties of the solvent, the interaction of alkali metal cations with thioselenophosphinate anoins might lead to the formation (depending on the size of M$^+$) of solvent-separated pairs, M$^+$[SeSPPh$_2$]$^-$ complexes, M$_2$[SeSPPh$_2$]$_2$ dimers, M$_n$[SeSPPh$_2$]$_n$ polymers, and other structural units. For example, if Li(Se$_2$PPh$_2$)·(THF)·(TMEDA) (TMEDA = tetramethylethylenediamine) is a monomer,[33] K$_2$(Se$_2$PPh$_2$)$_2$·(THF)$_2$ isolated from the mixture of THF/toluene represents a dimer,[34] and [Na$_2$(Se$_2$PPh$_2$)·THF·5H$_2$O] obtained under more polar conditions (THF/EtOH) is a polymer.[35]

A detailed investigation of the structure of thioselenophosphinate salts with alkali metals (depending on properties of medium and cations) is a very laborious task and lies far beyond the scope of this study.

Conclusion

In summary, a novel, general, and high-yield method for the synthesis of diverse Li, Na, K, Rb, and Cs thioselenophosphinates has been developed by exploiting the one-pot multicomponent reaction between secondary phosphanes, sulfur, selenium, and metal hydroxides. The reaction proceeds under mild conditions to provide the new or previously unavailable alkali metal thioselenophosphinates that bear alkyl, aralkyl, hetaralkyl, and aryl substituents. The structure of the [SeSPPh$_2$]$^-$ anion and its coordination toward Li$^+$, Na$^+$, and K$^+$ cations have been studied theoretically by DFT (B3LYP) calculations. The reactivity as well as the synthetic usefulness of the prepared thioselenophosphinates has been demonstrated by reactions with organic halides, iodine, and the cation exchange, which leads to the earlier unknown or unavailable thioselenophosphinic derivatives. The sodium thioselenophosphinates have been used as precursors of Ni^{II}–thioselenophosphinato square-planar complexes. According to X-ray analysis of the latter, the [SeSPR$_2$] ligands coordinate to the Ni^{II} ion in a S,Se-bidentate fashion to form Ni(PSeS)$_2$ metallobicycles. The results obtained significantly contribute to the fundamental chemistry of thio- and selenophosphorus compounds.

Experimental Section

Materials and Methods: All manipulations were performed under an argon atmosphere. Melting points (uncorrected) were measured with a Stuart SMP3 apparatus. The microanalyses were performed with a Flash EA 1112 CHNS elemental analyzer. FTIR spectra were performed with a Bruker Vertex 70 FT-IR spectrometer. The ^{1}H, ^{13}C, ^{31}P, and ^{77}Se NMR spectra were recorded with a Bruker AV-400 spectrometer (400.13, 100.61, 161.98, and 76.31 MHz, respectively) at ambient temperature using the solvent as reference, except for the ^{31}P and ^{77}Se NMR spectroscopy, in which the chemical shifts are relative to H_3PO_4 (85% in D_2O) and Me_2Se, respectively.

Ethanol (5% water content) and benzene were employed as received. Diethyl ether and 1,4-dioxane were distilled from metallic Na and Na/benzophenone, respectively, before use. Dicyclohexylphosphane (**1a**) and diphenylphosphane (**1f**) were purchased from Aldrich, whereas secondary phosphanes **1b**–**e** were prepared in a single step from red phosphorus and styrene,[36a] α-methylstyrene,[36a] 4-methoxystyrene,[36b] or 2-vinylfuran[36a] according to literature methods. Organic halides were distilled prior to use. All other chemicals were obtained commercially and used without further purification.

Safety Note: Selenium and its derivatives are toxic! These materials should be handled with great care.

Typical Procedure for Synthesis of Alkali Metal Thioselenophosphinates 2a–l: See Table 1. Powdered S_8 (32 mg, 0.125 mmol) was added to a solution of freshly distilled secondary phosphane **1a**–**f** (1 mmol) in EtOH (7 mL), and the mixture was stirred at room temp. until the dissolution of sulfur residue (ca. 20 min). Amorphous gray selenium (79 mg, 1.00 mmol) and a solution of $MOH{\cdot}nH_2O$ (n = 0 for Li and Na; n = 0.5 for K; n = 1 for Rb and Cs; 1.0 mmol) in EtOH (8 mL) were consecutively added to the transparent solution thus obtained. The resulting mixture was stirred at 40–50 °C until the dissolution of the selenium powder (ca. 10 min). The solvent was removed under reduced pressure, then the residue was washed with dry Et_2O (2 × 10 mL) and dried under vacuum (1 Torr, 40–45 °C) to afford thioselenophosphinates **2a**–**l**.

Alkylation of Alkali Metal Thioselenophosphinates 2a,c–e,j,k with Organic Halides: See Table 2. A corresponding organic halide (1.1 mmol) [for the preparation of bis-ester **3g**, 1,3-bis(chloromethyl)benzene (0.5 mmol) was used (Scheme 5)] was added at room temp. to a solution of thioselenophosphinate **2a**,**c**–**e**,**j**,**k** (1 mmol) in EtOH (8 mL). The mixture was stirred for 10 min at 40–43 °C. The solvent and the excess amount of organic halide were removed under reduced pressure, and dry Et_2O (10 mL) was added to the residue. The precipitated white powder (alkali metal halide) was removed by filtration, and Et_2O was evaporated from the filtrate. The residue obtained was dried under vacuum (1 Torr, 40–45 °C) to afford the corresponding *Se*-esters of thioselenophosphinic acids **3a**–**g**.

One-Pot Synthesis of *Se*-Esters of Thioselenophosphinic Acids 3a–f: See Scheme 6. Powdered S_8 (32 mg, 0.125 mmol) was added to a solution of freshly distilled secondary phosphane **1a**,**b**,**f** (1 mmol) in EtOH (7 mL), and the mixture was stirred at room temp. until the dissolution of sulfur residue (ca. 20 min). Amorphous gray selenium (78.9 mg, 1.00 mmol) and a solution of NaOH (40 mg, 1 mmol) in EtOH (8 mL) were consecutively added to the transparent solution thus obtained. The resulting mixture was stirred at 40–50 °C until the dissolution of the selenium powder (ca. 10 min), and corresponding organic halide (1 mmol) was added. The mixture was stirred for 10 min at 40–43 °C. The solvent and the excess amount of organic halide were removed under reduced pressure, and dry Et_2O (10 mL) was added to the residue. The precipitated white powder (alkali metal halide) was removed by filtration, and Et_2O was evaporated from the filtrate. The residue obtained was dried under vacuum (1 Torr, 40–45 °C) to afford the target *Se*-esters of thioselenophosphinic acids **3a**–**f**.

Oxidative Coupling of Thioselenophosphinate 2a,b,e,k by the Action of Iodine: Table 3. A solution of elemental iodine (254 mg, 1 mmol) in 1,4-dioxane (10 mL) was added dropwise at room temp. to a stirring solution of thioselenophosphinate **2a**,**b**,**e**,**k** (2 mmol) in 1,4-dioxane (10 mL). A white precipitate (alkali metal iodide) formed immediately. The resulting mixture was then diluted with water (30 mL) and extracted with benzene (2 × 20 mL). The extract was dried with Na_2SO_4 and concentrated to one-tenth of its volume. Upon addition of hexane (15 mL) to the resulting solution and exposure at 5–8 °C overnight, diselenide **4a**–**c** was precipitated as a microcrystalline solid. The latter was washed with cooled hexane (5 mL) and dried under vacuum (1 Torr). Single crystals of **4a**,**b** suitable for an X-ray analysis were obtained by cooling of their benzene/hexane solutions up to 3–5 °C over several days.

Synthesis of Diethylammonium Salt 2m: Scheme 7. A solution of hydrochloric acid (1 M, 1 mL, ca. 1 mmol) in methanol was added at room temp. to a solution of the potassium thioselenophosphinate **2k** (335 mg, 1 mmol) in MeOH (6 mL). The mixture was stirred for 5 min at the same temperature, and diethylamine (73 mg, 1 mmol) was added. The KCl precipitate was removed by filtration, and solvent was evaporated from the filtrate. The residue obtained was washed with dry Et_2O (2 × 5 mL) and dried under vacuum (1 Torr) to give thioselenophosphinate **2m** in 89% yield. Single crystals of **2m** were grown by slow evaporation of its ethanol solution at 3–5 °C.

Synthesis of Ni^{II} Thioselenophosphinates: See Scheme 8. A solution of thioselenophosphinate ligand **2c** or **2k** (1 mmol) in EtOH (5 mL) was added to a suspension of $NiBr_2$ (109 mg, 0.5 mmol) in CH_2Cl_2 (20 mL). The mixture was stirred for 10 min at room temp. and diluted with H_2O (30 mL). The organic layer was additionally washed with H_2O (2 × 10 mL), dried with Na_2SO_4, and evaporated under vacuum. The solid was dissolved in CH_2Cl_2 (10 mL) and layered with hexane (15 mL) to afford complexes **5a**,**b** as dark-green crystals.

X-ray Diffraction Analysis: X-ray crystallography studies of the crystals were carried out with a Bruker Kappa Apex II CCD diffractometer using ϕ,ω scans of narrow (0.5°) frames with Mo-K_α radiation (λ = 0.71073 Å) and a graphite monochromator. The structure was solved by direct methods and refined by full-matrix least-squares methods against all F^2 in an anisotropic approximation using the SHELX-97 programs set.[37] In the case of **4b** and **2m**, the C atoms of the benzene molecule and the minor S′ and Se′ atoms were refined isotropically with geometrical restrictions. The positions of the hydrogen atoms were calculated with the riding model. Absorption corrections were applied using the empirical multiscan method with the SADABS program.[38]

The obtained crystal structures were analyzed for short contacts between nonbonded atoms using PLATON[39] and MERCURY programs.[40]

CCDC-894978 (for **2m**), -894980 (for **4a**), -894979 (for **4b**), -901601 (for **5a**), and -901600 (for **5b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): X-ray crystallographic data for **2m**, **4a**, **4b**, **5a**, and **5b** as well as analytical data for the synthesized compounds.

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