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New Sulfanyl- and Selanyl-Substituted Schiff Bases Derived from 2-Chalcogenoalkylamines and Aromatic Aldehydes. Synthesis and Complex Formation Reactions

A. N. Chernysheva[a], E. K. Beloglazkina[a], R. L. Antipin[a], A. A. Moiseeva[a], and N. V. Zyk[a, b]

[a] *Faculty of Chemistry, Moscow State University, Leninskie gory 1, Moscow, 119992 Russia*
e-mail: bel@org.chem.msu.ru

[b] *Institute of Physiologically Active Compounds, Russian Academy of Sciences, Chernogolovka, Moscow oblast, Russia*

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Abstract—A number of β-phenyl(or benzyl)selanyl- and β-phenylsulfanyl-substituted imines possessing an additional donor nitrogen, oxygen, or sulfur atom were synthesized by reaction of 2-phenylsulfanylethanamine, 2-phenylsulfanylcyclohexanamine, 2-phenylselanylcyclohexanamine, and 2-benzylselanylaniline with salicylaldehyde, 2-pyridinecarbaldehyde, or 2-*tert*-butylsulfanylbenzaldehyde. The resulting Schiff bases were tested as ligands in the complex formation with nickel(II) and copper(II), and mononuclear (L–H)MCl or $LMCl_2$ coordination compounds were isolated (L = sulfur- or selenium-containing imine). The redox properties of the selenium-containing ligands and complexes were studied by cyclic voltammetry. The complexes were found to undergo reduction of the metal ion in two one-electron steps. The reduction is reversible for copper complexes and irreversible for nickel complexes.

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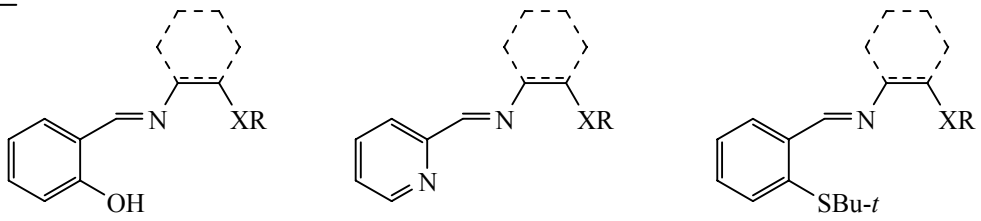
Organosulfur and organoselenium compounds are important intermediate products in organic synthesis and convenient models for studying organic and bioorganic reaction mechanisms. Low-molecular weight N,S,Se-containing ligands and coordination compounds based thereon attract considerable interest from the viewpoint of their potential catalytic activity, e.g., as models of natural metalloenzymes. Low-molecular complexes of transition metals are now used to catalyze many organic reactions, including asymmetric synthesis, epoxidation of alkenes [1–3], cyclopropanation [4], aziridination [5, 6], reactions of sulfides with diazo esters [7], Diels–Alder cycloadditions [8], C–H bond activation [9, 10], oxirane ring opening [11–16], etc.

The present study was aimed at developing procedures for the preparation of novel N,S- and N,Se-ligands containing azomethine and alkyl aryl sulfide (or selenide) fragments, as well as additional donor oxygen, nitrogen, or sulfur atoms. The structures of the synthesized Schiff bases are shown below:



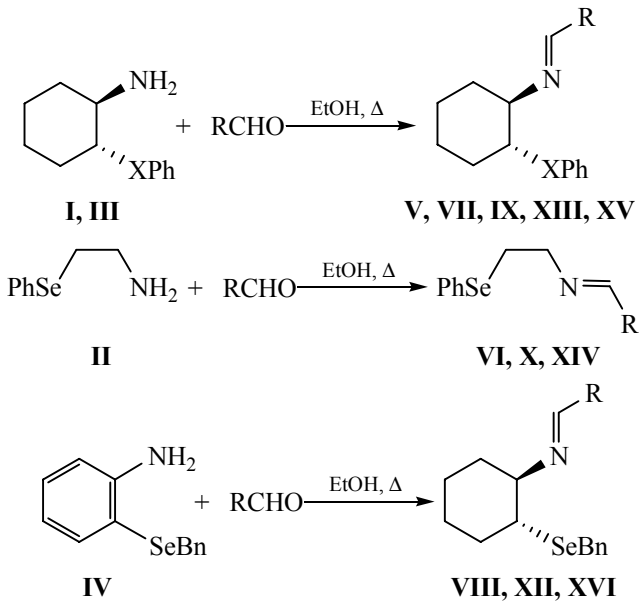
XR = SPh, SePh, SeBn.

These compounds are tridentate N,O,X-, N,S,X- or N,N,X-ligands (X = S, Se) potentially capable of forming mono- and dinuclear coordination compounds, so that they were brought into complex formation reactions with nickel(II) and copper(II) salts. With a view to assess the possibility of using the obtained

complexes as redox catalysts, electrochemical properties of the ligands and coordination compounds were studied.

As starting compounds for the synthesis of Schiff bases **V**–**XVI** we used 2-chalcogen-substituted amines **I**–**IV** and aromatic aldehydes, namely salicylaldehyde, pyridine-2-carbaldehyde, and 2-*tert*-butylsulfanylbenzaldehyde. The latter may be regarded as benzenethiol derivative protected at the sulfur atom; unlike ArSH compounds readily oxidizable on exposure to air, *S*-*tert*-butyl derivative is stable to oxygen; on the other hand, *tert*-butyl group can readily be removed via reaction with metal salts (Lewis acid) [17] to afford a thiolate complex.

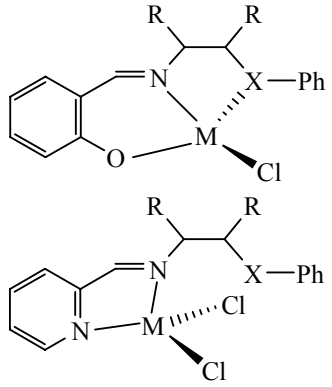
The reactions were carried out by heating the reactants in boiling ethanol or EtOH–CH_2Cl_2 mixture over a period of 3–7 h (the progress of reactions was monitored by TLC following the disappearance of the initial aldehyde). All Schiff bases **V**–**XVI** except for 2-*tert*-butylsulfanylbenzaldehyde derivative **XIII** were isolated as a single isomer. The *E* configuration of **XIV** was confirmed by NOE experiment: irradiation at a frequency corresponding to the HC=N resonance (δ 9.13 ppm) gave a response at a δ 4.0 ppm (CH_2N). Compound **XIII** was formed as a mixture of *E* and *Z* isomers at a ratio of 5 : 1, which was estimated from the intensity ratio of the HC=N signals at δ 9.06 and 8.67 ppm in the ^{1}H NMR spectrum.



I, **V**, **IX**, **XIII**, X = S; **III**, **VII**, **XI**, **XV**, X = Se; **V**–**VIII**, R = 2-HOC_6H_4; **IX**–**XII**, R = pyridin-2-yl; **XIII**–**XVI**, R = 2-*t*-$BuSC_6H_4$.

The Schiff bases were brought into reactions with nickel(II) and copper(II) chlorides by heating in boiling ethanol. The structure of the coordination compounds thus obtained was determined by elemental analysis, mass spectrometry, and electronic and IR spectroscopy. Their elemental compositions, yields, and colors are given in Table 1. The reactions of nickel(II) and copper(II) chlorides with salicylaldehyde derivatives **VI** and **VII** gave coordination compounds **XVII**–**XIX** which were assigned the composition (L–H)MCl on the basis of their elemental analyses (Table 1). Mononuclear structure of these complexes was confirmed by the MALDI mass spectra; according to their electronic absorption spectra, the central metal ion in **XVII**–**XIX** has tetrahedral configuration.

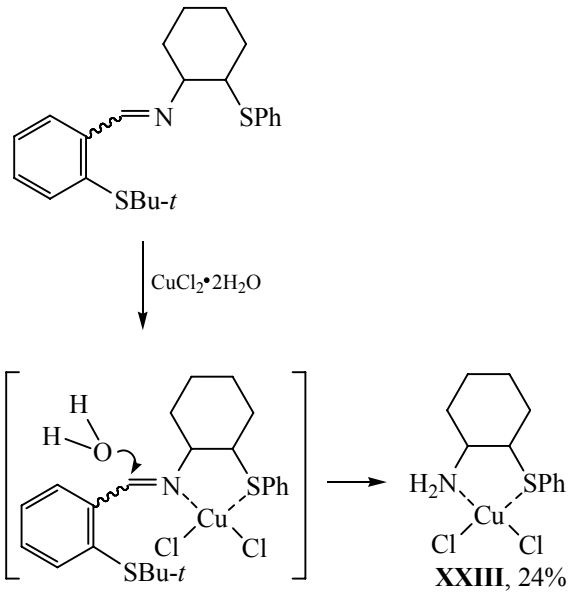
Ligands **IX**–**XI** reacted with nickel(II) and copper(II) chlorides to produce $LMCl_2$ complexes. Their electronic absorption spectra also indicated tetrahedral configuration of the coordination environment. The results of semiempirical quantum-chemical calculations (PM3) [18] showed that coordination of two nitrogen atom of the organic ligand and two halide ions to the metal ion is energetically more favorable than coordination modes involving the chalcogen atom. The propused structures of coordination compounds **XVII**–**XXII** are shown below.



XVII, **XXI**, R = H; **XVIII**–**XX**, **XXII**, RR = $(CH_2)_4$; **XVII**, **XX**, X = S; **XVIII**, **XIX**, **XXI**, **XXII**, X = Se; **XVII**, **XVIII**, **XXI**, M = Ni; **XIX**, **XX**, **XXII**, M = Cu.

Presumably, the reactions of *tert*-butylsulfanyl-substitued ligands **XIII**–**XV** with metal chlorides were accompanied by hydrolysis of the CH=N bond. The only product isolated in the reaction of **XIII** with $CuCl_2 \cdot 2H_2O$ was that whose elemental composition corresponded to copper(II) chloride complex **XXIII** with 2-phenylsulfanylcyclohexanamine. Compound

XXIII displayed in the IR spectrum absorption bands at 3220 and 3200 cm^{-1} due to primary amino group.



XXIII, 24%

We failed to obtain crystalline products by reactions of benzylselanyl derivatives **VIII**, **XII**, and **XVI** with metal chlorides under analogous conditions.

The redox properties of ligands **X** and **XI** and coordination compounds **XVII**, **XVIII**, and **XXI** were examined by cyclic and rotating disk electrode voltammetry using glassy carbon and gold electrodes in DMF with 0.1 M Bu_4NClO_4 as supporting electrolyte. The oxidation and reduction potentials are given in Table 2. Ligands **X** and **XI** are reduced in two steps at potentials higher than 1.0 V and are oxidized either in two steps at potentials of –1.8 to –1.9 and ca. –2.5 V. The reduction of pyridine-containing complexes **XXI** and **XXII** occurs at the metal ion in two one-electron steps; further reduction involves the ligand. The first oxidation step is oxidation of the coordinated chloride ion at 1.04–1.16 V (Fig. 1).

Copper complex **XXII** is reduced at the metal ion at a potential of +0.14 V via transfer of two electrons (Fig. 1). The subsequent ligand reduction peaks are strongly shifted to the anodic region compared to the free ligand, i.e., the presence of copper ion considerably facilitates reduction of the ligand. The reduced complex is stable; it remained unchanged in electrochemical experiments on both glassy carbon and gold electrodes, as followed from the absence of copper metal desorption peak on the reverse scan curve (Fig. 1).

Table 1. Compositions, colors, and electronic absorption spectra of coordination compounds **XVII**–**XXII**

Ligand	Complex	Color	Electronic spectrum, λ_{max}, nm (ε, l mol^{-1} cm^{-1})
VI	**XVII**, (L–H)NiCl	Yellow–green	325.0 (28561) 365.0 (22219) 419.0 (12988) 617.0 (492)
VII	**XVIII**, (L–H)NiCl·$2H_2O$	Yellow–green	317.5 (72277) 378.5 (24218) 473.5 (7035) 664.0 (5303)
	XIX, (L–H)CuCl	Light brown	337.0 (94371) 370.5 (65777) 470.0 (4231) 661.0 (3258)
IX	**XX**, $LCuCl_2$	Green	327.5 (29966) 711.5 (2689)
X	**XXI**, $LNiCl_2$	Green	344.0 (14314) 398.0 (15031) 736.0 (2831)
XI	**XXII**, $LCuCl_2$	Green	402.0 (11033) 416.0 (6124) 718.5 (3910)

Nickel complex **XXI** is reduced at the first step irreversibly via single electron transfer, and its one-electron reduction in the second step is quasi-reversible. Nickel complexes derived from salicylaldehyde imines **XVII** and **XVIII** displayed analogous electrochemical properties. Their oxidation occurred in two irreversible steps; four irreversible peaks were observed on the cathodic branch (Fig. 2), the first two of which corresponded to reduction of the metal ion ($Ni^{2+} \rightarrow Ni^{1+} \rightarrow Ni^0$).

Thus the results of electrochemical study showed that the examined complexes are initially reduced at the metal ion in two one-electron steps. The reduction of the copper complexes is reversible, whereas the nickel complexes are reduced irreversibly.

EXPERIMENTAL

The ^1H and ^{13}C NMR spectra were recorded at 25° C on Varian Mercury-400 and Bruker Avance-400 spectrometers at 400 and 100 MHz, respectively. The IR spectra were measured on a UR-20 spectrometer from samples dispersed in mineral oil and on a ThermoNicolet IR200 spectrometer with Fourier

Table 2. Oxidation (E^{ox}) and reduction potentials (E^{red}) of ligands **X** and **XI** and coordination compounds **XVII**, **XVIII**, **XXI**, **XXII**, **XXIV**, and **XXV**, determined by cyclic voltammetry (relative to $Ag|AgCl|KCl_{sat}$) using a glassy carbon electrode in DMF (0.1 M Bu_4NClO_4 as supporting electrolyte); potential scan rate 200 mV s^{-1}; potentials of reverse scan peaks are given in parentheses

Comp. no.	E_p^{red}	E_p^{ox}
X	–1.91 (–1.86); –2.67[a]	1.06; 1.30
XI	–1.83 (–1.75); –2.51	1.16; 1.46
XVII	–1.14; –1.33 (–1.27); –1.89; –2.39	0.84; 1.08
XVIII	–0.92; –1.36; –1.89; –2.39	1.08; 1.21
XXI	–0.93 (–0.86); –1.21 (–1.16); –1.91; –2.09 (–2.01)	1.15; 1.23
XXII	0.14 (–0.25, 0.49); –1.67; 1.87 (–1.76)[b,c]	1.17[b]

[a] Additional adsorption prepeaks were also observed at –1.26 and –2.31 V. [b] Initial potential 0.7 V. [c] Additional adsorption prepeak was observed at –1.43 V.

transform (USA) from films. The electronic absorption spectra were recorded on Perkin Elmer Lambda 25 and Hitachi U-2900 spectrophotometers from solutions in DMF with a concentration of 10^{-3} M.

The MALDI mass spectra were obtained on a Bruker Autoflex II instrument (FWHM resolution 18000) equipped with a nitrogen laser (λ 337 nm) and a time-of-flight mass analyzer (accelerating voltage 20 kV); samples were applied to a polished steel support; positive ions were detected; the resultant spectrum was the sum of 300 spectra recorded for different points of a sample; 2,5-dihyidroxybenzoic acid (99%, Acros) and α-cyano-4-hydroxycinnamic acid (99%, Acros) were used as matrices. The isotope ratios for all MS peaks given in Experimental are consistent with the calculated values.

The electron-impact mass spectra (70 eV) were recorded on Finnigan MAT SSQ 7000 [25-m quartz capillary column, stationary phase OV-I, oven temperature programming from 70°C (2 min) to 280°C (10 or 30 min) at a rate of 20 deg /min] and Kratos MS-30 instruments (England) (direct inlet probe, ion source temperature 200°C).

Electrochemical studies were carried out on a PI-50-1.1 potentiostat coupled with a PR-8 programmer according to a three-electrode scheme. A glassy carbon (d = 2 mm), platinum (d = 3 mm), or gold disk (d = 2 mm) was used as working electrode, Ag/AgCl/KCl (sat.) was used as reference electrode, and secondary electrode was a platinum plate; supporting electrolyte 0.1 M solution of Bu_4NClO_4 in DMF. The working electrode surface was polished with aluminum oxide powder (particle size <10 μm; Sigma–Aldrich). The potential scan rate was 200 (cyclic voltammetry) or

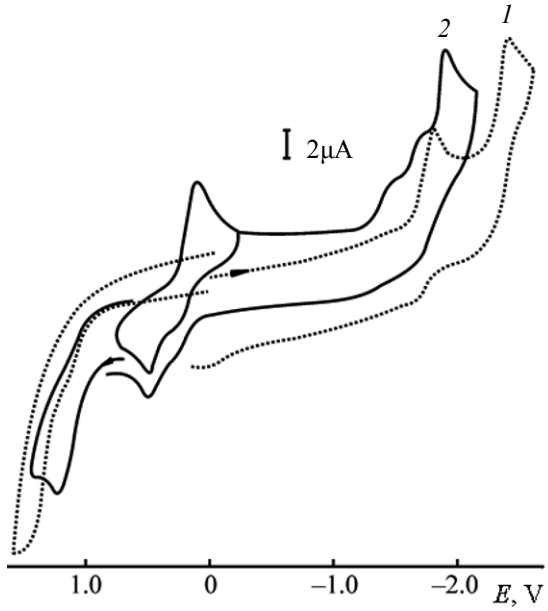


Fig. 1. Cyclic voltammograms of (*1*) ligand **XI** and (*2*) complex **XXII**; concentration 10^{-3} M, glassy carbon electrode, DMF, Bu_4NClO_4.

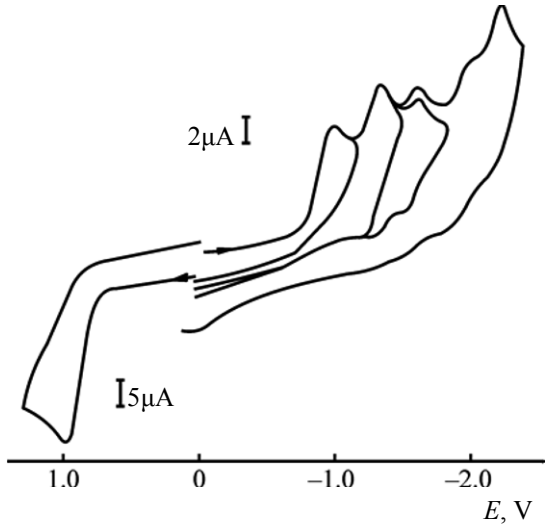


Fig. 2. Cyclic voltammograms of nickel complex **XVIII**; concentration 10^{-3} M, glassy carbon electrode, DMF, Bu_4NClO_4.

20 mV/s (rotating disk electrode). The potentials are given with correction for *iR*-compensation. The number of transferred electrons was determined by comparing the limiting wave current in rotating disk electrode experiment with the one-electron oxidation current of ferrocene at the same concentration. All measurements were performed under dry argon; samples were dissolved in pre-liminarily deoxygenated anhydrous solvent. Dimethyl-formamide of pure grade was purified by stirring for 4 days over freshly calcined potassium carbonate, followed by distillation under reduced pressure first over P_2O_5 and then over anhydrous $CuSO_4$.

trans-2-(Phenylsulfanyl)cyclohexan-1-amine (**I**), 2-(phenylselanyl)ethanamine (**II**) hydrochloride, and *trans*-(2-phenylselanyl)cyclohexan-1-amine (**III**) were synthesized as described in [19, 20]; 2-(benzylselanyl) aniline (**IV**) was prepared according to [21]; and 2-*tert*-butylsulfanylbenzaldehyde was synthesized as described in [22].

2-[2-(Phenylsulfanyl)cyclohexyliminomethyl]phenol (V). Salicylaldehyde, 0.09 ml (0.9 mmol), was added under stirring to a solution of 0.18 g (0.9 mmol) of 2-(phenylsulfanyl)cyclohexan-1-amine (**I**) in 10 ml of ethanol, and the mixture was heated under reflux until the initial aldehyde disappeared (TLC). The solvent was removed under reduced pressure to isolate 0.25 g (91%) of compound **V** as a yellow oily substance. IR spectrum (film), ν, cm^{-1}: 3070, 1640, 1590. ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 13.29 br.s (1H, OH), 8.36 s (1H, CH=N), 7.37 m (2H, H_{arom}), 7.32 d.d.d (1H, H_{arom}, *J* = 0.8, 1.6, 6.7), 7.27 d.d (1H, H_{arom}, *J* = 1.6, 7.6), 7.23–7.17 m (3H, H_{arom}), 6.95 d (1H, H_{arom}, *J* = 8.3), 6.89 t (1H, H_{arom}, *J* = 6.7), 3.21 d. t (1H, HCN, *J* = 4.2, 9.7), 3.17 d. t (1H, HCS, *J* = 4.2, 9.7), 2.23 m (1H, 3-H), 1.95 m (1H, 6-H), 1.83 m (2H, 3-H, 6-H), 1.69 m (1H, 4-H), 1.55–1.40 m (3H, 5-H, 4-H). Mass spectrum (EI): *m*/*z* 311 $[M]^+$.

2-[2-(Phenylselanyl)ethyliminomethyl]phenol (VI). A solution of 0.12 g (2.1 mmol) of potassium hydroxide in a minimal volume of ethanol was added to a solution of 0.5 g (2.1 mmol) of 2-(phenylselanyl) ethanamine (**II**) hydrochloride in 10 ml of ethanol. The mixture was stirred until complete precipitation of potassium chloride (white flakes). The precipitate was filtered off, 0.22 ml (2.1 mmol) of salicylaldehyde was added to the filtrate under stirring, and the mixture was heated under reflux until salicylaldehyde disappeared (TLC). Removal of the solvent under reduced pressure gave 0.63 g (99%) of compound **VI** as a yellow oily substance which gradually crystallized on storage. ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 12.69 br. s (1H, OH), 8.30 s (1H, CH=N), 7.60 d (1H, H_{arom}, *J* = 7.8), 7.52 m (2H, H_{arom}), 7.25 m (3H, H_{arom}), 7.18 t (1H, H_{arom}, *J* = 7.4), 6.91 d (1H, H_{arom}, *J* = 8.4), 6.83 t (1H, H_{arom}, *J* = 7.4), 3.89 t (2H, CH_2, *J* = 6.8); 3.04 t (2H, CH_2, *J* = 7.0).

2-[2-(Phenylselanyl)cyclohexyliminomethyl]phenol (VII). Salicylaldehyde, 0.05 ml (0.5 mmol), was added under stirring to a solution of 0.13 g (0.5 mmol) of 2-(phenylselanyl)cyclohexan-1-amine (**III**) in 7 ml of ethanol, and the mixture was heated under reflux until salicylaldehyde disappeared (TLC). The solvent was removed under reduced pressure to leave 0.16 g (91%) of **VII** as a yellow oily substance. ^1H NMR spectrum (C_6D_6), δ, ppm (*J*, Hz): 13.57 br. s (1H, OH), 7.98 s (1H, CH=N), 7.58 d.d (2H, H_{arom}, *J* = 2.2, 7.2), 7.20 m (2H, H_{arom}), 7.07 m (4H, H_{arom}), 6.81 d.d.d (1H, H_{arom}, *J* = 0.8, 2.2, 7.2), 3.17 d.t (1H, HCN, *J* = 4.1, 9.8), 2.99 d. t (1H, HCSe, *J* = 4.1, 9.8), 2.22 d.d (1H, 3-H, *J* = 4.1, 13.3), 1.65 d (1H, 6-H, *J* = 13.3), 1.54 m (3H, 3-H, 4-H, 6-H), 1.38 m (1H, 5-H), 1.11 m (2H, 4-H, 5-H).

2-[2-(Benzylselanyl)cyclohexyliminomethyl]phenol (VIII). Salicylaldehyde, 0.06 ml (0.6 mmol), was added under stirring to a solution of 0.15 g (0.6 mmol) of 2-(benzylselanyl)aniline (**IV**) in 10 ml of CH_2Cl_2–EtOH (1 : 1), and the mixture was heated under reflux until salicylaldehyde disappeared (TLC). The solvent was removed under reduced pressure to obtain 0.22 g (99%) of **VIII** as a yellow oily substance which gradually crystallized on storage. ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 13.05 br.s (1H, OH), 8.62 s (1H, HC=N), 7.45 m (2H, H_{arom}), 7.39 m (2H, H_{arom}), 7.31 m (7H, H_{arom}), 7.07 d (1H, H_{arom}, *J* = 8.4), 6.95 t (1H, H_{arom}, *J* = 7.6), 3.73 s (2H, CH_2). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 162.58, 138.97, 133.04, 132.16, 129.31, 129.11, 128.40, 126.75, 121.24, 118.76, 117.49, 96.28, 32.53, 27.44.

2-Phenylsulfanyl-*N*-(pyridin-2-ylmethylidene)-cyclohexan-1-amine (IX). Pyridine-2-carbaldehyde, 0.08 ml (0.9 mmol), was added under stirring to a solution of 0.18 g (0.9 mmol) of 2-(phenylsulfanyl) cyclohexan-1-amine (**I**) in 10 ml of ethanol, and the mixture was heated for 8 h under reflux (TLC) and evaporated under reduced pressure. Yield 0.23 g (91%), red oily substance. IR spectrum (nujol), ν, cm^{-1}: 1655, 1590, 1570. ^1H NMR spectrum ($CDCl_3$), δ, ppm

(*J*, Hz): 8.52 d (1H, Py, *J* = 5.6), 8.27 s (1H, HC=N), 7.78 d (1H, Py, *J* = 7.9), 7.55 t (1H, Py, *J* = 7.9), 7.27 d (2H, Ph, *J* = 8.2), 7.16 t (1H, Py, *J* = 5.6), 7.08 t (2H, Ph, *J* = 8.2), 7.01 m (1H, Ph), 3.23 m (2H, 1-H, 2-H), 2.12 m (1H, 3-H), 1.77 m (3H, 3-H, 6-H), 1.66 m (1H, 5-H), 1.45–1.36 m (3H, 4-H, 5-H).

2-Phenylselanyl-*N*-(pyridin-2-ylmethylidene)-ethanamine (X). A solution of 0.09 g (1.7 mmol) of potassium hydroxide in a minimal volume of ethanol was added to a solution of 0.40 g (1.7 mmol) of 2-(phenylselanyl)ethanamine (**II**) hydrochloride in 5 ml of ethanol. The mixture was stirred until complete precipitation of potassium chloride (white flakes). The precipitate was filtered off, 0.16 ml (1.7 mmol) of pyridine-2-carbaldehyde was added under stirring, and the mixture was heated for 7 h under reflux (TLC) and evaporated under reduced pressure. Yield 0.46 g (94%), brown oily substance which gradually crystallized on storage. IR spectrum (film), ν, cm^{-1}: 1650, 1590, 1570. ^1H NMR spectrum, $CDCl_3$, δ, ppm (*J*, Hz): 8.63 d (1H, Py, *J* = 4.9), 8.34 s (1H, HC=N), 7.9 d (1H, Py, *J* = 7.8), 7.69 t (1H, Py, *J* = 7.8), 7.51 d. d (2H, Ph, *J* = 1.4, 7.8), 7.23 m (4H, Ph, Py), 3.96 t (2H, CH_2, *J* = 7.8), 3.23 t (CH_2, *J* = 7.8). Mass spectrum (EI): *m*/*z* 290 $[M]^+$.

2-Phenylselanyl-*N*-(pyridin-2-ylmethylidene)-cyclohexan-1amine (XI). Pyridine-2-carbaldehyde, 0.05 ml (0.5 mmol), was added under stirring to a solution of 0.13 g (0.5 mmol) of 2-(phenylselanyl) cyclohexan-1-amine (**III**) in 7 ml of ethanol, the mixture was heated for 3 h under reflux (TLC), and the solvent was removed under reduced pressure. Yield 0.17 g (99%), brown oily substance. ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 8.59 d (1H, Py, *J* = 4.1), 8.35 s (1H, HC=N), 7.80 d (1H, Py, *J* = 7.8), 7.62 d.t (1H, Py, *J* = 1.2, 7.8), 7.47 m (2H, Ph), 7.24 d.d.d (1H, Py, *J* = 1.2, 4.1, 7.8), 7.14 m (3H, H_{arom}), 3.46 d.d.d (1H, 1-H, *J* = 4.1, 9.7, 13.7), 3.33 d. t (1H, 2-H, *J* = 4.1, 9.7), 2.21 d (1H, 3-H, *J* = 4.1), 1.75 m (4H, 3-H, 4-H, 6-H), 1.55 m (1H, 5-H), 1.38 m (2H, 4-H, 5-H). Mass spectrum (MALDI-TOF): *m*/*z* 344 $[M]^+$.

2-(Benzylselanyl)-*N*-(pyridin-2-ylmethylidene)-aniline (XII). Pyridine-2-carbaldehyde, 0.06 ml (0.6 mmol), was added under stirring to a solution of 0.15 g (0.6 mmol) of 2-(benzylselanyl)aniline (**IV**) in 10 ml of CH_2Cl_2–EtOH (1:1), the mixture was heated for 7 h under reflux (TLC), and the solvent was removed under reduced pressure. Yield 0.20 g (99%), red–brown oily substance which gradually crystallized on storage. ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 8.66 m (1H, Py), 8.58 s (1H, HC=N), 8.26 t.d (1H, Py, *J* = 1.0, 7.9), 7.76 d.d (1H, Py, *J* = 1.0, 7.9), 7.38 t (2H, Ph, *J* = 7.9), 7.31 d.d.d (1H, Py, *J* = 1.0, 4.8, 7.9), 7.27–7.18 m (7H, Ph, Py), 3.66 s (2H, CH_2). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 160.47, 154.98, 151.09, 149.34, 138.96, 135.99, 129.04, 128.32, 128.16, 126.97, 126.61, 126.48, 124.59, 121.36, 121.09, 96.21, 27.36.

***N*-[2-(*tert*-Butylsulfanyl)phenylmethylidene]-2-(phenylsulfanyl)cyclohexan-1-amine (XIII).** 2-*tert*-Butylsulfanylbenzaldehyde, 0.14 g (0.7 mmol), was added under stirring to a solution of 0.15 g (0.7 mmol) of 2-(phenylsulfanyl)cyclohexan-1-amine (**I**) in 10 ml of ethanol. The mixture was heated for 5 h under reflux (TLC), and the solvent was removed under reduced pressure. Yield 0.27 g (99%; a mixture of *E* and *Z* isomers at a ratio of 5:1), yellow oily substance. IR spectrum (film), ν, cm^{-1}: 1640, 1590, 1530. ^1H NMR spectrum, $CDCl_3$, δ, ppm (*J*, Hz): *E* isomer: 9.06 s (1H, CH=N), 8.00 d.d (1H, H_{arom}, *J* = 2.2, 7.4), 7.51 d.d (1H, H_{arom}, *J* = 2.2, 6.6), 7.34 m (4H, H_{arom}), 7.17 m (3H, H_{arom}), 3.33 t (1H, HCN, *J* = 7.4), 3.25 m (1H, HCS), 2.23 m (1H, 3-H), 1.79 m (4H, 3-H, 6-H), 1.44 m (3H, 4-H, 5-H), 1.28 s (9H, *t*-Bu); *Z* isomer: 8.67 s (1H, CH=N), 7.94 d (1H, H_{arom}, *J* = 7.4), 7.83 d (1H, H_{arom}, *J* = 7.4), 7.46 d (1H, H_{arom}, *J* = 6.7), 7.34 m (4H, H_{arom}), 7.09 d (2H, H_{arom}, *J* = 7.4), 3.33 t (1H, HCN, *J* = 7.4), 3.25 m (1H, HCS), 2.23 m (1H, 3-H), 1.74 m (4H, 3-H, 6-H), 1.51 m (3H, 4-H, 5-H), 1.28 s (9H, *t*-Bu). Mass spectrum: *m*/*z* 326 $[M]^+$.

***N*-[2-(*tert*-Butylsulfanyl)phenylmethylidene]-2-(phenylsulfanyl)ethanamine (XIV).** A solution of 0.03 g (0.5 mmol) of potassium hydroxide in a minimal amount of ethanol was added to a solution of 0.13 g (0.5 mmol) of 2-(phenylselanyl)ethanamine (**II**) hydrochloride in 5 ml of ethanol. The mixture was stirred until complete precipitation of potassium chloride as white flakes. The precipitate was filtered off, 0.11 g (0.5 mmol) of 2-*tert*-butylsulfanyl-benzaldehyde was added under stirring, the mixture was heated for 7 h under reflux (TLC), and the solvent was removed under reduced pressure. Yield 0.20 g (99%), amber yellow oily substance. ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 9.09 s (1H, CH=N), 8.05 d.d (1H, H_{arom}, *J* = 2.2, 7.2), 8.01 d.d (1H, H_{arom}, *J* = 2.2, 7.6), 7.64 m (1H, H_{arom}), 7.57 m (2H, H_{arom}), 7.40 d. t (1H, H_{arom}, *J* = 2.2, 7.2), 7.27 m (3H, H_{arom}), 3.98 d. t (2H, CH_2, *J* = 2.2, 7.6), 3.70 d.t (2H, CH_2, *J* = 2.2, 7.6), 1.31 s (9H, *t*-Bu).

***N*-[2-(*tert*-Butylsulfanyl)phenylmethylidene]-2-(phenylselanyl)cyclohexan-1-amine (XV).** 2-*tert*-butylsulfanylbenzaldehyde, 0.1 g (0.5 mmol), was added under stirring to a solution of 0.13 g (0.5 mmol) of 2-(phenylselanyl)cyclohexan-1-amine (**III**) in 7 ml of ethanol, the mixture was heated for 5 h under reflux (TLC), and the solvent was removed under reduced pressure. Yield 0.21 g (98%), yellow oily substance. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 9.08 s (1H, CH=N), 8.07 d.d (1H, H_{arom}, *J* = 2.2, 7.2), 8.02 d.d (1H, H_{arom}, *J* = 2.2, 7.2), 7.62 m (2H, H_{arom}), 7.55 m (2H, H_{arom}), 7.40 d.t (1H, H_{arom}, *J* = 2.2, 7.2), 7.24 m (2H, H_{arom}), 3.20 d.t (1H, HCN, *J* = 4.1, 9.8), 2.92 d.t (1H, HCSe, *J* = 4.1, 9.8), 2.24 m (1H, 3-H), 1.68 m (1H, 6-H), 1.50 m (3H, 3-H, 4-H, 6-H), 1.32 m (1H, 5-H), 1.28 s (9H, *t*-Bu), 1.09 m (2H, 4-H, 5-H).

2-(Benzylselanyl)-*N*-[2-(*tert*-butylsulfanyl)phenylmethylidene]aniline (XVI). 2-*tert*-butylsulfanylbenzaldehyde, 0.11 g (0.6 mmol), was added under stirring to a solution of 0.15 g (0.6 mmol) of 2-(benzylselanyl)aniline (**IV**) in 10 ml of CH_2Cl_2–EtOH (1:1), the mixture was heated for 7 h under reflux (TLC), and the solvent was removed under reduced pressure. Yield 0.24 g (96%), yellow oily substance. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 9.30 s (1H, HC=N), 8.39 d.d (1H, H_{arom}, *J* = 1.4, 7.7), 7.61 d (1H, H_{arom}, *J* = 6.4), 7.51 t (1H, H_{arom}, *J* = 7.7), 7.42 m (3H, H_{arom}), 7.28–7.21 m (7H, H_{arom}), 3.69 s (2H, CH_2), 1.34 s (9H, *t*-Bu). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 159.74, 139.56, 130.37, 129.31, 129.06, 128.35, 128.16, 126.63, 125.84, 121.09, 96.24, 31.09, 27.38.

{2-[2-(Phenylselanyl)ethyliminomethyl]phenolato}nickel(II) chloride (XVII). Compound **VI**, 0.07 g (0.2 mmol), was dissolved on heating in a minimal volume of ethanol, a solution of 0.06 g (0.2 mmol) of nickel(II) chloride hexahydrate or 0.03 g (0.2 mmol) of anhydrous nickel(II) chloride in 2–3 ml of ethanol was added, and the mixture was heated for 5 h under reflux. The precipitate was filtered off, washed with ethanol, and dried in air. Yield 0.01 g (13%), yellow–green crystals, mp 142°C. IR spectrum (nujol), ν, cm^{-1}: 3470, 1645, 1600, 1545. Mass spectrum (MALDI-TOF): *m*/*z* 362 $[M]^+$.

Coordination compounds with ligand VII *(general procedure).* Compound **VII**, 1 equiv, was dissolved on heating in a minimal volume of ethanol, a solution of 1 equiv of the corresponding metal chloride in ethanol was added, and the mixture was heated for 5 h under reflux. The precipitate was filtered off, washed with ethanol, and dried in air.

{2-[2-(Phenylselanyl)cyclohexyliminomethyl]-phenolato}nickel(II) chloride dihydrate (XVIII) was synthesized from 0.08 g (0.2 mmol) of **VII**, 0.05 g (0.2 mmol) of $NiCl_2·6H_2O$ or 0.03 g (0.2 mmol) of $NiCl_2$. Yield 0.01 g (11%), yellow–green crystals, mp 240°C. IR spectrum (nujol), ν, cm^{-1}: 3480, 1630, 1600, 1565. Mass spectrum (MALDI-TOF): *m*/*z* 416 $[M]^+$. Found, %: C 47.22; H 4.63; N 3.00. $C_{19}H_{20}ClN·NiOSe·2H_2O$. Calculated, %: C 46.81; H 4.96; N 2.87.

{2-[2-(Phenylselanyl)cyclohexyliminomethyl]-phenolato}copper(II) chloride (XIX) was synthesized from 0.08 g (0.2 mmol) of **VII** and 0.04 g (0.2 mmol) of $CuCl_2·2H_2O$ or 0.03 g (0.2 mmol) of $CuCl_2$. Yield 0.04 g (34%), light brown crystals, mp 188°C. IR spectrum (nujol), ν, cm^{-1}: 3420, 1635, 1600, 1560. Mass spectrum (MALDI-TOF): *m*/*z* 421 $[M]^+$. Found, %: C 49.55; H 4.44; N 3.07. $C_{19}H_{20}Cl·CuNOSe$. Calculated, %: C 50.01; H 4.42; N 3.07.

[2-(Phenylsulfanyl)-*N*-(pyridin-2-ylmethylidene)-cyclohexan-1-amine]copper(II) dichloride (XX). Ethanol, 1 ml, was added to a solution of 0.05 g (0.2 mmol) of compound **IX** in 2 ml of methylene chloride until the mixture separated into layers. A solution of 0.03 g (0.2 mmol) of $CuCl_2·2H_2O$ in 2 ml of EtOH was slowly added, and the mixture was left to stand in a tightly capped vessel until it became homogeneous. The resulting solution was transferred into an open micro test tube which was placed in a tightly capped vessel charged with diethyl ether and left to stand therein until crystals separated. Yield 0.06 g (84%), green crystals, mp 170°C. Found, %: C 50.04; H 4.84; N 6.41; S 7.19. $C_{18}H_{20}Cl_2CuN_2S$. Calculated, %: C 50.18; H 4.68; N 6.50; S 7.44.

[2-(Phenylselanyl)-*N*-(pyridin-2-ylmethylidene)-ethanamine]nickel(II) dichloride (XXI). A solution of 0.06 g (0.3 mmol) of $CuCl_2·2H_2O$ in 5 ml of ethanol was added to a solution of 0.10 g (0.3 mmol) of compound **X** in 5 ml of ethanol. The mixture was heated for 5 h under reflux and cooled to room temperature, and the precipitate was filtered off, washed with small portions of diethyl ether, and dried in air. Yield 0.05 g (31%), green crystals, mp 170°C (decomp.). IR spectrum (nujol), ν, cm^{-1}: 1650, 1600, 1575. Mass spectrum (MALDI-TOF): *m*/*z* 388 $[M]^+$. Found, %: C 39.42; H 3.41; N 6.40. $C_{14}H_{14}Cl_2·CuN_2Se$. Calculated, %: C 39.69; H 3.33; N 6.61.

[2-(Phenylselanyl)-*N*-(pyridin-2-ylmethylidene)-cyclohexan-1-amine]copper(II) dichloride (XXII). A solution of 0.03 g (0.3 mmol) of $CuCl_2$ in 5 ml of

ethanol was added to a solution of 0.09 g (0.3 mmol) of compound **XI** in 3 ml of ethanol. The mixture was heated for 4 h under reflux and cooled to room temperature, and the precipitate was filtered off, washed with small portions of diethyl ether, and dried in air. Yield 0.07 g (58%), green crystals, mp 202°C (decomp.). IR spectrum (nujol), ν, cm^{-1}: 1640, 1595, 1470. Mass spectrum (MALDI-TOF): *m*/*z* 442 $[M]^+$.

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