Synthesis and Structural Studies of Pyridine-2-selenolates − Reactions with Electrophilic Phosphorus(III) Compounds and Related Complex Chemistry

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Dedicated to Professor Henning Hopf on the occasion of his 60th birthday

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The reaction intermediates in the synthesis of 2,2′-bis(pyridyl) diselenide (2,2′-Py_2Se_2) have been determined. The reaction of Na_2Se_2 with 2-BrC_5H_4N (2-BrPy) leads to a tautomeric mixture of pyridine-2-selenol (2-PySeH) and pyridine-2(1*H*)-selone (2-PyHSe), which have been investigated by spectroscopic means. Additionally, the crystal structure of the latter has been determined. Reductive cleavage of the Se–Se bond in 2,2′-Py_2Se_2 with K*B*s*Bu*$_3$H leads to K-2-SePy, which was trapped, either as [(18-crown-6)K]$^+$[2-PySe]$^-$, whose structure contains polymeric cation–anion chains, or as [Et_4N]$^+$[2-PySe]$^-$. Reactions of K-2-SePy or [Et_4N]$^+$[2-PySe]$^-$ with Ph_2PCl, *t*Bu_2PCl, or *t*$BuPBr_2$ lead to the corresponding, extremely air-sensitive (pyridyl)selenophosphanes Ph_2P-2-SePy, *t*Bu_2P-2-SePy, and *t*BuP(2-SePy)$_2$. The latter was trapped as *t*BuP(O)(2-SePy)$_2$, whose crystal structure has been determined. Metal complexes of these (pyridyl)selenophosphanes have been prepared starting from the phosphane and CuBr, AgBr, (tht)AuCl (tht = tetrahydrothiophene), or [(η^6-C_7H_8)Mo(CO)$_3$], in one-pot syntheses. All crystal structures of the resulting metallacycles [({(C$_5$H$_4$N-2-Se)*t*Bu_2P}-*N,P*)Cu(μ-Br)]$_2$, [({(C$_5$H$_4$N-2-Se)*t*Bu_2P}-*N,P*)Ag(μ-Br)]$_2$, [({(C$_5$H$_4$N-2-Se)*t*Bu_2P}-*P*)AuCl], and [({(C$_5$H$_4$N-2-Se)$_2$*t*BuP}-*N,N′,P*)Mo(CO)$_3$], were determined. Additionally, comprehensive spectroscopic investigations are presented.

Introduction

Recent research in our laboratory has shown that 2,2′-bis(pyridyl) diselenide (Py_2Se_2) is a useful starting material for the preparation of (pyridyl-2-selenolato)metal complexes.[1] The most common reaction mechanisms comprise oxidative addition of Py_2Se_2 to unsaturated metal centres and reductive cleavage of the Se−Se bond with organoboron hydrides, and subsequent reactions of the formed $PySe^-$ anion with halometal complexes. Additionally, oxidative addition of Py_2Se_2 to finely divided elemental metals could be employed, as shown for In.[2]

Apart from homoleptic (pyridineselenolato)metal complexes, which can serve as volatile starting materials for the preparation of thin metal selenide layers,[3] the coordination chemistry of ligands that contain the soft/hard Se/N donor set is surprisingly unexplored,[4] although Py_2Se_2 was first synthesized in 1962,[5] and its use in organic syntheses[6] and biochemistry[7] is well documented. The mechanism of Py_2Se_2 formation from Na_2Se_2 and 2-BrPy under acidic conditions is also not well understood. Py_2Se_2 is usually synthesized by oxidation of Py-2-SeH with various oxidising agents, but the reported syntheses of Py-2-SeH are often unreliable for different reasons.[3a,5][7c,8] In the first part of this paper, we report on the synthesis and characterization of Py-2-SeH and its tautomeric form pyridine-2(1*H*)-selone PyH-2-Se, together with the synthesis of the useful starting material in pyridineselenolate chemistry, [Et_4N][2-PySe]. We also report the crystal structure of PyH-2-Se and [(18-crown-6)K][2-PySe].

(Organoseleno)phosphanes are relatively rare in the literature, and apart from $P(SePh)_3$, no crystal structure has been published.[9] Heteroatom-substituted phosphanes were shown to be useful ligands that display enhanced catalytic activities,[10] as described for the reaction of ketones with propane-2-ol to form corresponding alcohols with [$RuCl_2(PPh_3)_3$] or [$RuCl_2(PPh_3)$(N,P,N)] [N,P,N = bis(2-oxazoline-2-yl-methyl)(phenyl)phosphane] as catalyst.[11] One possibility for controlling the reaction pathways and the selectivity of phosphane-containing catalysts is the modification of the surrounding phosphane by varying the donor atom sets, which are usually C, N, and P. The introduction of selenium offers different coordination modes with hard and soft metal centres. In the second part of the paper, we therefore describe the syntheses of (pyridylseleno)-phosphanes and related metal complexes, together with the crystal structures of *t*BuP(O)(2-SePy)$_2$, [({(C$_5$H$_4$N-2-Se)*t*Bu_2P}-*N,P*)Cu(μ-Br)]$_2$, [({(C$_5$H$_4$N-2-Se)*t*Bu_2P}-*N,P*)Ag-(μ-Br)]$_2$, [({(C$_5$H$_4$N-2-Se)*t*Bu_2P}-*P*)AuCl], and [({(C$_5$H$_4$N-2-Se)$_2$*t*BuP}-*N,N′,P*)Mo(CO)$_3$].

Results and Discussion

Pyridine-2-selenol (1), Pyridine-2(1*H*)-selone (2), and Related Selenolates

Our previously described synthesis of Py-2-SeH is strongly dependent on the reaction conditions.[1a] All attempts to repeat the synthesis at slightly different temper-

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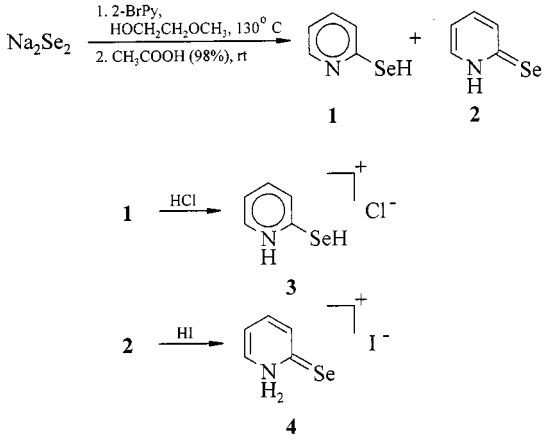
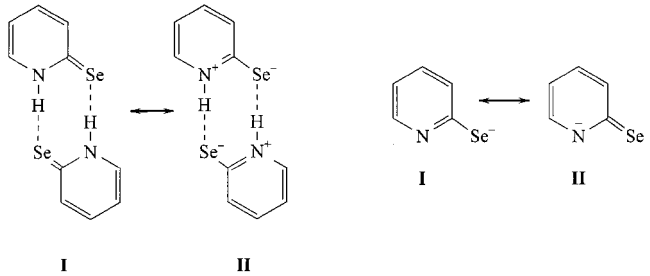
atures or pH values have been unsuccessful. This prompted us to examine this reaction in more detail. The results are shown in Scheme 1.



Scheme 1. Synthesis of 2-pyridineselenol (**1**) and pyridine-2(1*H*)-selone (**2**) and their reactions with HCl and HI

The acidification of the reaction mixture Na_2Se_2/2-BrPy, after refluxing it for 24 h in glycol monomethyl ether, with glacial acetic acid, leads to a mixture of Py-2-SeH (**1**) and PyH-2-Se (**2**) (ratio 1:6). These could be easily separated, since **1** and **2** have different physical properties: **1** is a light-yellow air-sensitive powder, soluble in polar solvents (alcohols, H_2O), but only sparingly soluble in CH_2Cl_2; **2** is a dark-yellow to orange air-stable and crystalline solid, soluble in polar solvents, but only sparingly soluble in H_2O. Once separated, **2** does not equilibrate to **1** in polar solvents. However, the mixture of **1** and **2** does not have to be separated for the synthesis of Py_2Se_2. The tautomerism of **1** and **2** was examined by spectroscopic means. It was shown that the UV/Vis spectrum of **2** is similar to the corresponding spectrum of 1-methylpyridine-2(1*H*)-selone, which gives a first hint of the selone structure.[5,12] Additional measurements of the dipole moment suggest the selone to be dimeric and resonance-stabilized (Scheme 2).



Scheme 2. Resonance forms of the dimeric pyridine-2(1*H*)-selone (**2**) and the 2-$PySe^-$ anion

The zwitterionic form **II** contributes markedly, since the dipole moment is relatively high and strongly solvent-dependent. ^{1}H NMR spectroscopic data show that the SeH signal of **1** (δ = 8.53) is shifted to low field in comparison with other organic selenols [PhSeH: δ = 1.36 (m); 2,4,6-$(CF_3)_3C_6H_2$SeH: δ = 2.36].[13] The tautomeric forms **1** and **2** are therefore easily distinguishable, since **2** displays a corresponding ^{1}H NMR resonance at a lower field (δ = 12−14; depending on the solvent and concentration). Further experiments showed that **1** and **2** react with acids to produce, e.g., the corresponding pyridinium hydrochloride and hydroiodide **3** and **4**. Protonation occurs exclusively at the nitrogen atom, and again the ^{1}H NMR spectroscopic data allow a clear distinction. Thus, the resonance for SeH of **3** appears at δ = 4.96, with an H−Se coupling constant of 14 Hz, derived from ^{77}Se satellites. The corresponding resonance of the amine proton is shifted to lower field (δ = 11.93). The ^{1}H NMR spectrum of **4** displays a resonance for the equivalent amine protons at δ = 8.88 (av. value of three measurements).

To confirm the NMR results, an X-ray structure analysis of **2** was performed (Figure 1). Alternative positions of the pyridine N atom and the *o*-carbon atom C2 were refined to establish the exact connectivity (see Exp. Sect.).

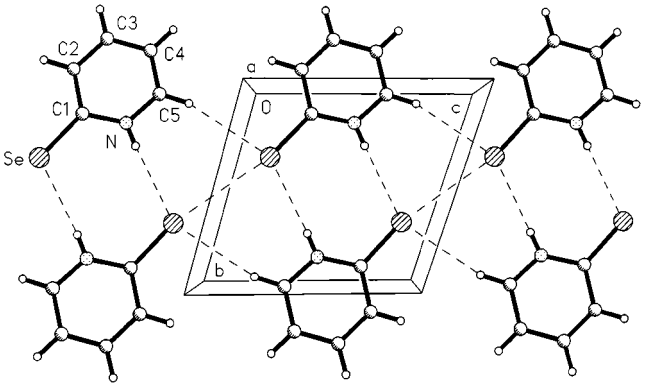


Figure 1. Molecular structure of PyH-2-Se (**2**) displaying intermolecular hydrogen bonding and weak Se−Se interactions (ellipsoids drawn at 50% probability level); selected bond lengths [pm] and angles [°]: Se−C1 184.6(8), N−C1 135.4(10), N−C5 133.8(10), N···Se^{i} 336.2(6), C5···Se^{ii} 386.0(8), Se···Se^{iii} 353.9(2); Se−C1−N 120.5(5), Se−C1−C2 124.8(6), C1−N−C5 125.5(7), N−C1−C2 114.7(7), N−H1···Se^{i} 164(8), C5−H5···Se^{ii} 163.7, C1−Se···Se^{iii} 167.7(2); *i*: x, y + 1, z; *ii*: x, y + 1, z + 1; *iii*: x, y + 1, z − 1

The crystal structure consists of dimeric pyridine-2(1*H*)-selones with planar monomeric units (max. dev. 8 pm for the N−H proton H1), connected via N−H···Se hydrogen bonds. The C=Se bond length of 184.6(8) pm is attributable to a resonance-stabilized C−Se double bond (Scheme 2). In selones not stabilized by resonance, the C=Se bonds are significantly shorter {1,5-dimethyl-3,7-dithiabicyclo[3.3.1]nonane-9-selone 177.4(6) pm; 4,4′-dimethoxyselenobenzophenone 179.0(4) pm; calculated value for selenoformaldehyde 173.9 pm}.[14] All other bond lengths are similar to those in pyridine.[15] Figure 2 shows the packing of **2**. The dimeric units are linked by weak Se···Se contacts of 353.9(2) pm and non-classical C−H···Se hydrogen bonds of C···Se 386.0(8) pm and H···Se 294 pm to form planar tapes, parallel to the *c* axis.

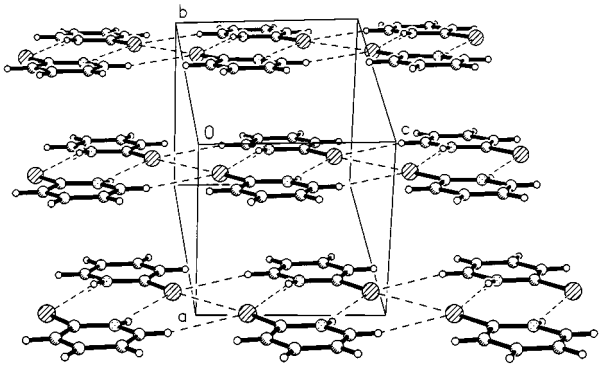
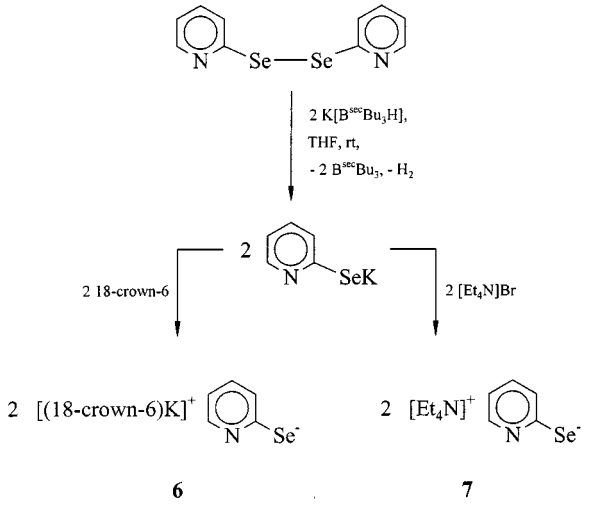


Figure 2. Packing diagram of (**2**) displaying the planar ribbons parallel to the *c* axis; radii are arbitrary; dashed lines correspond to N−H···Se hydrogen bonds, Se···Se contacts, and C−H···Se hydrogen bonds

To exploit the synthetic potential of the strongly nucleophilic 2-$PySe^-$ anion, it was necessary to introduce a new starting material with suitable properties, since many known syntheses of $PySe^-$ often suffer from a lack of reliability. One possible starting material is the pale-yellow compound $[Et_4N][2\text{-SePy}]$ (**7**), which can be easily prepared as described in Scheme 3.



Scheme 3. Synthesis of the stable pyridine-2-selenolates [(18-crown-6)K][2-SePy] (**6**) and $[Et_4N][2\text{-SePy}]$ (**7**)

The synthesis strongly depends on the reducing agent for 2,2′-Py_2Se_2 (**5**). Usually, reactions with 2-$PySe^-$ are performed in situ with Na, NaH, or MBR_3H (M = Li, Na) as reducing agents for **5**. The disadvantages of such procedures are as follows: (i) an excess of Na or NaH is difficult to remove from the reaction mixture, and can lead to undesired side-reactions if the reactants are redox-sensitive; (ii) the concentration of commercially available MBR_3H solutions is neither stable nor easy to monitor. In the case of **7**, these problems do not occur, since K*B*s*Bu*$_3$H solutions can be used in excess, and $[Et_4N]Br$ is not redox-sensitive. Additional advantages are the low solubility of $[Et_4N]Hal$ (Hal = Cl^-, Br^-) in many organic solvents, which can be regarded as the driving force in reactions of **7** with halogen derivatives, and the easy handling of the less air-sensitive **7**, which can be weighed in air.

A second possibility for stabilizing the 2-$PySe^-$ anion is the reaction of K-2-SePy with 18-crown-6 ether. The colourless oily product [(18-crown-6)K][2-SePy] (**6**) could be crystallised from ethanol/diethyl ether in moderate yield. The resonances in the ^{77}Se NMR spectra appear at low field [**2**: δ = 314.0 ($CDCl_3$), δ = 214.9 (H_2O); **6**: δ = 441.8 (CD_3OD); **7**: δ = 359.6 (CD_3OD)]. The values for **6** and **7** indicate a strong contribution of the ionic and the amide mesomeric form, as depicted in Scheme 2. This is in agreement with the shift of the resonance of **2** to higher field, when changing the solvent to H_2O, in which the ionic mesomeric form is more favoured. In systems where mesomeric forms display markedly different contributions, the resonances of the selenolates are usually shifted to higher field, compared with the corresponding selenols.[16] Unfortunately, appropriate data for **1** are not available.

The crystal structure of **6** is shown in Figure 3. It consists of cation−anion pairs with the potassium ion 82.8(3) pm outside the ideal plane through the oxygen atoms, linked by short K···N and K···Se contacts of 276.5(6) and 348.5(2) pm, respectively. Comparable, slightly smaller values for K···Se contacts were observed in $\{K[Ph_2P(Se)NSiMe_3]\cdot THF\}_2$ [336.6(5) and 338.9(4) pm] and 2-$MeOC_6H_4COSeK$ [330.9(1) pm].[17] In all such compounds, the negative charge at the selenium atom is delocalized; crystal structures with the negative charge centred at the selenium atom are unknown. Weak non-classical C−H···O hydrogen bonds of 264.4 and 255.5 pm (H···O) link the cation−anion pairs to infinite chains along the *a* axis. The Se−C bond, at 186.6(6) pm, is only slightly longer than the corresponding one in **2**, and can therefore also be described as a resonance-stabilized C−Se double bond (Scheme 3). Similar

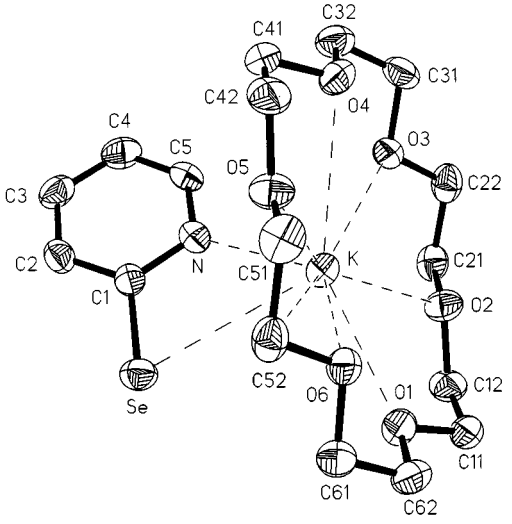


Figure 3. Molecular structure of $[(18\text{-crown-6})K]^+[2\text{-PySe}]^-$ (**6**) (ellipsoids drawn at 50% probability level): H atoms omitted for clarity; selected bond lengths [pm] and angles [°]: Se−C1 186.6(6), N−C1 136.1(8), N−C5 133.6(8), K−O 280.3(4) to 314.1(4), K···Se 348.5(2), K···N 276.5(6); C1−N−C5 117.5(6), N−C1−C2 120.0(6), N−C5−C4 125.3(6), N−C1−Se 118.3(5)

bonding patterns were detected in the corresponding thiolate [(18-crown-6)K][2-SPy] with a K···N contact of 285.4(3) and a K···S contact of 325.58(1) pm.[18]

(2-Pyridylseleno)phosphanes and Related Complexes

K-2-SePy and [Et_4N][2-SePy] (**7**) are useful starting materials for introducing 2-$PySe^-$ into phosphanes (Scheme 4).

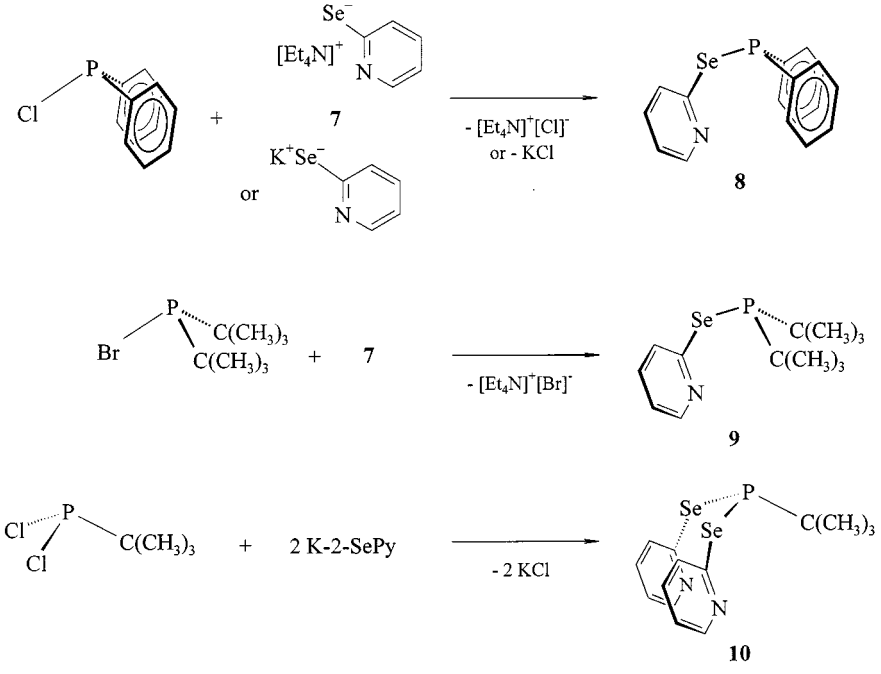
The nature of the products in such reactions is strongly dependent on the nucleophilicity of the starting material used, as shown for the reaction of Ph_2PCl with NaSePh, which leads quantitatively to Ph_3PSe even at low temperatures.[19] Apart from *t*Bu_2P(2-SePy) (**9**), which can be crystallised as an analytically pure yellow compound at low temperatures, the resulting yellow (2-pyridylseleno)phosphanes Ph_2P(2-SePy) (**8**) and *t*BuP(2-SePy)$_2$ (**10**) are extremely air-sensitive and oily compounds. Therefore, reactions with **8** and **10** should be performed in situ. The synthesis of **10** cannot be performed with **7** as starting material, since the nucleophilicity is not sufficient at room temperature. Performing the reaction at higher temperatures leads to an inseparable mixture of phosphorus-containing compounds. During the synthesis of **10** with K-2-SePy at room temperature, KCl forms an emulsion, which leads to difficulties in the workup procedure. Attempts to remove KCl resulted in complete oxidation of **10** to the corresponding phosphane oxide *t*BuP(O)(2-SePy)$_2$ **11**, whose crystal structure was determined (vide infra).

Compounds **9** and **11** have been fully characterized, whereas **8** and **10** have only been characterized by ^{31}P NMR spectroscopy. All (2-pyridylseleno)phosphanes and the phosphane oxide derivative display singlets in the ^{31}P NMR spectra in the range $\delta = +20$ to $+110$. The ^{31}P-^{77}Se coupling constants derived from ^{77}Se satellites (219−236 Hz for **8**, **9**, and **10**; 413 Hz for **11**) are typical values for P−Se single bonds, and the greater magnitude of the value for **11** shows the typical influence of the oxidation state change from P^{III} to P^{V}, accompanied by the introduction of an electron-withdrawing substituent.[16] Similar values of the chemical shift and the ^{31}P-^{77}Se coupling constant were found in Me_2PSeMe ($\delta = 0.8$, 218 Hz), $(CF_3)_2$PSeMe ($\delta = 27.9$, 294 Hz), and [Ph_2PSePPh_2Cr(CO)$_5$] [$\delta = 25.7$ with 244 Hz (λ^3-P), $\delta = 78.6$ with 312 Hz (λ^4-P)].[20] The corresponding resonance signals in the ^{77}Se NMR spectra appear at $\delta = +271$ for **9** and $\delta = +437.8$ for **11**, as doublets with coupling constants of the same magnitude.

The crystal structure of **11** is shown in Figure 4. It consists of loose dimers, linked by non-classical C−H···O hydrogen bonds with H···O = 259 pm. Additionally, intramolecular C−H···O hydrogen bonds with H···O = 245 pm are observed. The angles at the selenium atom differ considerably with values of 95.28(12)° and 104.92(12)°, probably associated with the intramolecular hydrogen bond. The observed P−Se bond lengths of 224.68(11) and 225.62(12) pm are attributable to P−Se single bonds and similar to the central P−Se bonds in [*t*BuP(Se)(μ-Se)]$_2$ with 226.9(2) pm.[21]

The (pyridylseleno)phosphanes **9** and **10** were treated with unsaturated metal complexes in order to examine which binding site of the potentially three- or five-atom donor set could be used for complexation reactions (Scheme 5, Scheme 6, and Scheme 7).

In the case of Cu^I and Ag^I, the doubly bromo-bridged dinuclear complexes [({(C_5H_4N-2-Se)*t*Bu_2P}-*N*,*P*)Cu(μ-Br)]$_2$ (**12**) and [({(C_5H_4N-2-Se)*t*Bu_2P}-*N*,*P*)Ag(μ-Br)]$_2$ (**13**) were formed in almost quantitative yield as air-stable pale-yellow to colourless solids. The reaction of **9** with (tht)AuCl



Scheme 4. Synthesis of the (2-pyridylseleno)phosphanes **8**−**10**

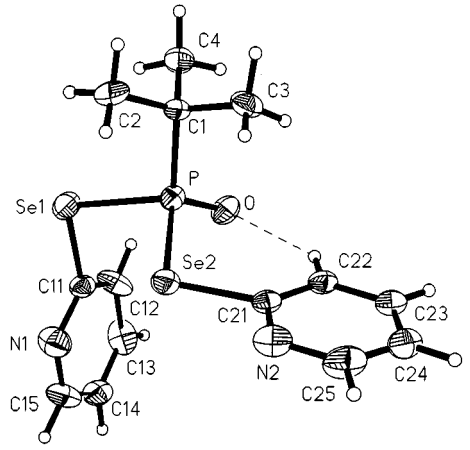
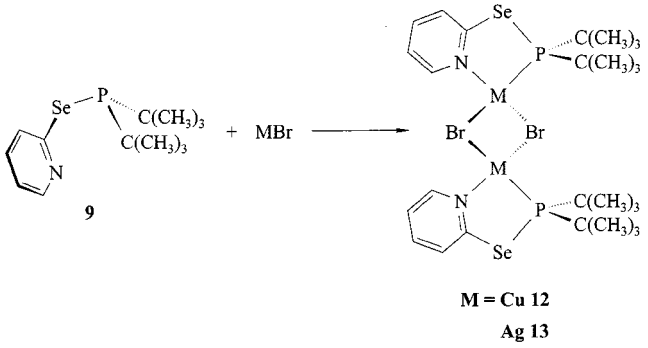
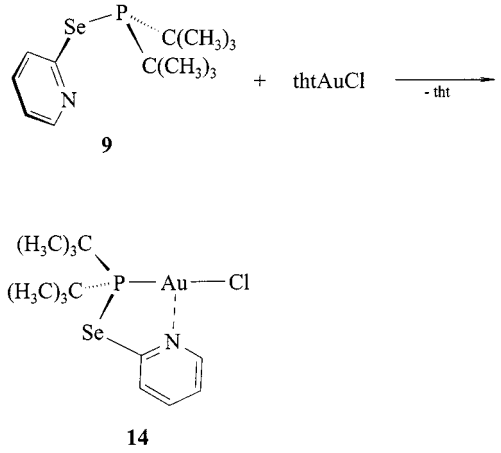


Figure 4. Molecular structure of *t*BuP(O)(2-SePy)$_2$ (**11**) (ellipsoids drawn at 50% probability level); selected bond lengths [pm] and angles [°]: P−Se1 224.68(11), P−Se2 225.62(12), P−O 147.0(3), Se1−C11 193.3(4), Se2−C21 195.1(4), C22···O 325.0(5), C23···O^{i} 317.7(5); O−P−C1 113.80(2), O−P−Se1 116.19(12), O−P−Se2 114.46(12), C1−P−Se1 103.82(13), C1−P−Se2 109.05(13), Se1−P−Se2 97.94(4), P−Se1−C11 95.28(12), P−Se2−C21 104.92(12); *i*: $-x + 1$, y, $-z + 0.5$

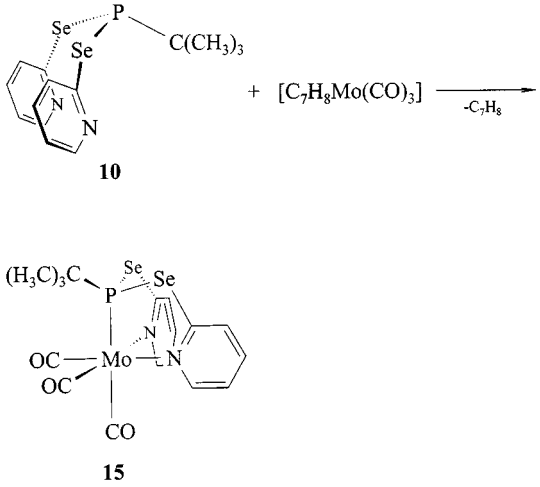


Scheme 5. Syntheses of the Cu^{I} and Ag^{I} complexes **12** and **13**



Scheme 6. Synthesis of the Au^{I} complex **14**

(tht = tetrahydrothiophene) leads in contrast to the mononuclear complex [({(C$_5$H$_4$N-2-Se)*t*Bu$_2$P}-*P*)AuCl] (**14**). Finally, the reaction of the bis(pyridylseleno)phosphane **10** with [(η^6-C$_7$H$_8$)Mo(CO)$_3$] leads to the deep-red mononuclear complex [({(C$_5$H$_4$N-2-Se)$_2$*t*BuP}-



Scheme 7. Synthesis of the Mo^{0} complex **15**

N,*N*′,*P*)Mo(CO)$_3$] (**15**) in moderate yield. All complexes were fully characterized, including crystal structure analyses.

The resonances in the ^{31}P NMR spectra show a shift to lower field, going from the Cu^{I} complex **12** to the Au^{I} complex **14**, with values of δ = 72.4 (**12**), δ = 84.7 (**13**), and δ = 117.3 (**14**) (chemical shift for **9**: δ = 90.3). By contrast, generally the opposite tendency is observed, caused by an increasing electron density from Cu to Au. This observation could be explained in terms of metal−nitrogen bonds of different strengths. The strongest metal−nitrogen bond in this row can be apparently found in **12**, leading to an increased electron density at Cu^{I}, whereas the Au^{I}−N bond in **14** must be considered as weak. This results in a stronger metal−phosphorus back donation, which explains the shift of the ^{31}P NMR resonances of **12** and **13** to higher field, compared with the uncomplexed phosphane. The explanation of the corresponding resonances in the ^{77}Se NMR spectra with values of δ = +520 (**12**), δ = +470 (**13**), and δ = +501 (**14**) (chemical shift for **9**: δ = +271) seems to be more complicated, since a clear tendency cannot be observed. Even the ^{77}Se-^{31}P coupling constants (240 to 322 Hz) are similar to that of the uncomplexed phosphane (235 Hz), so that the interpretation of the electron densities in the examined nuclei, as derived from ^{77}Se NMR spectroscopic data, is not reasonable. In the case of the Mo^{0} complex **15**, the ^{31}P NMR resonance with δ = 155.9 is strongly shifted to lower field, compared with the corresponding value for **10** (δ = 101). Additionally, the equivalent Se atoms display a chemical shift in the ^{77}Se NMR spectrum at extremely low field (δ = +761.1). Unfortunately, the corresponding data for **10** are not available, since its instability does not permit ^{77}Se NMR experiments. Since **12** and **13** are isostructural, their crystal structures are discussed together (Figure 5).

The common feature in both structures is that two monomeric units are doubly bridged by bromide to form dinuclear complexes. The resulting central four-membered M$_2$Br$_2$ rings are folded across the M···M vector, with corresponding interplanar angles of 20.25(5)° for **12** and 24.62(3)° for

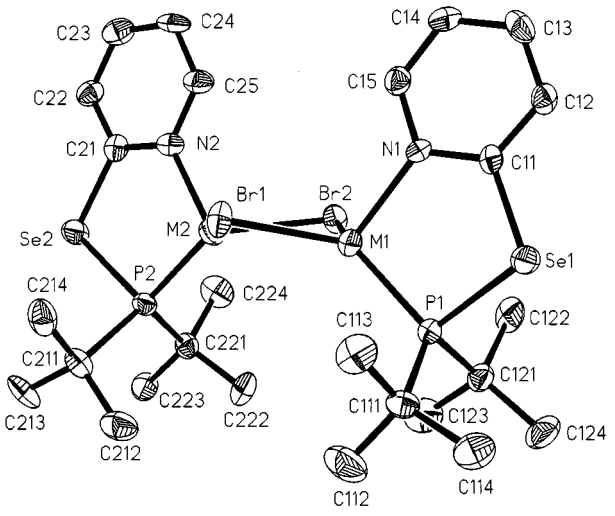


Figure 5. Molecular structures of [({$(C_5H_4N$-2-Se)tBu$_2$P}-*N*,*P*)M(μ-Br)]$_2$ [M = Cu (**12**), Ag (**13**)] (ellipsoids drawn at 50% probability level); H atoms omitted for clarity; selected bond lengths [pm] and angles [°] (the second value corresponds to the silver complex **13**): M1−N1 210.9(4)/245.6(3), M2−N2 210.4(5)/248.8(3), M1−P1 220.15(17)/241.16(11), M2−P2 220.09(17)/241.76(11), M1−Br1 245.96(10)/263.12(6), M1−Br2 249.77(10)/270.17(6), M2−Br1 248.43(10)/265.32(7), M2−Br2 247.73(10)/267.84(6), P1−Se1 226.41(17)/225.45(12), P2−Se2 226.92(17)/225.37(12), Se1−C11 191.8(6)/194.5(4), Se2−C21 192.7(6)/194.3(4), M1···M2 314.30(11)/313.33(6), Br1···Br2 377.66(10)/421.53(8); N1−M1−P1 95.11(14)/85.14(8), M1−P1−Se1 101.07(7)/105.33(5), P1−Se1−C11 99.31(17)/100.98(12), Se1−C11−N1 119.7(4)/119.2(3), C11−N1−M1 121.8(4)/122.9(3), N2−M2−P2 94.74(14), M2−P2−Se2101.52(7)/106.76(5), P2−Se2−C21 99.6(2)/101.66(13), Se2−C21−N2 120.1(4)/120.5(3), C21−N2−M2 123.2(4)/124.5(3)

13, which leads to relatively short metal−metal contacts of 314.30(11) and 313.33(6) pm, respectively. These values and corresponding bonding parameters are often found in Cu_2Br_2 and Ag_2Br_2 rings.[22] The (2-pyridylseleno)phosphane ligands act as chelates and are bound through the phosphorus and nitrogen atoms. The P−Se bond lengths in both complexes are 226.41(17) and 226.92(17) pm for **12**, and 225.45(12) and 225.37(12) pm for **13**, which correspond to P−Se single bonds. The strength of the metal−nitrogen bond may be assumed to be greater in **12** [210.9(4), 210.4(5) pm] than in **13** [245.6(3), 248.8(3) pm], consistent with the greater hardness of Cu^I centres compared with Ag^I centres. The molecular structure of the Au^I complex **14** is shown in Figure 6.

In contrast to the dimeric complexes **12** and **13**, complex **14** forms a simple monomer with a semi-chelating (2-pyridylseleno)phosphane ligand and essentially linear bonding at Au. An additional Au···N contact of 282.8(7) pm, which is too long for a bonding interaction is also formed. Normal Au−N single bonds in Au^I−amine complexes are much shorter (ca. 200 pm).[23] The P−Se bond length of 225.3(2) pm is again assignable to a P−Se single bond. In the molecular structure of the Mo^0 complex **15**, the bis(2-pyridylseleno)phosphane **10** acts as a tridentate chelating ligand (Figure 7).

Complex **15** crystallized with one disordered CH_2Cl_2 molecule per asymmetric unit, which was refined in two alternative positions. The coordination sphere of the molybdenum centre is slightly distorted octahedral, with angles ranging from 82.91(8) to 96.77(13)° and 175.26(13) to 177.08(13)°. The ligand is exclusively bound through both nitrogen and phosphorus atoms in a *fac* arrangement, and shows a strong *trans* influence with Mo−C bond lengths of 194.2(4) pm (av. value, carbonyl groups *cis* to the P atom) and 200.9(4) pm (carbonyl group *trans* to the P atom). The P−Se bond lengths of 226.59(10) and 227.12(10) pm match the observed values in **12**, **13**, and **14**, and therefore again correspond to P−Se single bonds. All other bonding para-

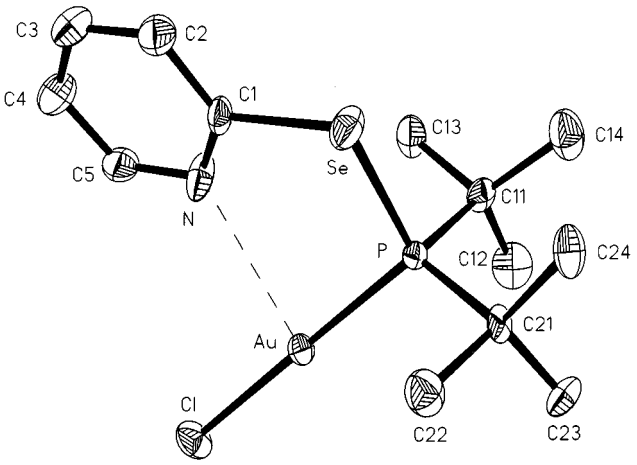


Figure 6. Molecular structure of [({$(C_5H_4N$-2-Se)tBu$_2$P}-*P*)AuCl] (**14**) (ellipsoids drawn at 50% probability level); H atoms omitted for clarity; selected bond lengths [pm] and angles [°]: Au−P 223.7(2), Au−Cl 230.2(2), P−Se 225.3(2), Se−C1 194.0(7), Au···N 282.8(8); P−Au−Cl 179.63(9), Au−P−Se 110.93(8), P−Se−C1 101.9(3), N···Au−Cl 101.02(14), N···Au−P 79.22(14)

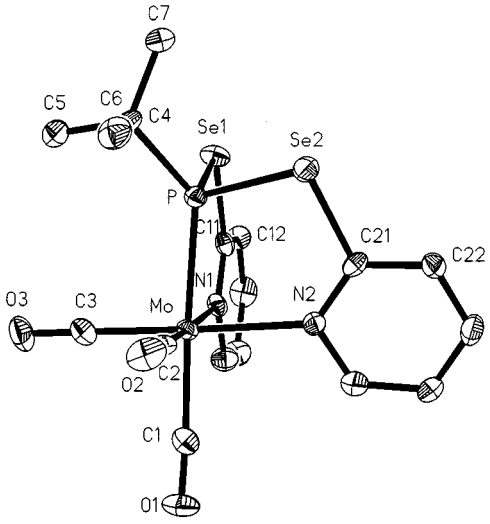


Figure 7. Molecular structure of [({$(C_5H_4N$-2-Se)$_2t$BuP}-*N*,*N*′,*P*)Mo(CO)$_3$] (**15**) (ellipsoids drawn at 50% probability level); H atoms and CH_2Cl_2 molecule omitted for clarity; selected bond lengths [pm] and angles [°]: Mo−P 239.24(10), Mo−N1 230.3(3), Mo−N2 230.1(3), P−Se1 226.59(10), P−Se2 227.12(10), Se1−C11 191.7(4), Se2−C21 192.2(4); P−Mo−N1 84.17(8), P−Mo−N2 82.91(8), N1−Mo−N2 84.78(10), Mo−P−C4 132.32(12), Mo−P−Se1 108.01(4), Mo−P−Se2 106.21(4), Se1−P−Se2 105.04(4), Se1−P−C4 101.31(12), Se2−P−C4 101.26(12), P−Se1−C11 97.79(11), P−Se2−C21 96.28(11)

meters in the complexes **12** to **15** are consistent with the usually observed values.

Experimental Section

General Techniques: All reactions were performed under dry dinitrogen using conventional Schlenk techniques. Solvents were dried and degassed using standard procedures prior to use. − NMR spectra were recorded with a Bruker AC 200 at room temperature [^{1}H: 200.1 MHz; ^{13}C: 50.32 MHz; ^{31}P: 81.0 MHz; ^{77}Se: 38.2 MHz; standards Me_4Si (^{1}H, ^{13}C); 85% H_3PO_4 (^{31}P); 100% Me_2Se (^{77}Se)]. − IR spectra were recorded in KBr with a Biorad FTS 165 spectrometer. − UV/Vis spectra were recorded with a Perkin−Elmer Lambda 15 spectrometer using quartz cuvettes with a diameter of 1 cm. − MS: Finnigan MAT 8430 at 70 eV. − Elemental analyses of the isolated products were performed by the analytical laboratory of this Institute. − (2,2′-Bispyridyl) diselenide was prepared according to a literature procedure.[1a] All other commercial-grade chemicals were used without further purification.

Py-2-SeH (1) and PyH-2-Se (2): Na_2Se_2 was prepared according to the procedure of Klayman et al. starting from grey selenium (30 g, 0.38 mol) and $NaBH_4$ (10 g, 0.27 mol) in 500 mL of ethanol.[24] After the reaction was complete, the solvent was removed in vacuo at 50 °C. Ethylene glycol monomethyl ether (500 mL) was added to the grey-violet solid, affording a dark-red solution. To this solution was added 2-BrPy (20.1 g, 0.127 mol), and the reaction mixture was allowed to reflux for 24 h. The resulting yellow-brown solution was filtered and concentrated, and H_2O (320 mL, degassed) was added. After addition of glacial acetic acid (80 mL) with stirring, red selenium precipitated, which was removed by filtration after 1 h of stirring at ambient temperature. The yellow filtrate was concentrated at 80 °C and the resulting yellow solid was extracted with CH_2Cl_2 (500 mL) using a Soxhlet apparatus. Concentration of the yellow extract afforded pale-yellow **1** (1.7 g, 9%). Subsequent evaporation of the solvent and storage at −30 °C afforded dark-yellow **2** (12 g, 60%) as a crystalline product. Suitable crystals of **2** for an X-ray structure analysis were obtained from liquid-liquid diffusion of hexanes into a CH_2Cl_2 solution. **1:** ^{1}H NMR ([D$_6$]DMSO): δ = 6.96 (m, 1 H, *p* to CSeH), 7.43 (m, 1 H, *p* to N), 7.61 (m, 1 H, *o* to N), 7.80 (m, 1 H *o* to CSeH), 8.53 (s, br, 1 H, SeH); ref.[1a] ($CDCl_3$): δ = 6.98, 7.38, 7.71, 7.86, 8.41. − **2:** M.p.: 137 °C. − C_5H_5NSe (158.06): calcd. C 37.99, H 3.19, N 8.86; found C 38.05, H 3.16, N 8.86. − IR (CH_2Cl_2, $\tilde{\nu}$ [cm^{-1}]): 1607 (m, br), 1572 (st), 1561 (st), 1420 (st, br), 1271 (st), 1244 (st), 1107 (m), 1078 (m), 1044 (w), 893 (vs), 774 (vs, br), 685 (vs, br). − ^{1}H NMR ($CDCl_3$): δ = 6.96 (m, 1 H, *p* to C=Se), 7.38 (m, 1 H, *p* to NH), 7.73 (m, 1 H, *o* to NH), 7.85 (m, 1 H, *o* to C=Se), 13.44 (s, br, 1 H, NH, av. value of six measurements with values of δ = 12.03 to 14.07). − ^{13}C NMR ($CDCl_3$): δ = 118.6 (s, *p* to C=Se), 131.3 (s, *o* to C=Se), 137.8 (s, *p* to NH), 143.4(s, *o* to NH), 162.0 (s, *C*=Se). − ^{77}Se NMR ($CDCl_3$): δ = 314.0 s; (H_2O with C_6D_6 capillary): δ = 214.9 s. − UV/Vis (10^{-3} M in H_2O, λ_{max} [nm]): 228, 283, 357; ref.[5] (H_2O, pH = 5.7): 227, 285, 358.

[HPy-2-SeH]$^+$Cl$^-$ (3): A suspension of **1** (500 mg, 3.16 mmol) in 40 mL of THF was treated with Ph_2PCl (698 mg, 3.16 mmol) at room temperature. A clear yellow solution was formed immediately. After 3 h of stirring, a pale yellow precipitate had formed, which was filtered off and dried in vacuo (370 mg, 60%). − ^{1}H NMR ([D$_6$]DMSO): δ = 4.96 [s, 1 H, Se*H*, ^{77}Se satellites, *J*(H,Se) = 14.2 Hz], 7.39 (m, 1 H, *p* to CSeH), 7.82 (m, 2 H, *o* and *p* to NH), 8.57 (m, 1 H, *o* to CSeH), 11.93 (s, br, 1 H, N*H*).

[H$_2$Py-2-Se]$^+$I$^-$ (4): A 57% HI solution in H_2O (3 mL) was added to a suspension of **2** (500 mg, 3.16 mmol) in 20 mL of H_2O. A clear yellow solution formed immediately. Removal of H_2O in vacuo gave **4** as a pale yellow solid in quantitative yield. Compound **4** decomposes in neutral H_2O, and is sparingly soluble in $CHCl_3$ and acetone. Solutions of **4** in methanol or DMSO are dark-yellow. − C_5H_6INSe (285.97): calcd. C 21.00, H 2.11, N 4.90; found C 20.81, H 2.11, N 4.72. − ^{1}H NMR ([D$_6$]DMSO): δ = 7.30 (m, 1 H, *p* to C=Se), 7.79 (m, 2 H, *o* and *p* to NH_2), 8.43 (m, 1 H, *o* to C=Se), 8.88 (s, br, 2 H, NH_2, av. value of two measurements with values of δ = 8.64 and 9.12).

[(18-crown-6)K]$^+$[2-PySe]$^-$ (6): A solution of KB*s*Bu$_3$H (6.33 mL of a 1 M solution in THF, 6.33 mmol) was added to a solution of 2,2′-Py_2Se_2 (**5**; 1 g, 3.16 mmol) in 40 mL of THF. Gas evolution occurred and a pale yellow solid precipitated, leaving a colourless supernatant solution. After 1 h of stirring at ambient temperature, the solvent was removed in vacuo and 20 mL of ethanol and solid 18-crown-6 ether (1.67 g, 6.33 mmol) was added. After 30 min, the product was crystallized with diethyl ether at −30 °C (450 mg, 15%). − M.p.: 152 °C. − $C_{17}H_{28}KNO_6Se$ (460.47): calcd. C 44.34, H 6.13, N 3.04; found C 44.72, 3.03, 6.19. − ^{1}H NMR (CD_3OD): δ = 3.66 (s, 24 H, CH_2), 6.92 (m, 1 H, *p* to CSe), 7.26 (m, 1 H, *p* to N), 7.71 (m, 1 H, *o* to N), 8.10 (m, 1 H, *o* to CSe). − ^{13}C NMR (CD_3OD): δ = 71.3 (s, *C*H$_2$), 118.6 (s, *p* to CSe), 132.7 (s, *o* to CSe), 135.8 (s, *p* to N), 148.9 (s, *o* to N), 164.5 (s, *C*Se). − ^{77}Se NMR (CD_3OD): δ = 441.8 s. − MS (FAB): *m*/*z* (%) = 303 (100) [(18-crown-6)K]$^+$, 158 (100) [2-PySe]$^-$.

[Et$_4$N]$^+$[2-PySe]$^-$ (7): K-2-SePy was prepared in the same manner as described for **6**, starting from 25.3 mL of a 1 M KB*s*Bu$_3$H solution in THF (25.3 mmol) and **5** (4 g, 12.65 mmol) in 100 mL of THF. The pale yellow solid was dissolved in 100 mL of ethanol and Et_4NBr (5.32 g, 25.31 mmol) was added. After 15 min of stirring at ambient temperature, the solvent was removed in vacuo and the remaining solid was suspended in 200 mL of acetone. The workup procedure comprised filtration and washing of the solid for several times with 20 mL of acetone until the filtrate became colourless. The combined acetone extracts were concentrated, washed with diethyl ether and dried in vacuo, leaving a pale yellow solid of **7** (5.98 g, 82%), soluble in polar organic solvents such as CH_3CN, DMSO or alcohols. − M.p.: 108 °C. − $C_{13}H_{24}N_2Se$ (287.31): calcd. C 54.35, H 8.42, N 9.75; found C 53.28, H 8.37, N 9.52. − ^{1}H NMR ([D$_6$]DMSO): δ = 1.15 [t, 12 H, CH_3, ^{3}*J*(H,H) = 7.2 Hz], 3.21 [q, 8 H, CH_2, ^{3}*J*(H,H) = 7.2 Hz], 6.49 (m, 1 H, *p* to CSe), 6.78 (m, 1 H, *p* to N), 7.26 (m, 1 H, *o* to N), 7.84 (m, *o* to CSe). − ^{13}C NMR ([D$_6$]DMSO): δ = 7.1 (s, *C*H$_3$), 51.4 (s, *C*H$_2$), 113.7 (s, *p* to CSe), 131.8 (s, *o* to CSe), 132.6 (s, *p* to N), 147.7 (s, *o* to N), 172.7 (s, *C*Se). − ^{77}Se NMR (CD_3OD): δ = 359.6 s. − UV/Vis (10^{-3} M in H_2O, λ_{max} [nm]): 233, 277, 352.

Ph$_2$P-2-SePy (8). − Route A: To a solution of K-2-SePy, prepared from a solution of **5** (1 g, 3.16 mmol) in 40 mL of diethyl ether and 6.33 mL of a 1 M KB*s*Bu$_3$H solution in THF at −70 °C, was added Ph_2PCl (1.41 g, 6.37 mmol) dropwise via a syringe. The reaction mixture was allowed to warm to room temperature within 1 h, and was stirred for additional 2 h at 25 °C and then filtered, leaving a dark-yellow filtrate. − **Route B:** Ph_2PCl (195 mg, 0.88 mmol) was added dropwise via a syringe to a solution of **7** (254 mg, 0.88 mmol) in 20 mL of CH_3CN at 0 °C. After 2 h of additional stirring, the mixture was filtered, leaving a dark-yellow filtrate (quantitative yield, monitored by ^{31}P NMR means). **8** was completely oxidized during the workup, leading to various unidentified products, but it is stable in solution under N_2. − ^{31}P NMR (THF

solution, C_6D_6 capillary): δ = 22.40 [s, ^{77}Se satellites, J(P,Se) = 219 Hz].

***t*Bu$_2$P-2-SePy (9):** A solution of *t*Bu$_2$PBr (1.21 g, 5.35 mmol) in 60 mL of CH_3CN was added dropwise to a solution of **7** (1.54 g, 5.35 mmol in 60 mL of CH_3CN). The reaction mixture was stirred for 3 h at room temperature, to leave a colourless solution. The workup procedure comprised removal of the solvent in vacuo, addition of 10 mL of diethyl ether, filtration of Et_4NBr and removal of the diethyl ether, leaving a pale yellow oil that crystallized upon standing at −30 °C in nearly quantitative yield. Compound **9** is soluble in nearly all common organic solvents. − M.p.: 28 °C. − $C_{13}H_{22}NPSe$ (302.26): calcd. C 51.66, H 7.34, N 4.63; found C 51.74, H 7.35, N 4.44. − ^{1}H NMR ([D$_6$]acetone): δ = 1.34 [d, 18 H, CH_3, ^3J(H,P) = 12 Hz], 7.13 (m, 1 H, *p* to CSe), 7.59 (m, 1 H, *p* to N), 7.91 (m, 1 H, *o* to N), 8.36 (m, 1 H, *o* to CSe). − ^{13}C NMR ($CDCl_3$): δ = 30.3 [d, *C*H$_3$, ^2J(C,P) = 15 Hz], 34.8 [d, *C*(CH$_3$)$_3$, J(C,P) = 32.9 Hz], 120.5 (s, *p* to CSe), 126.5 [d, *o* to CSe, ^3J(C,P) = 12.9 Hz], 136.3 (s, *p* to N), 149.6 [d, *o* to N, ^4J(C,P) = 2.4 Hz], 156.8 [d, *C*Se, ^2J(C,P) = 17.5 Hz]. − ^{31}P NMR ($CDCl_3$): δ = 90.33 [s, ^{77}Se satellites, J(P,Se) = 235.5 Hz]. − ^{77}Se NMR ($CDCl_3$): δ = 271 [d, J(Se,P) = 235.1 Hz]. − MS (EI): *m*/*z* (%): 303 (2) [M]$^+$, 246 (100) [M − *t*Bu]$^+$.

***t*BuP(2-SePy)$_2$ (10) and *t*BuP(O)(2-SePy)$_2$ (11):** K-2-SePy was prepared from **5** (1.74 g, 5.51 mmol) in 40 mL of THF and 11.01 mL of a 1 M K*B*s*Bu*$_3$H solution (11.01 mmol) in THF. A solution of *t*BuPCl$_2$ (876 mg, 5.51 mmol) in 20 mL of THF was added over 30 min. The yellow reaction mixture was stirred for additional 2 h, and contained **10** and KCl as an emulsion. − ^{31}P NMR (THF, C_6D_6 capillary): δ = 101.0 [s, ^{77}Se satellites, J(P,Se) = 228.4 Hz]. − Removal of the solvent in vacuo led to an oily solid mixture, which was then suspended in 50 mL of CH_2Cl_2 and filtered through silica. The dark-yellow filtrate was reduced to 10 mL and crystallized by addition of hexanes and storage at −30 °C (1.43 g, 62%, yellow prisms). − M.p.: 85 °C. − $C_{14}H_{17}N_2OPSe_2$ (418.20): calcd. C 40.21, H 4.10, N 6.70; found C 39.83, H 4.12, N 6.59. − ^{1}H NMR ([D$_6$]acetone): δ = 1.30 [d, 9 H, CH_3, ^3J(H,P) = 21.7 Hz], 7.36 (m, 2 H, *p* to CSe), 7.73 (m, 2 H, *p* to N), 7.94 (m, 2 H, *o* to N), 8.48 (m, 2 H, *o* to CSe). − ^{13}C NMR ($CDCl_3$): δ = 25.0 [d, *C*H$_3$, ^2J(C,P) = 1.4 Hz], 46.0 [d, *C*(CH$_3$)$_3$, J(C,P) = 49 Hz], 123.2 (s, *p* to CSe), 131.6 [d, *o* to CSe, ^3J(C,P) = 1.7 Hz], 137.0 (s, *p* to N), 150.3 (s, *o* to N), 151.2 [d, *C*Se, ^2J(C,P) = 5.7 Hz]. − ^{31}P NMR ([D$_6$]acetone): δ = 72.1 [s, ^{77}Se satellites, J(P,Se) = 412.5 Hz]. − ^{77}Se NMR ($CDCl_3$): δ = 437.8 [d, J(Se,P) = 417.8 Hz]. − MS (CI): *m*/*z* (%): 376 (100) [M − *t*Bu]$^+$, 262 (2) [M − SePy]$^+$.

[({(C$_5$H$_4$N-2-Se)*t*Bu$_2$P}-*N*,*P*)Cu(μ-Br)]$_2$ (12), [({(C$_5$H$_4$N-2-Se)*t*Bu$_2$P}-*N*,*P*)Ag(μ-Br)]$_2$ (13), and [({(C$_5$H$_4$N-2-Se)*t*Bu$_2$P}-*P*)AuCl] (14): Complex **12** was prepared from CuBr (176 mg, 1.23 mmol) and **9** (371 mg, 1.23 mmol), complex **13** from AgBr (391 mg, 2.08 mmol) and **9** (629 mg, 2.08 mmol), and complex **14** from thtAuCl (774 mg, 2.41 mmol) (tht = tetrahydrothiophene) and **9** (730 mg, 2.41 mmol), by addition of a solution of the metal halide to a solution of **9** (in the case of **12**), or addition of a solution of **9** to a solution of the metal halide (in the case of **13**, **14**) in CH_3CN (60 mL), and stirring for 3 h at room temperature under exclusion of light. The solvent was removed in vacuo, and crystallisation from a CH_2Cl_2 solution by layering with hexanes afforded colourless (**13**) to pale-yellow (**12**, **14**) solids. Single crystals suitable for an X-ray analysis were obtained directly from the reaction mixture in all cases.

12: Nearly quantitative yield, M.p.: 233 °C. − $C_{26}H_{44}Br_2Cu_2N_2P_2Se_2$ (891.42): calcd. C 35.03, H 4.98, N 3.03; found C 35.09, H 4.98, N 3.03. − ^{1}H NMR ($CDCl_3$): δ = 1.45 [d, 36 H, CH_3, ^3J(H,P) = 15.4 Hz], 7.20 (m, 2 H, *p* to CSe), 7.52 (m, 4 H, *o* and *p* to N), 8.87 (m, 2 H, *o* to CSe). − ^{13}C NMR (CD_2Cl_2): δ = 30.4 [d, *C*H$_3$, ^2J(C,P) = 9.8 Hz], 37.0 [d, *C*(CH$_3$)$_3$, J(C,P) = 4.5 Hz], 122.3 [d, *p* to CSe, ^5J(C,P) = 1.9 Hz], 126.2 (s, *o* to CSe), 137.6 [d, *p* to N, ^4J(C,P) = 1.5 Hz], 151.1 [d, *o* to N, ^4J(C,P) = 2.5 Hz], 155.4 [d, *C*Se, ^2J(C,P) = 6.5 Hz]. − ^{31}P NMR ($CDCl_3$): δ = 72.4 (s, br). − ^{77}Se NMR (CD_2Cl_2): δ = 520.4 [d, J(Se,P) = 240 Hz]. − MS (EI): *m*/*z* (%) {monomer = [M]$^+$}: 445 (31) [M]$^+$, 246 (100) [2-SePyP*t*Bu]$^+$.

13: 882 mg, 87%, M.p.: 189 °C. − $C_{26}H_{44}Ag_2Br_2N_2P_2Se_2$ (980.07): calcd. C 31.86, H 4.53, N 2.86; found C 31.87, H 4.52, N 2.84. − ^{1}H NMR ($CDCl_3$): δ = 1.43 [d, 36 H, CH_3, ^3J(H,P) = 15.8 Hz], 7.16 (m, 2 H, *p* to CSe), 7.47 (m, 4 H, *o* and *p* to N), 8.77 (m, 2 H, *o* to CSe). − ^{13}C NMR (CD_2Cl_2): δ = 30.4 [d, *C*H$_3$, ^2J(C,P) = 11 Hz], 37.2 [d, *C*(CH$_3$)$_3$, J(C,P) = 8.8 Hz], 122.4 [d, *p* to CSe, ^5J(C,P) = 1.5 Hz], 127.1 (s, *o* to CSe), 137.6 [d, *p* to N, ^4J(C,P) = 1.4 Hz], 151.7 (s, *o* to N), 152.0 [d, *C*Se, ^2J(C,P) = 2.6 Hz]. − ^{31}P NMR ($CDCl_3$): δ = 84.7 (s, br). − ^{77}Se NMR (CD_2Cl_2): δ = 470.2 [d, J(Se,P) = 273.8 Hz]. − MS (EI): *m*/*z* (%): 246 (100) [2-SePyP*t*Bu]$^+$.

14: 1.16 g, 90%, M.p.: > 126 °C (dec.). − $C_{13}H_{22}AuClNPSe$ (534.68): calcd. C 29.20, H 4.15, N 2.62; found C 29.00, H 4.19, N 2.48. − ^{1}H NMR (CD_2Cl_2): δ = 1.49 (d, 18 H, CH_3, ^3J(H,P) = 17.2 Hz), 7.30 (m, 1 H, *p* to CSe), 7.60 (m, 1 H, *p* to N), 7.75 (m, 1 H, *o* to N), 8.50 (m, 1 H, *o* to CSe). − ^{13}C NMR (CD_2Cl_2): δ = 30.0 [d, *C*H$_3$, ^2J(C,P) = 6.5 Hz], 40.1 [d, *C*(CH$_3$)$_3$, J(C,P) = 14 Hz], 123.8 (s, *o* to N), 131.4 [d, *o* to CSe, ^3J(C,P) = 2.2 Hz], 137.8 (s, *p* to N), 151.0 (s, *o* to N), 151.8 (s, CSe). − ^{31}P NMR (CD_2Cl_2): δ = 117.3 [s, ^{77}Se satellites, J(P,Se) = 319.8 Hz]. − ^{77}Se NMR (CD_2Cl_2): δ = 501.0 [d, J(Se,P) = 322.3 Hz]. − MS (EI): *m*/*z* (%): 535 (31) [M]$^+$, 246 (100) [2-SePyP*t*Bu]$^+$.

[({(C$_5$H$_4$N-2-Se)$_2$*t*BuP}-*N*,*N*′,*P*)Mo(CO)$_3$] (15): The yellow reaction mixture of **10** (5.1 mmol) was concentrated to dryness, and the remaining solid was suspended in 40 mL of toluene. A solution of [(η^6-C$_7$H$_8$)Mo(CO)$_3$] (1.38 g, 5.1 mmol) in 50 mL of toluene was added dropwise at room temperature under exclusion of light to the reaction mixture. After 12 h of stirring at room temperature, the solvent was removed in vacuo. The workup procedure comprised addition of 60 mL of CH_2Cl_2, filtration through silica, and column chromatography on silica (40 × 3 cm; eluent: CH_2Cl_2/hexanes, 75:25). After four fractions (yellow, orange, brown, red) that contained traces of unidentified by-products, the deep-red main fraction of **15** eluted. Crystals of the CH_2Cl_2 hemisolvate were obtained by layering a CH_2Cl_2 solution (20 mL) with hexanes (150 mL) at room temperature. − Yield: 1.15 g, 34%, M.p.: > 125 °C (dec.). − $C_{17.5}H_{18}ClMoN_2O_3PSe_2$ (624.63): calcd. C 33.65, H 2.90, N 4.48; found C 33.56, H 2.89, 4.39. − IR (CH_2Cl_2, ṽ [cm^{-1}]): 1931 vs, 1838 st, br, 1815 st, br (Mo−*CO*). − ^{1}H NMR ([D$_6$]acetone): δ = 1.67 [d, 9 H, CH_3, ^3J(H,P) = 17.7 Hz], 5.62 (s, 1 H, CH_2Cl_2), 7.18 (m, 2 H, *p* to CSe), 7.61 (m, 2 H, *p* to N), 7.75 (m, 2 H, *o* to N), 9.49 (m, 2 H, *o* to CSe). − ^{13}C NMR ([D$_6$]acetone): δ = 28.6 [d, *C*H$_3$, ^3J(C,P) = 6.2 Hz], 41.5 [d, *C*(CH$_3$)$_3$, J(C,P) = 10.9 Hz], 54.9 (s, *C*H$_2$Cl$_2$), 122.8 (s, *p* to CSe), 127.6 [d, *o* to CSe, ^3J(C,P) = 2.7 Hz], 138.0 (s, *p* to N), 154.4 [d, *o* to N, ^4J(C,P) = 5.6 Hz], 163.3 [d, *C*Se, ^2J(C,P) = 10.8 Hz], 222.8, 227.2, 227.3 (s, Mo*C*O). − ^{31}P NMR ([D$_6$]acetone): δ = 155.9 [s, ^{77}Se satellites, J(P,Se) = 257.1 Hz]. − ^{77}Se NMR ([D$_6$]acetone): δ = 761.1 [d, J(Se,P) = 258.8 Hz]. − MS (EI): *m*/*z* (%): 582 (1) [M]$^+$, 246 (32) [PySeP*t*Bu]$^+$, 57 (100) [*t*Bu]$^+$.

Crystal Structure Analyses: The crystal structures for **2**, **6**, **11**, **12**, **13**, **14**, and **15** were performed with a Siemens P4 diffractometer

Table 1. Crystal data for the compounds **2**, **6**, and **11**

	2	**6**	**11**
Empirical formula	C_5H_5NSe	$C_{17}H_{28}KNO_6Se$	$C_{14}H_{17}N_2OPSe_2$
Molecular mass [gmol^{-3}]	158.06	460.46	418.19
Crystal size [mm]	0.26 × 0.20 × 0.14	0.30 × 0.16 × 0.12	0.40 × 0.32 × 0.24
Space group	$P\bar{1}$ (No. 2)	$P1$ (No. 1)	$C2/c$ (No. 15)
Crystal system	triclinic	triclinic	monoclinic
a [pm]	660.2(2)	827.9(3)	1718.7(2)
b [pm]	685.6(2)	834.4(3)	755.90(8)
c [pm]	693.6(2)	900.5(2)	2470.0(3)
α [°]	103.93(2)	74.10(2)	90
β [°]	94.61(2)	66.52(2)	97.509(8)
γ [°]	111.98(2)	63.97(3)	90
V [nm^3]	0.2775(1)	0.5090(3)	3.1814(7)
Z	2	1	8
$d_{calcd.}$ [gcm^{-3}]	1.892	1.502	1.746
μ [cm^{-1}]	66.24	20.80	47.46
$2\Theta_{max}$	50	50	50
Data (total)	1882	3522	4190
Data (independent)	948	3290	2753
Restraints	0	3	0
Parameters	68	235	184
S (F^2)	1.004	1.045	0.858
R_1	0.0629	0.0459	0.0326
wR_2	0.1585	0.1107	0.0651

Table 2. Crystal data for the compounds **12**, **13**, **14**, and **15**

	12	**13**	**14**	**15**·0.5 CH_2Cl_2
Empirical formula	$C_{26}H_{44}Br_2Cu_2N_2P_2Se_2$	$C_{26}H_{44}Ag_2Br_2N_2P_2Se_2$	$C_{13}H_{22}AuClNPSe$	$C_{17.5}H_{18}ClMoN_2O_3PSe_2$
Molecular mass [gmol^{-3}]	891.42	980.05	534.66	624.62
Crystal size [mm]	0.26 × 0.18 × 0.16	0.30 × 0.24 × 0.24	0.24 × 0.20 × 0.20	0.50 × 0.30 × 0.20
Space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
Crystal system	triclinic	triclinic	monoclinic	monoclinic
a [pm]	968.71(12)	990.34(10)	1367.8(2)	1591.15(14)
b [pm]	1223.32(14)	1245.15(14)	1220.6(2)	1164.74(14)
c [pm]	1493.14(18)	1483.4(2)	1040.3(2)	1197.08(10)
α [°]	92.497(10)	93.551(10)	90	90
β [°]	93.076(10)	94.787(10)	105.95(2)	102.496(6)
γ [°]	106.182(10)	104.200(8)	90	90
V [nm^3]	1.6937(4)	1.7604(4)	1.6699(5)	2.1660(4)
Z	2	2	4	4
d_c [gcm^{-3}]	1.748	1.849	2.127	1.915
μ [cm^{-1}]	58.76	55.58	112.30	41.84
$2\Theta_{max}$	50	50	50	50
Data (total)	6268	10239	5956	3998
Data (independent)	5965	6195	2929	3799
Restraints	0	0	0	146
Parameters	337	338	169	265
S (F^2)	0.758	0.856	0.761	0.873
R_1	0.0376	0.0287	0.0279	0.0280
wR_2	0.0563	0.0546	0.0488	0.0537

(graphite-monochromated Mo-K_α radiation, λ = 71.073 pm) at −100 °C in the ω-scan mode (Table 1 and Table 2). Cell parameters were refined from setting angles at 2Θ = 20−24°. Absorption corrections based on Ψ-scans were applied. The structures were solved by direct methods using SHELXS-86/97,[25] and subjected to full-matrix least-squares refinement on F^2 using SHELXL-93/97,[26] with anisotropic displacement parameters for non-H atoms. Correct positions for nitrogen and carbon atoms in the crystal structure of **2** were established from the refinement of alternative positions and subsequent comparison of the R values and the final electron density ($wR2$: 0.1585 vs. 0.1703, ρ_{max} 1.28·10^{-6} e pm^{-3}). Methyl groups were treated as rigid groups and N-bonded hydrogen atoms were refined freely. All other hydrogen atoms were included using a riding model. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications no. CCDC-150945 (**2**), -150946 (**6**), -150947 (**11**), -150948 (**12**), -150949 (**13**), -150950 (**14**), and -150951 (**15**). Copies

of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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