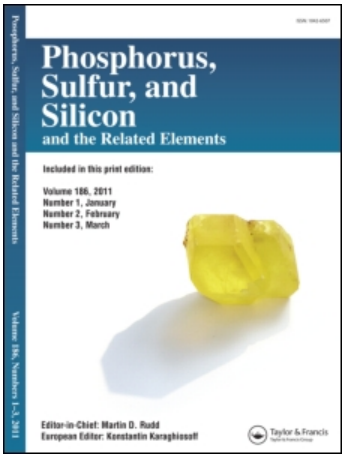

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Laube, Jörg and Thöne, Carsten(2001) 'The Novel Multidentate Ligands $^{t}BU_2P(2\text{-SePy})$ and $^{t}BUP(2\text{-SePy})_2$; Py = Pyridyl. Synthesis, Reactivity and Crystal Structures of Mo-, Cu- and Ag-Complexes', Phosphorus, Sulfur, and Silicon and the Related Elements, 169: 1, 173 — 176
To link to this Article: DOI: 10.1080/10426500108546618
URL: http://dx.doi.org/10.1080/10426500108546618

Phosphorus, Sulfur and Silicon, 2001, Vol. 169, pp. 173-176
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The Novel Multidentate Ligands $^tBU_2P(2\text{-SePy})$ and $^tBUP(2\text{-SePy})_2$; Py = Pyridyl. Synthesis, Reactivity and Crystal Structures of Mo-, Cu- and Ag-Complexes

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2-Pyridylseleno-phosphines can easily be synthesized via reaction of appropriate halophosphines with K(2-SePy) or [Et_4N][2-SePy]. The phosphines are extremely sensitive to oxygen and can be trapped as Cu-, Ag- or Mo-complexes via reaction with CuBr, AgBr and $[(\eta^6\text{-}C_7H_8)Mo(CO)_3]$. The crystal structures of $^tBuP(O)(2\text{-SePy})_2$ **7**, $[\{^tBu_2P(2\text{-SePy})\}\text{-}P,N\text{-}MBr]_2$, M = Cu **8**, Ag **9** and $[^tBuP(2\text{-SePy})_2\text{-}N,N',P\text{-}Mo(CO)_3]$ **10** have been determined.

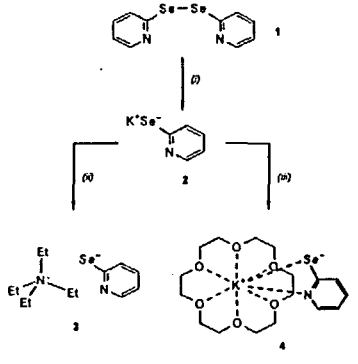
Keywords: Pyridiylselenolate; phosphine; metal complex

The current interest in the chemistry of heteroatom-substituted phosphines arises from their potential use in catalytical processes. One possibility of controlling the reaction pathways and the selectivity of phosphine-containing catalysts is the modification of the surrounding phosphine ligands by varying the donor-atom sets, which are usually C, N and P[1,2].

Here, we describe the synthesis and reactivity of novel 2-pyridylseleno-phosphine ligands that contain N-, P-, Se-donor sets. Recently, a few complexes containing the $SePy^-$ anion appeared in the literature, mainly in combination with Cd, Hg and Pd, as single-source precursors for metal selenides[3]. Starting from 2,2'-bis(pyridyl)diselenide[4] **1**, the $SePy^-$ anion can easily be obtained as depicted in Scheme 1. Reactions with K(*2*-SePy) **2** are usually performed *in situ*. [Et_4N][*2*-SePy] **3** is a useful derivative, because it can be stored under N_2 for a prolonged time without decomposition[5].

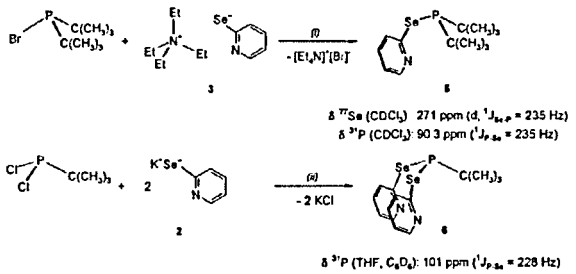
$^tBu_2P$(*2*-SePy) **5** and ^tBuP(*2*-SePy)$_2$ **6** can easily be prepared from halophosphines via reactions with **2** or **3** (Scheme 2)[6] in nearly quantitative yield (for **6** by NMR means).

5 and **6** are extremely air-sensitive oily liquids (**5** solidifies at 25°C). During the work-up procedure, **6** was fully oxidized to the corresponding phosphine oxide $^tBuP(O)$(*2*-SePy)$_2$ **7** (Fig. 2), which was characterized by spectroscopic and crystallographic means [δ ^{77}Se ($CDCl_3$): 438 ppm ($^1J_{Se\text{-}P}$ 418 Hz); δ ^{31}P (D_6-acetone): 72.1 ppm ($^1J_{P\text{-}Se}$ 413 Hz)] [6]. **7** represents the first crystal structure of a bis(pyridylseleno)phosphine oxide. The observed P-Se bond lengths are attributable to P-Se single bonds



SCHEME 1: Reaction conditions: *(i)* KB^{sec}Bu$_3$H, THF, 25°C; *(ii)* [Et_4N]Br, EtOH, 25°C; *(iii)* 18-crown-6, EtOH, 25°C.

and comparable to the central P-Se bonds in $[^tBuP(Se)(\mu\text{-}Se)]_2$ (2.269(2) Å)[7]. **5** and **6** were trapped as Cu-, Ag- and Mo-complexes via reactions with CuBr, AgBr or $[\eta^6\text{-}C_7H_8)Mo(CO)_3]$; tht = tetrahydrothiophene, C_7H_8 = cyclooctatriene) in excellent yield[6]. The reactions were performed under exclusion of light.



SCHEME 2: Synthesis of pyridylseleno-phosphines, reaction conditions: *(i)* CH_3CN, rt, 1h; *(ii)* THF, rt, 3h.

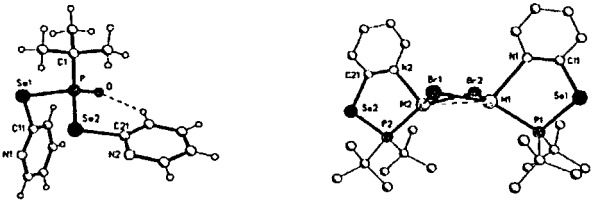


FIGURE 1: The crystal structures of **7** (left, *C*2/c, Z = 8) and the crystal structures of **8** and **9** (right, *P*-1, Z = 2) displaying the five-membered MPSeCN-rings. Selected bond lengths [Å] and angles [°]: **7** P-Se1 2.2468(11), P-Se2 2.2562(12), P-O 1.470(3), Se1-C11 1.933(4), Se2-C21 1.951(4); C11-Se1-P 95.28(12), C21-Se2-P 104.92(12). **8** [**M = Cu**] Cu-P1 2.2015(17), P1-Se1 2.2641(17), Se1-C11 1.918(6), C11-N1 1.344(6), Cu-N1 2.109(4), Cu-Br1 2.4596(10), Cu-Br2 2.4977(10), Cu---Cu 3.1430(11), Br---Br 3.7766(10); N1-Cu1-P1 95.11(14), Cu-P1-Se1 101.07(7), P1-Se1-C11 99.31(17). **9** [**M = Ag**] Ag-P1 2.4116(11), P1-Se1 2.2545(12), Se1-C11 1.945(4), C11-N1 1.325(5), Ag-N1 2.456(3), Ag-Br1 2.6312(6), Ag-Br2 2.7017(6), Ag---Ag 3.1333(6), Br---Br 4.2153(8); N1-Ag-P1 85.14(8), Ag-P1-Se1 105.33(5), P1-Se1-C11 100.98(12).

The molybdenum complex is shown in Fig. 2. Mo is coordinated octahedrally with a fac-pyridylseleno-phosphine ligand.

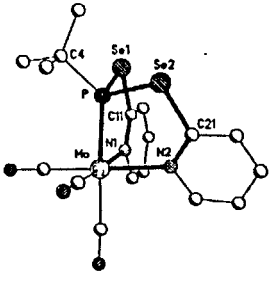


FIGURE 2: The molecular structure of **10**. Selected bond lengths [Å] and angles [°]: Mo-P 2.3924(10), P-Se1 2.2659(10), P-Se2 2.2712(10), Mo-N 2.302(3) av., Se-C 1.920(4) av.; Se1-P-Mo 108.01(4), Se2-P-Mo 106.21(4), C4-P-Mo 132.32(12), C4-P-Se1 101.31(12), C4-P-Se2 101.26(12), P-Se1-C11 97.79(11), P-Se2-C21 96.28(11).

Acknowledgements

We thank Prof. Peter G. Jones for generous support, A. Weinkauf for diffractometer maintenance and the Fonds der Chemischen Industrie for financial support.

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