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Phosphine Chalcogenides

Tri(3-pyridyl)- and Tri(4-pyridyl)phosphine Chalcogenides and Their Complexes with ZnTPP (TPP = Tetraphenylporphyrinate)

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Abstract: The preparation, spectroscopic characterization (NMR and IR spectroscopy), and solid-state structures of tri(3-pyridyl)- and tri(4-pyridyl)phosphine chalcogenides (E = O, S, Se) as well as their ability to behave as ligands for ZnTPP (TPP = tetraphenylporphyrinate) moieties are reported. In the solid state, the compounds from this family are three-bladed molecular propellers that crystallize as racemates. Both triorganophosphine sulfides and selenides, $(3\text{-Py})_3$PE [Py = pyridyl, NC_5H_4; E = S (**2**), Se (**3**)] and $(4\text{-Py})_3$PE [E = S (**6**), Se (**7**)], quantitatively form complexes with ZnTPP by selective coordination of all three pyridyl groups of a molecular unit to three metalloporphyrin moieties. The formation of these complexes in chlorinated solvents is unambiguously proven by spectroscopic methods (i.e., multinuclear NMR and UV/Vis spectroscopy). The affinity of these ligands towards ZnTPP is different in benzene, yielding a mixture of products in solution.

Introduction

Heterometallic complexes are expected to possess novel properties with respect to their homometallic counterparts.[1] This particularity can be exploited in many applications, especially in cooperative and tandem catalysis.[2] Ligands able to form such coordinative heterometallic species have to be intelligently designed to be able to selectively coordinate different metal centers. Tri(3-pyridyl)phosphane achieves this goal and furthermore its heterometallic complex formed with ZnTPP and $RhH(CO)_3$ showed excellent selectivity in the hydroformylation of *trans*-2-alkenes.[3] Such ligands containing nitrogen donor groups and a P^{III} center have been found to bind tetracoordinate Zn complexes selectively through the pyridyl moieties with no affinity of the phosphorus for zinc.[3,4] This is due to the more pronounced σ-donor character of the nitrogen atom. On the other hand, a transition metal will selectively bind to the P^{III} center, the bond being stabilized by the π-acceptor character of the later. This is perhaps the reason why organophosphorus(III) ligands benefit and have benefited from such a high level of interest in coordination chemistry.[5] Despite this fact, organophosphorus compounds can successfully be used as ligands even when phosphorus is in oxidation state V. In such compounds, phosphorus loses its electron-donating ability, but keeps its other most important role as an NMR active nucleus with a high sensitivity to its chemical environment. Trialkyl- and triarylphosphine chalcogenides, R_3PE (E = O, S, Se), readily form complexes with various main group and transition metals.[6] Our aim within this research was to prepare and to structurally characterize tri(3-pyridyl)- and tri(4-pyridyl)phosphine chalcogenides and then to study their coordination behavior. These proligands possess two different donor atoms (nitrogen and chalcogen), which can coordinate to different metal centers. They might, thus, be useful as tetrahedral tectons to build heterometallic supramolecular architectures and their coordination behavior can be monitored through ^{31}P NMR spectroscopy.

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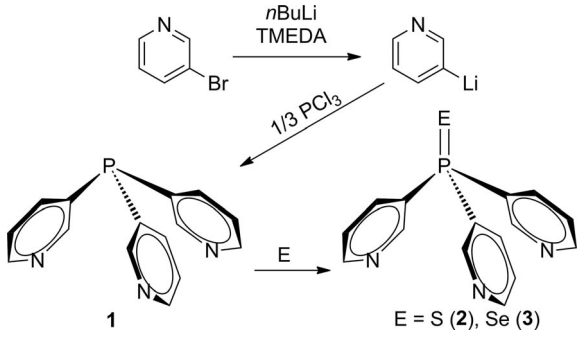
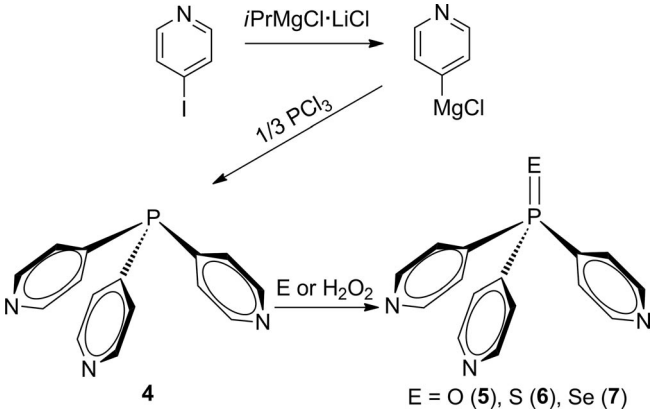
Results and Discussion

Preparation

Tri(3-pyridyl)phosphane (**1**) was prepared according to a published method (Scheme 1).[7] The 4-pyridyl analog was obtained by using 4-iodopyridine, which was converted into the corresponding Grignard reagent[8] by using *i*PrMgCl·LiCl and was subsequently reacted with PCl_3 in a 3:1 molar ratio. After working up, the crude reaction product consisted of a complex mixture with the tri(4-pyridyl)phosphane (**4**) being the major product (Scheme 2). The use of a 6:1 molar ratio for the same reaction between 4-PyMgCl and PCl_3 yielded similar patterns in the ^{31}P NMR spectrum of the crude product, but with a lower yield. Pure **4** crystallizes from the brown oily crude when left standing for a few days. Oxidation reactions were carried out with hydrogen peroxide, elemental sulfur, and selenium. The oxidation of P^{III} to P^{V} with hydrogen peroxide was optimized first for triphenylphosphine (see the Supporting Information). Similarly, attempts were made for the oxidation of triphenylphosphine to the corresponding telluride, Ph_3PTe. However, elemental tellurium was found to be unreactive towards Ph_3P even when dissolved in a mixture of ethylene diamine and 2-mercaptoethanol (4:1). Similar mixtures have been reported to easily dissolve elemental selenium and tellurium.[9]



Scheme 1. Synthesis of tri(3-pyridyl)phosphine chalcogenides.

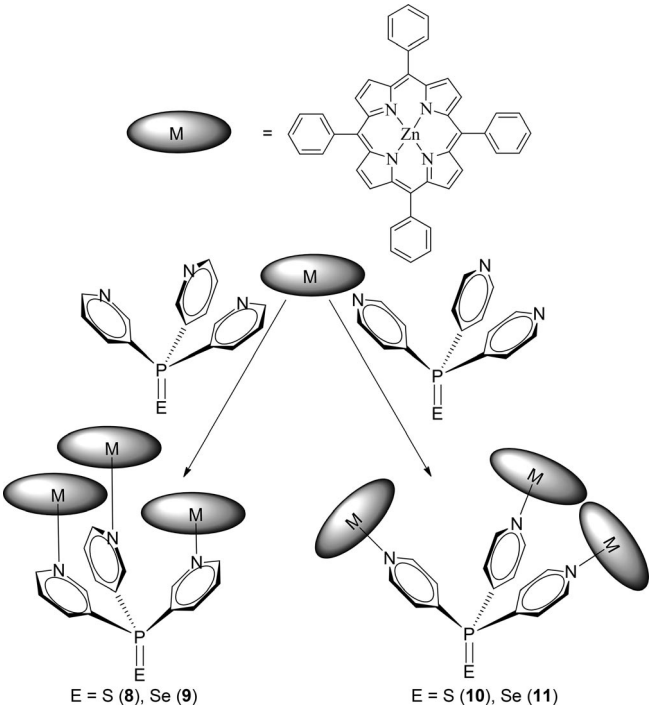


Scheme 2. Synthesis of tri(4-pyridyl)phosphine chalcogenides.

Heating crude tri(3-pyridyl)phosphane (**1**) at reflux overnight in toluene with excess elemental S or Se, respectively, yielded the corresponding sulfide (**2**) and selenide (**3**) (Scheme 1). The excess sulfur was removed by filtration from an Et_2O solution of the sulfide **2**. The selenide **3** was obtained by extraction with CH_2Cl_2 from the crude product. Both compounds were obtained as pure colorless (**2**) and pale yellow (**3**) solids after working up the crude products.

Phosphane **4** can easily be oxidized to the corresponding oxide **5** and sulfide **6** by using H_2O_2 or elemental sulfur, respectively (Scheme 2). During the preparation of the sulfide **6**, the formation of the oxide **5** has to be avoided as these compounds cannot be separated by fractional crystallization or by chromatographic methods. The selenide **7** was obtained by heating crude **4** at reflux with excess elemental selenium. After working up the crude products, the chalcogenides **5**, **6**, and **7** were obtained as colorless solids.

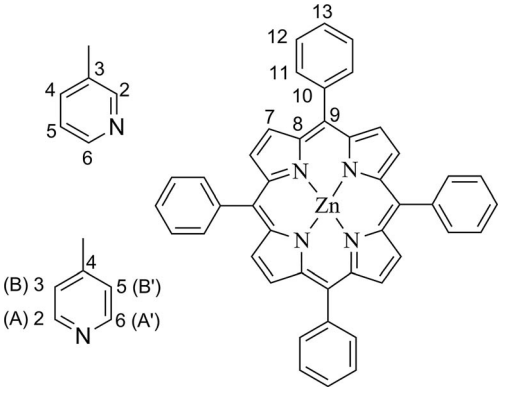
The reaction of the parent triorganophosphine chalcogenides **2**, **3**, **6**, and **7** with three equivalents of ZnTPP (TPP = tetraphenylporphyrinate), in chlorinated solvents, readily form the corresponding metal complexes **8**–**11** (Scheme 3) as deep-purple solids. Attempts to grow X-ray quality crystals by diffusion of hydrocarbons into $CHCl_3$ or CH_2Cl_2 solutions of the complexes yielded only amorphous solids. On the other hand, similar attempts using hydrocarbons/benzene solutions led to the crystallization of free ZnTPP. This observation is consistent with the weak pyridine–ZnTPP interaction reported for similar species.[4a]



Scheme 3. Synthesis of ZnTPP complexes of triorganophosphine chalcogenides **2**, **3**, **6**, and **7**.

Spectroscopic Studies

All the new triorganophosphine chalcogenides were investigated by using multinuclear NMR spectroscopy. The ^1H and ^{13}C resonances for all compounds reported in this work were assigned by using 2D NMR experiments according to the numbering scheme shown in Scheme 4. As expected, the ^1H NMR spectra of the tri(3-pyridyl)phosphine sulfide **2** and selenide **3** display four resonances corresponding to protons in positions 2, 4, 5, and 6. It is worthwhile to note that the coupling constant $^3J_{PH}$ has values of 13.8 Hz (for **2**) and 14.2 Hz (for **3**) for H-4, whereas smaller $^3J_{PH}$ values were observed for the coupling for **3** (7.7 Hz). The ^1H NMR spectra for all the tri(4-pyridyl)phosphine chalcogenides display two multiplet resonances corresponding to H-2/H-6 and H-3/H-5 in an AA'BB' pattern for phosphorus with H-2 of the pyridyl ring, with $^3J_{PH}$ = 8.0 Hz (for **2**). The ^{13}C NMR spectra display doublet resonances in the cases of



Scheme 4. Numbering scheme for NMR spectra assignments.

all the title triorganophosphine chalcogenides with J_{PC} coupling constants ranging from 2.5 to 100.1 Hz. The $^1J_{PC}$ value varies linearly in the series of the tri(4-pyridyl)phosphine chalcogenides with values of 100.1 Hz (oxide **5**), 80.3 Hz (sulfide **6**), and 71.2 Hz (selenide **7**), respectively.

The chemical shifts observed in the ^{31}P and ^{77}Se NMR spectra of all compounds are summarized in Table 1. Within the series of tri(4-pyridyl)phosphine chalcogenides (oxide, sulfide, selenide) the chemical shifts of the ^{31}P resonances range from δ = 22.4 ppm for oxide **5** to δ = 38.4 ppm for sulfide **6**. Selenide **7** yields a resonance in-between at δ = 31.4 ppm. Similarly, in the case of the tri(4-pyridyl)phosphine chalcogenides, the ^{31}P resonance observed for the sulfide **2** at δ = 33.2 ppm is more shielded than the corresponding resonance at δ = 23.7 ppm for the selenide **3**. The ^{77}Se NMR spectra of the selenides **3** and **7** display doublet resonances at δ = –275.5 and –304.7 ppm owing to coupling with phosphorus.

Table 1. The ^{31}P and ^{77}Se NMR chemical shifts (ppm; solvent: $CDCl_3$) observed for **1**–**7**.

	δ (^{31}P)	δ (^{77}Se)	Ref.
1	–24.7(s)	–	[6]
2	33.2(s) ($^1J_{PC}$ = 83.9 Hz)	–	this work
3	23.7 ($^1J_{PC}$ = 75.9 Hz, $^1J_{PSe}$ = 770.1 Hz)	–275.5(d) ($^1J_{PSe}$ = 770.1 Hz)	this work
4	–10.8(s)	–	[6]
5	22.4(s)	–	this work
6	38.4(s)	–	this work
7	31.4(s) ($^1J_{PC}$ = 70.4 Hz $^1J_{PSe}$ = 784.7 Hz)	–304.7(d) ($^1J_{PSe}$ = 785.9 Hz)	this work
8	27.4(s)	–	this work
9	18.9(s) ($^1J_{PSe}$ = 790.9 Hz)	–253.6(d) ($^1J_{PSe}$ = 791.0 Hz)	this work
10	35.2(s)	–	this work
11	28.6(s) ($^1J_{PSe}$ = 798.7 Hz)	–298.7(d) ($^1J_{PSe}$ = 799.2 Hz)	this work

Evidence of the formation of the complexes **8**–**11** in solution is provided by their ^{1}H NMR spectra. In all these cases, the resonances corresponding to the pyridyl groups are significantly shifted upfield owing to the shielding effect of the metalloporphyrin. This upfield shift ranges from $\Delta\delta$ = 1.88 ppm for H-2 in complex **9** compared with ligand **3**, to $\Delta\delta$ = 6.43 ppm for H-5 in complex **11** compared with ligand **7**. The selective complexation of triorganophosphine selenides **3** and **7** with ZnTPP through the nitrogen atoms of the pyridyl rings can be best evidenced by the ^{77}Se NMR spectra. In both cases, the resonances found for the complexes are slightly shifted downfield with respect to the corresponding free ligands (Table 1). The ^{77}Se NMR spectrum of complex **9** displays one doublet resonance at δ = –253.6 ppm versus –275.5 ppm ($\Delta\delta$ = 21.9 ppm) in the free selenide **3**. The deshielding induced by complexation of **7** (δ = –304.7 ppm) to form complex **11** (δ = –298.7 ppm) is even less ($\Delta\delta$ = 6 ppm). Considering the high sensitivity of ^{77}Se NMR spectroscopy, these variations suggest no significant change in the environment around the Se centers in the respective species. The resonances observed in the ^{31}P NMR spectra for the complexes **9** and **11** are slightly more deshielded than in the corresponding free ligands **3** and **7**, respectively [$\Delta\delta$ = 4.8 ppm (**3** vs. **9**) and $\Delta\delta$ = 2.8 ppm (**7** vs. **11**)]. These differences are very similar for the analogous sulfide free ligand/complex pairs [$\Delta\delta$ = 5.8 ppm (**2** vs. **8**) and $\Delta\delta$ = 3.2 ppm (**6** vs. **10**)]. Therefore, by analogy to the complexation behavior of selenides **3** and **7**, which could easily be investigated by ^{77}Se NMR spectroscopy, we can state that sulfides **2** and **6** will coordinate to ZnTPP exclusively through the pyridyl moieties.

The lack of significant change in the magnitude of the ν(P=E) (E = S, Se) stretching vibration observed for the free triorganophosphine chalcogenides **2**, **3**, **6**, and **7** and for the corresponding metal complexes **8**–**11** suggests that in the solid state the ZnTPP moieties are coordinated only to the nitrogen atoms of the triorganophosphine chalcogenides.

ESI+ HRMS spectra recorded for **9**, postulated as a 1:3 complex, reveal associations with ligand-to-ZnTPP ratios up to 1:4 (see the Experimental Section for details). On the other hand, fragments corresponding to 1:1 ligand-to-ZnTPP ratios could be observed in the HRMS ESI+ spectra of complexes **10** and **11**, whereas for **8** no fragments containing both the ligand and ZnTPP could be detected.

To obtain further insight into the behavior of the obtained complexes in solution, we selected the system $(4\text{-Py})_3$PSe/ZnTPP for a model study through detailed multinuclear NMR investigations. Owing to the dynamic behavior, that is, a rapid de-coordination–re-coordination process, even for a 1:1 molar ratio between $(4\text{-Py})_3$PSe (**7**) and ZnTPP, the room-temperature ^{1}H NMR spectrum displays only one set of resonances for the pyridyl groups owing to their equivalence on the NMR timescale. This behavior is preserved even at –60 °C. The binding stoichiometry between $(4\text{-Py})_3$PSe (**7**) and ZnTPP was investigated by NMR and UV/Vis spectroscopy. Job plot analysis based on ^{1}H and ^{31}P NMR spectroscopy shows the formation of a 1:3 complex, that is, **11** (see the Supporting Information). Binding constants of the ZnTPP units to $(4\text{-Py})_3$PSe were determined by using UV/Vis titration. According to the findings from the Job plot analyses, the titration curve was fitted against a 1:3 model to give the association constants K_{a1} [$(10.9 \pm 0.3) \times 10^3$ M^{-1}], K_{a2} [$(2.8 \pm 0.7) \times 10^3$ M^{-1}], and K_{a3} [$(2.1 \pm 1.1) \times 10^3$ M^{-1}] for the first, second, and third bindings of ZnTPP to $(4\text{-Py})_3$PSe (**7**). The binding of ZnTPP to $(4\text{-Py})_3$PSe through the nitrogen atoms is very selective. This is supported by the UV/Vis titrations of ZnTPP with Ph_3PSe, which shows no interaction between these two species (see the Supporting Information).

X-ray Crystallography

The molecular structures were determined for tri(3-pyridyl)-phosphine sulfide (**2**) and selenide (**3**), tri(4-pyridyl)phosphane (**4**), tri(4-pyridyl)phosphine oxide (**5**) and selenide (**7**) and are depicted in Figure 1, while selected interatomic distances and angles are summarized in Table 2.

Compounds from this family can be regarded as three-bladed molecular propellers of Py_3PE type (E = chalcogen, lone pair of electrons) with the pyridyl groups being the blades and the phosphorus atom being the propeller hub.[10] The *propeller*

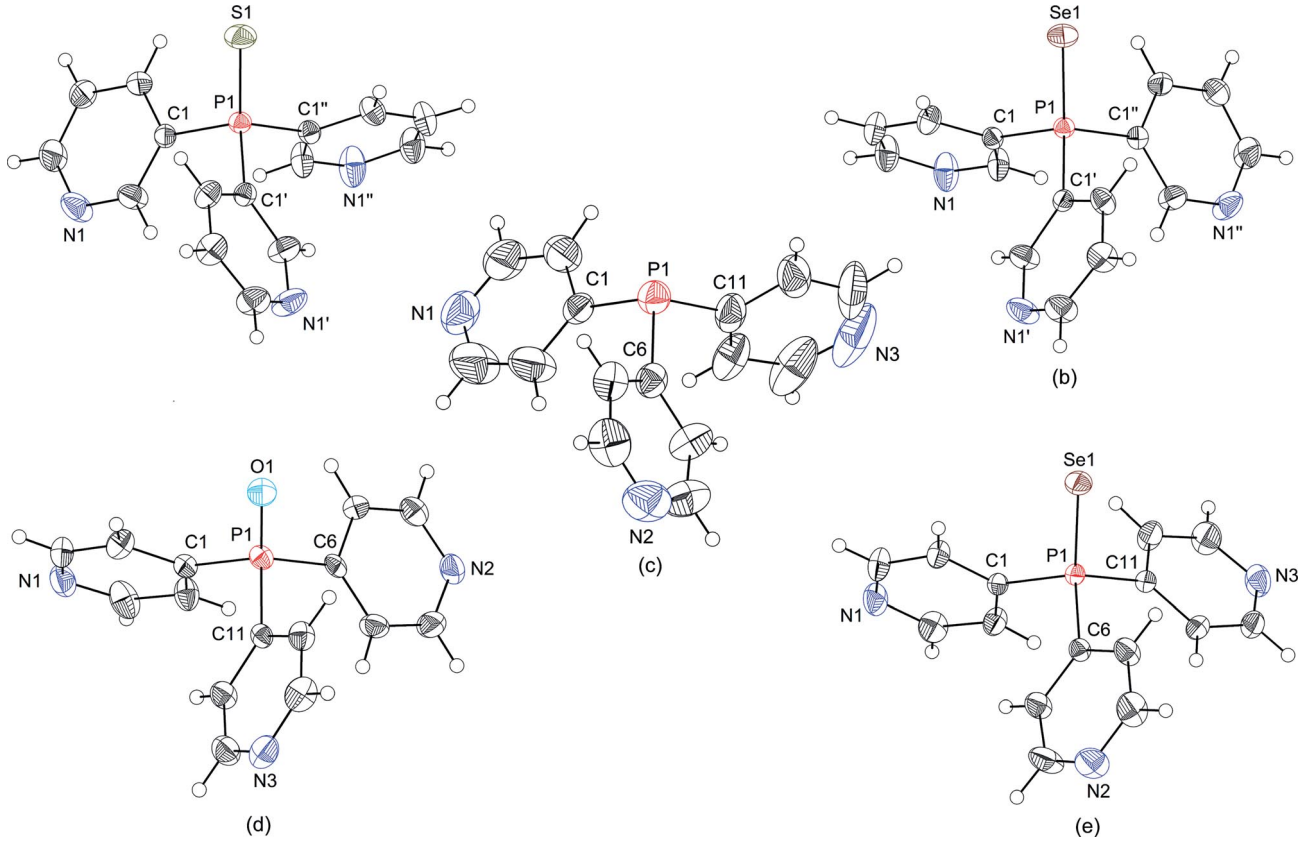


Figure 1. ORTEP representations (at the 30 % probability level) of (a) sulfide **2** (*M* isomer); (b) selenide **3** (*P* isomer); (c) phosphane **4** (*M* isomer); (d) oxide **5** (*P* isomer); (e) selenide **7** (*M* isomer). For **2** and **3**, the symmetry equivalent atoms (2 – *x* + *y*, 1 – *x*, *z*) and (1 – *y*, –1 + *x* – *y*, *z*) are given by "prime" and "double prime", respectively.

Table 2. Selected bond lengths [Å] and angles [°] for **2**, **3**, **4**, **5**, and **7**.

	2	**3**		**4**	**5**	**7**
P(1)–C(1)	1.812(4)	1.808(5)	P(1)–C(1)	1.820(5)	1.803(6)	1.817(3)
			P(1)–C(6)	1.832(5)	1.808(6)	1.817(3)
			P(1)–C(11)	1.826(5)	1.821(6)	1.816(3)
P(1)–E(1)	1.946(2)	2.102(2)	P(1)–E(1)	–	1.473(4)	2.101(1)
C(1)–P(1)–C(1′)[a]	105.3(1)	105.6(2)	C(1)–P(1)–C(6)	102.7(2)	105.1(1)	105.8(1)
C(1)–P(1)–C(1″)[a]	105.3(1)	105.6(2)	C(1)–P(1)–C(11)	101.8(2)	105.2(3)	106.3(1)
C(1′)–P(1)–C(1″)[a]	105.3(1)	105.6(2)	C(6)–P(1)–C(11)	102.3(2)	105.9(2)	105.7(1)
Σ[C–P–C]	315.9	316.8		306.8	316.2	317.8
E(1)–P(1)–C(1)	113.4(1)	113.1(2)	E(1)–P(1)–C(1)	–	113.6(3)	113.5(1)
			E(1)–P(1)–C(6)	–	113.5(2)	112.9(1)
			E(1)–P(1)–C(11)	–	112.7(3)	112.0(1)
α(C1)[b]	42.0(1)	42.6(1)	α(C1)[b]	52.9(2)	38.4(3)	29.4(1)
			α(C6)[b]	39.9(2)	43.9(2)	45.4(1)
			α(C11)[b]	23.0(2)	38.8(2)	67.2(1)

[a] Symmetry equivalent atoms (2 – *x* + *y*, 1 – *x*, *z*) and (1 – *y*, –1 + *x* – *y*, *z*) are given by "prime" and "double prime", respectively. [b] For the definition of the dihedral angle α(C*x*), see the text.

plane (or *reference plane*) is defined by the *ipso* carbon atoms of the pyridyl rings. The axis of rotation is defined by the P=E bond or the axis of the orbital occupied by the lone pair and it is perpendicular to the propeller plane. Although the tri(4-pyridyl)phosphane and its chalcogenides only possess two enantiomeric forms (*M* and *P*), the tri(3-pyridyl)phosphane and chalcogenide analogs have more possible diastereoisomers owing to the possible placement of the pyridyl nitrogen atom above or below the propeller plane.[11] Both in the tri(3-pyridyl)phosphine sulfide **2** and in the related selenide **3** the nitrogen atoms of the pyridyl rings are placed on the opposite sides of the propeller plane with respect to the phosphorus atom.

All compounds, for which X-ray quality crystals were obtained, crystallize as racemates regarding the helical chirality. The rotation of the pyridyl rings is correlated, as this conformation is energetically favored.[12] The pitch of these propellers depends on the dihedral angle α(C*x*) between a blade and the plane defined by the *ipso* carbon atom (C*x*) of the respective blade, the phosphorus, and the chalcogen atom (or lone pair of electrons on phosphorus for the phosphane **4**). An α(C*x*) angle of 0° would mean an infinite pitch, whereas a value of 90° for the α angle will correspond to zero pitch.

Although the molecules of the tri(3-pyridyl)phosphine sulfide **2** and selenide **3** possess a C_3 axis, the tri(4-pyridyl)phosphane **4** and its corresponding oxide **5** and selenide **7** all have C_1 symmetry. As a consequence, all blades of compounds **2** and **3** will have the same pitch, whereas in the case of **4**, **5**, and **7** the pitch of the blades varies significantly within one molecule by as much as 37.8° in **7**.

The value of the P=O bond length [1.473(3) Å] in **5** is slightly shorter than that in Ph_3P=O [1.492(1) Å],[13] whereas the P=S bond length of 1.946(2) Å in **2** is almost identical to that found in Ph_3P=S [1.950(3) Å].[14] The P=Se bond lengths of 2.102(2) Å in **3** and 2.101(1) Å in **7** are equivalent to the analogous bond lengths in triphenylphosphine selenide [2.105(2), 2.107(2) Å].[15] The sums of the C–P–C angles at the phosphorus atom in the triphenylphosphine oxide (319.4°), sulfide (316.9/317.4°), and selenide (317.2/316.6°) are very similar to the values found in the tripyridylphosphine chalcogenides reported herein (see Table 1).

Conclusions

The preparation and structural characterization in solution and in the solid state of tri(3-pyridyl)- and tri(4-pyridyl)phosphine chalcogenides are described herein. All compounds from this class can be regarded as three-bladed molecular propellers. Compounds **2**, **3**, **4**, **5**, and **7** crystallized as racemates (*M* and *P* isomers) regarding this type of helical chirality. The blades of tri(3-pyridyl)phosphine sulfide and selenide have identical pitch and C_3 symmetry, whereas the 4-pyridyl derivatives have C_1 symmetry and significant differences between the pitch of the blades within a molecule. Selective complexation of the tripyridylphosphine sulfides and selenides through the nitrogen centers was achieved with ZnTPP. Formation of the new Zn complexes is quantitative in chlorinated solvent solutions. In benzene, on the other hand, presumably solvation of the ZnTPP by π···π interactions prevents the formation of 1:3 complexes; the ^{31}P NMR spectra of the reaction mixture exhibited a more complex pattern and attempts to isolate solid products yielded X-ray quality crystals of free ZnTPP. Formation of heterometallic complexes (monomeric or polymeric) using these proligands is currently under investigation.

Experimental Section

General Measurements and Analysis Instrumentation: Multinuclear NMR spectra (^{1}H, ^{13}C, ^{31}P, ^{77}Se) were recorded at room temperature with a Bruker Avance III 400 or Bruker Avance III 600 instrument. The ^{1}H chemical shifts are reported in δ units (ppm) relative to the residual peak of the deuterated solvent ($CHCl_3$, 7.26 ppm). The ^{13}C chemical shifts are reported in δ units (ppm) relative to the peak of the deuterated solvent ($CDCl_3$, 77.16 ppm).[16] The ^{31}P chemical shifts are reported relative to H_3PO_4 85 % in H_2O (δ = 0 ppm), which was used as the external standard. The ^{77}Se chemical shifts are reported relative to Me_2Se (δ = 0 ppm) by using an external standard of Ph_2Se_2 (δ = 461 ppm).[17] The ^{1}H and ^{13}C resonances were assigned by using 2D NMR experiments (COSY, ROESY, HSQC, HMBC). The NMR spectra were processed by using the *MestReC* and *MestReNova* software.[18] HRMS APCI(+) and ESI(+) spectra were recorded with a Thermo Scientific Orbitrap XL spectrometer. Data analysis and calculations of the theoretical isotopic patterns were carried out with the Xcalibur software package.[19] Infrared spectra were recorded in the range 4000–500 cm^{-1} with a Bruker Vector 22 spectrometer. A Jasco V-550 UV/Vis spectrophotometer with double beam system with single monochromator (Tokyo, Japan), in absorbance mode, was used for spectra acquisition in the range 200–800 nm. The acquired spectra of the CH_2Cl_2 solutions were stored after the smoothing process. The Spectra Manager for Windows 95/NT version 1.53.04 (1995–2002, Jasco Corporation) software package was used for the spectra acquisition control, smoothing process, storage, and spectroscopic data digitization.

Crystal Structure Determination: Suitable crystals for X-ray diffraction were obtained by slow evaporation of the solvent (1:1 mixture of CH_2Cl_2 and Et_2O) from solutions of compounds **2**, **3**, **5**, and **7**. The oily brown crude of **4** affords X-ray quality crystals upon standing at room temperature for approximately 3 days. Crystallographic data were collected with a Bruker SMART APEX diffractometer using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). The structures were solved by using SHELXS-97[20] and refined, with anisotropic thermal parameters for all non-hydrogen atoms, by using SHELXL-2013 or SHELXL-2014/6.[21] The isotropic displacement parameters for the hydrogen atoms were set with respect to those of the atom to which they are directly attached. The details of the crystal structure determination and refinement are given in Tables S1 and S2 (see the Supporting Information). The drawings were created with the Diamond program.[22]

CCDC 1437261 (for **2**), 1437262 (for **3**), 1437263 (for **4**), 1437264 (for **5**), and 1437265 (for **7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Materials and Procedures: All manipulations involving air-sensitive compounds were carried out under an inert atmosphere of argon by using Schlenk techniques. Tetrahydrofuran, diethyl ether, and toluene were freshly distilled prior to use, under an argon atmosphere, from sodium or potassium as drying agents. All other solvents were used as received. PCl_3 was distilled under argon before use. 4-Iodopyridine,[23] Turbo Grignard reagent,[24] ZnTPP,[25] and tri(3-pyridyl)phosphane (**1**)[7] were prepared according to literature procedures.

Tri(3-pyridyl)phosphine Sulfide (2): Crude tri(3-pyridyl)phosphane (**1**), prepared from excess 3-lithiopyridine and PCl_3 (7 mmol), was heated at reflux with elemental sulfur (2.44 g, 76 mmol) in toluene (70 mL) under an argon atmosphere. After evaporation of the solvent, the residue was extracted with Et_2O (2 × 100 mL). Upon cooling to –20 °C, the concentrated extract (ca. 20 mL) gave the title compound as a colorless solid, yield 1.52 g (30 %), m.p. 155–157 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 8.80 (m, 6 H, 5-H and 6-H), 8.17 (ddt, $^3J_{PH}$ = 13.8, $^3J_{HH}$ = 7.9, $^4J_{HH}$ = 2.0 Hz, 3 H, 4-H), 7.48 (ddd, $^3J_{PH}$ = 8.0, $^4J_{HH}$ = 4.8, $^4J_{HH}$ = 2.3 Hz, 3 H, 2-H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$, 20 °C): δ = 153.12 (d, $^4J_{PC}$ = 2.5 Hz, C-6), 152.25

(d, $^3J_{PC}$ = 11.9 Hz, C-5), 140.03 (d, $^2J_{PC}$ = 9.8 Hz, C-4), 127.90 (d, $^1J_{PC}$ = 84.3 Hz, C-3), 124.0 (d, $^2J_{PC}$ = 9.6 Hz, C-2) ppm. ^{31}P NMR (162 MHz, $CDCl_3$, 20 °C): δ = 33.2 (s, $^1J_{PC}$ = 83.9 Hz) ppm. IR (KBr): $\tilde{\nu}$ = 656 (m) (P=S) cm^{-1}. HRMS (APCI+): calcd. for $[C_{15}H_{13}N_3PS]^+$: 298.05623; found: 298.05600.

Tri(3-pyridyl)phosphine Selenide (3): Crude tri(3-pyridyl)phosphane (**1**), prepared from excess 3-lithiopyridine and PCl_3 (7 mmol), was heated at reflux with Se (6 g, 76 mmol) in toluene (70 mL) under an argon atmosphere. After evaporation of the solvent, the residue was extracted with CH_2Cl_2 (2 × 100 mL). The solvent was removed from the clear extract and the remaining product was washed with cold acetone and Et_2O to give a pale-yellow solid, yield 1.96 g (34 %), m.p. 203–205 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 8.77 (m, 6 H, 5-H, 6-H), 8.19 (ddt, $^3J_{PH}$ = 14.2, $^3J_{HH}$ = 8.0, $^4J_{HH}$ = 2.0 Hz, 3 H, 4-H), 7.47 (ddd, $^3J_{PH}$ = 7.7, $^4J_{PH}$ = 4.8, $^4J_{HH}$ = 2.3 Hz, 3 H, 2-H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$, 20 °C): δ = 153.07 (d, $^4J_{PC}$ = 2.5 Hz, C-6), 152.31 (d, $^3J_{PC}$ = 11.5 Hz, C-5), 140.62 (d, $^2J_{PC}$ = 10.4 Hz, C-4), 126.66 (d, $^1J_{PC}$ = 75.2 Hz, C-3), 123.99 (d, $^2J_{PC}$ = 9.7 Hz, C-2) ppm. ^{31}P NMR (162 MHz, $CDCl_3$, 20 °C): δ = 23.7 (s, $^1J_{PC}$ = 75.9, $^1J_{PSe}$ = 770.1 Hz) ppm. ^{77}Se NMR (76 MHz, $CDCl_3$, 20 °C): δ = –275.5 (d, $^1J_{PSe}$ = 770.1 Hz) ppm. IR (KBr): $\tilde{\nu}$ = 574 (m) (P=Se) cm^{-1}. HRMS (APCI+): calcd. for $[C_{15}H_{13}N_3PSe]^+$: 346.00068; found: 346.00027.

Tri(4-pyridyl)phosphane (4): A solution of *i*PrMgCl·LiCl in THF (3.84 mL, 1.27 M) was added dropwise to a stirred solution of 4-iodopyridine (1 g, 4.88 mmol) in anhydrous Et_2O (50 mL) at –60 °C. After stirring for 90 min at this temperature, a solution of PCl_3 (0.22 g, 1.6 mmol) in anhydrous Et_2O (20 mL) was slowly added to the reaction mixture. Stirring was continued overnight and the temperature was allowed to reach room temperature. The reaction mixture was poured into degassed water and the phases were separated. The aqueous phase was extracted with CH_2Cl_2 and the combined organic phases were dried with Na_2SO_4. After evaporation of the solvents, the crude brown oil afforded colorless X-ray quality crystals upon standing at room temperature for a few days. The NMR spectra were identical to those reported.[7] Yield 0.19 g (45 %).

Tri(4-pyridyl)phosphine Oxide (5): A solution of **4** (0.15 g, 0.56 mmol) in CH_2Cl_2 (20 mL) was treated with H_2O_2 (6 mL, 3 %) and stirred for 3 h. The aqueous layer was discarded and evaporation of the solvent from the organic phase yielded the title compound as a colorless solid, yield 0.15 g (95 %), m.p. 117 °C (dec.). ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 8.84 (m, AA′BB′ spin system, 6 H, 2-H and 6-H), 7.53 (m, 6 H, 3-H and 5-H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$, 20 °C): δ = 150.65 (d, $^2J_{PC}$ = 9.9 Hz, C-2 and C-6), 138.92 (d, $^1J_{PC}$ = 100.1 Hz, C-4), 125.38 (d, $^3J_{PC}$ = 8.1 Hz, C-3 and C-5) ppm. ^{31}P NMR (162 MHz, $CDCl_3$, 20 °C): δ = 22.4 (s) ppm. IR (KBr): $\tilde{\nu}$ = 1262 (s), 1017 (s) (P=O) cm^{-1}. HRMS (APCI+): calcd. for $[C_{15}H_{13}N_3PO]^+$: 282.07908; found: 282.07902.

Tri(4-pyridyl)phosphine Sulfide (6): A solution of *i*PrMgCl·LiCl in THF (3.84 mL, 1.27 M) was added dropwise to a stirred solution of 4-iodopyridine (1 g, 4.88 mmol) in anhydrous Et_2O (50 mL) at –60 °C. After stirring for an additional 90 min at this temperature, a solution of PCl_3 (0.22 g, 1.6 mmol) in anhydrous Et_2O (20 mL) was slowly added to the reaction mixture. Stirring was continued overnight and the temperature was allowed to reach room temperature, after which the solvent was evaporated in vacuo and dry hot toluene was added over the remaining solid. The remaining solid was filtered off with a cannula and the clear solution was heated at reflux with elemental sulfur (0.1 g, 3.2 mmol) for 8 h. After evaporation of the solvent, the residue was extracted with Et_2O (2 × 50 mL). Upon cooling to –20 °C, the concentrated extract (ca. 10 mL) gave the title compound as a colorless solid, yield 0.14 g (30 %), m.p. 118–120 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 8.82 (m, AA′BB′ spin system, 6 H, 2-H and 6-H), 7.57 (m, 6 H, 3-H and 5-H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$, 20 °C): δ = 150.63 (d, $^2J_{PC}$ = 9.8 Hz, C-2 and C-6), 139.91 (d, $^1J_{PC}$ = 80.3 Hz, C-4), 125.38 (d, $^3J_{PC}$ = 8.4 Hz, C-3 and C-5) ppm. ^{31}P NMR (162 MHz, $CDCl_3$, 20 °C): δ = 38.4 (s) ppm. IR (KBr): $\tilde{\nu}$ = 640 (s) (P=S) cm^{-1}. HRMS (APCI+): calcd. for $[C_{15}H_{13}N_3PS]^+$: 298.05623; found: 298.05596.

Tri(4-pyridyl)phosphine Selenide (7): Crude **4**, obtained as described above from PCl_3 (1.6 mmol), was heated at reflux with Se powder (0.25 g, 3.2 mmol) in toluene (50 mL) in an inert atmosphere for 8 h. After evaporation of the solvent, the residue was extracted with CH_2Cl_2. After removal of dichloromethane from the clear extract, the remaining product was washed with cold acetone and Et_2O to give a colorless solid, yield 0.21 g (38 %), m.p. 240 °C (dec.). ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 8.79 (m, AA′BB′ spin system, 6 H, 2-H and 6-H), 7.56 (m, 6 H, 3-H and 5-H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$, 20 °C): δ = 150.59 (d, $^2J_{PC}$ = 9.8 Hz, C-2 and C-6), 138.73 (d, $^1J_{PC}$ = 71.2 Hz, C-4), 125.89 (d, $^3J_{PC}$ = 8.6 Hz, C-3 and C-5) ppm. ^{31}P NMR (162 MHz, $CDCl_3$, 20 °C): δ = 31.4 (s, $^1J_{PC}$ = 70.4, $^1J_{PSe}$ = 784.7 Hz) ppm. ^{77}Se NMR (76 MHz, $CDCl_3$, 20 °C): δ = –304.7 (d, $^1J_{PSe}$ = 785.9 Hz) ppm. IR (KBr): $\tilde{\nu}$ = 575 (m) (P=Se) cm^{-1}. HRMS (APCI+): calcd. for $[C_{15}H_{13}N_3PSe]^+$: 346.00086; found: 346.00054.

General Procedure for the Preparation of $(ZnTPP)_3(R_3PE)$ (R = 3-Py, 4-Py; E = S, Se) Complexes (8–11): The corresponding tripyridylphosphine chalcogenides were stirred in 1:3 molar ratio with ZnTPP in CH_2Cl_2 for 30 min. Evaporation of the solvent in vacuo yielded quantitatively the corresponding complexes as deep-purple solids, which decompose without melting.

$(ZnTPP)_3[(3\text{-}Py)_3PS]$ (8): From **2** (20.0 mg, 0.07 mmol) and ZnTPP (136.8 mg, 0.21 mmol), in CH_2Cl_2 (25 mL). ^{1}H NMR (600 MHz, $CDCl_3$, 20 °C): δ = 8.71 (s, 24 H, 7-H), 7.95 (d, $^3J_{HH}$ = 7.4 Hz, 24 H, 11-H), 7.74 (t, $^3J_{HH}$ = 7.5 Hz, 12 H, 13-H), 7.56 (t, $^3J_{HH}$ = 7.6 Hz, 24 H, 12-H), 5.51 (br. s, 3 H, 2-H), 4.95 (br. s, 3 H, 4-H), 3.39 (br. s, 3 H, 6-H), 2.65 (br. s, 3 H, 5-H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$, 20 °C): δ = 149.83 (s, C-8), 146.74 (s, C-6) 146.33 (d, $^3J_{PC}$ = 14.3 Hz, C-5), 142.92 (s, C-10), 137.02 (d, $^2J_{PC}$ = 7.8 Hz, C-4), 134.52 (s, C-11), 131.70 (s, C-7), 127.27 (s, C-13), 126.33 (s, C-12), 124.78 (d, $^1J_{PC}$ = 85.6 Hz, C-3), 122.04 (d, $^2J_{PC}$ = 9.4 Hz, C-2), 120.63 (s, C-9) ppm. ^{31}P NMR (243 MHz, $CDCl_3$, 20 °C): δ = 27.4 (s) ppm. IR (KBr): $\tilde{\nu}$ = 661 (m) (P=S) cm^{-1}.

$(ZnTPP)_3[(3\text{-}Py)_3PSe]$ (9): From **3** (25.0 mg, 0.07 mmol) and ZnTPP (147.8 mg, 0.21 mmol), in CH_2Cl_2 (25 mL). ^{1}H NMR (600 MHz, $CDCl_3$, 20 °C): δ = 8.70 (s, 24 H, 7-H), 7.94 (d, $^3J_{HH}$ = 7.2 Hz, 24 H, 11-H), 7.70 (t, $^3J_{HH}$ = 7.6 Hz, 12 H, 13-H), 7.53 (t, $^3J_{HH}$ = 7.5 Hz, 24 H, 12-H), 5.59 (br. s, 3 H, 2-H), 5.07 (br. s, 3 H, 4-H), 3.73 (br. s, 3 H, 6-H), 3.16 (br. s, 3 H, 5-H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$, 20 °C): δ = 149.96 (s, C-8), 147.36 (m, C-5, C-6), 143.04 (s, C-10), 137.65 (d, $^2J_{PC}$ = 8.6 Hz, C-4), 134.63 (s, C-11), 131.82 (s, C-7), 127.37 (s, C-13), 126.42 (s, C-12), 123.96 (d, $^1J_{PC}$ = 75.9 Hz, C-3), 122.18 (d, $^2J_{PC}$ = 9.3 Hz, C-2) 120.76 (s C-9) ppm. ^{31}P NMR (243 MHz, $CDCl_3$, 20 °C): δ = 18.9 (s, $^1J_{PSe}$ = 790.9 Hz) ppm. ^{77}Se NMR (76 MHz, $CDCl_3$, 20 °C): δ = –253.6 (d, $^1J_{PSe}$ = 791.0 Hz) ppm. IR (KBr): $\tilde{\nu}$ = 574 (m) (P=Se) cm^{-1}. HRMS (ESI+, MeOH): calcd. for $[C_{191}H_{125}N_{19}PSeZn_4]^+$: 3050.64053; found: 3050.64759; calcd. for $[C_{147}H_{96}N_{15}PSeZn_3]^+$: 2374.48231; found: 2374.47376; calcd. for $[C_{103}H_{69}N_{11}PSeZn_2]^+$: 1698.32177; found: 1698.32120; calcd. for $[C_{59}H_{41}N_7PSeZn]^+$: 1022.16123; found: 1022.16111.

$(ZnTPP)_3[(4\text{-}Py)_3PS]$ (10): From **6** (20.0 mg, 0.07 mmol) and ZnTPP (136.8 mg, 0.21 mmol), in CH_2Cl_2 (25 mL). ^{1}H NMR (600 MHz, $CDCl_3$, 20 °C): δ = 8.90 (s, 24 H, 7-H), 8.16 (d, $^3J_{HH}$ = 7.2 Hz, 24 H, 11-H), 7.79 (t, $^3J_{HH}$ = 7.5 Hz, 12 H, 13-H), 7.73 (t, $^3J_{HH}$ = 7.5 Hz, 24 H, 12-H), 4.57 (dd, $^3J_{PH}$ = 13.6, $^3J_{HH}$ = 5.5 Hz, 6 H, 3-H and 5-H), 2.43 (br.

s, 6 H, 2-H and 6-H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$, 20 °C): δ = 150.20 (s, C-8), 143.76 (d, $^3J_{PC}$ = 10.2 Hz, C-2 and C-6), 143.05 (s, C-10), 137.48 (d, $^1J_{PC}$ = 78.8 Hz, C-4), 134.57 (s, C-11), 132.00 (s, C-7), 127.56 (s, C-13), 126.63 (s, C-12), 123.26 (d, $^2J_{PC}$ = 9.1 Hz, C-3 and C-5), 121.06 (s, C-9) ppm. ^{31}P NMR (243 MHz, $CDCl_3$, 20 °C): δ = 35.2 (s) ppm. IR (KBr): $\tilde{\nu}$ = 659 (m) (P=S) cm^{-1}. HRMS (ESI+, MeOH): calcd. for $[C_{59}H_{41}N_7PSZn]^+$: 974.21677; found: 974.21886.

$(ZnTPP)_3[(4\text{-}Py)_3PSe]$ (11): From **7** (25.0 mg, 0.07 mmol) and ZnTPP (147.8 mg, 0.21 mmol), in CH_2Cl_2 (25 mL). ^1H NMR (600 MHz, CD_2Cl_2, 20 °C): δ = 8.82 (s, 24 H, 7-H), 8.07 (d, $^3J_{HH}$ = 7.3 Hz, 24 H, 11-H), 7.81 (t, $^3J_{HH}$ = 7.4 Hz, 12 H, 13-H), 7.73 (t, $^3J_{HH}$ = 7.5 Hz, 24 H, 12-H), 4.60 (dd, $^3J_{PH}$ = 14, $^3J_{HH}$ = 5.3 Hz, 6 H, 3-H and 5-H), 2.36 (br. s, 6 H, 2-H and 6-H) ppm. ^{13}C NMR (151 MHz, CD_2Cl_2, 20 °C): δ = 150.42 (s, C-8), 143.86 (d, $^3J_{PC}$ = 10.3 Hz, C-2 and C-6), 143.59 (s, C-10), 136.70 (d, $^1J_{PC}$ = 70.0 Hz, C-4), 134.99 (s, C-11), 132.14 (s, C-7), 127.88 (s, C-13), 126.99 (s, C-12), 124.36 (d, $^2J_{PC}$ = 9.2 Hz, C-3 and C-5), 121.15 (s, C-9) ppm. ^{31}P NMR (243 MHz, CD_2Cl_2, 20 °C): δ = 28.6 (s, $^1J_{PSe}$ = 798.7 Hz) ppm. ^{77}Se NMR (76 MHz, CD_2Cl_2, 20 °C): δ = –298.7 (d, $^1J_{PSe}$ = 799.2 Hz) ppm. IR (KBr): $\tilde{\nu}$ = 575 (m) (P=Se) cm^{-1}. HRMS (ESI+, MeOH): calcd. for $[C_{59}H_{41}N_7PSeZn]^+$: 1022.16123; found: 1022.16163.

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