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# Unexpected One-Electron Oxidation of a Secondary Phosphite Selenide $Cp(CO)_2FeP(Se)(OiPr)_2$ by $GaCl_3$ and $InCl_3$ – Rare Examples of Di- and Triselenide Formation

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The reactions of the neutral phosphonoselenoate  $[Cp(CO)_2FeP(Se)(OiPr)_2]$  (1) with Lewis acids  $(GaCl_3, InCl_3)$  produce dicationic complexes  $[\{Cp(CO)_2FeP(OiPr)_2\}_2-Se_n][GaCl_4]_2$ , [n = 2 (2), 3 (3)] and  $[\{Cp(CO)_2FeP(OiPr)_2\}_2-Se_n][InCl_4]_2$  [n = 2 (4), 3 (5)] in good yields; the complexes comprise an Se<sub>3</sub> (or Se<sub>2</sub>) chain that bridges two FpP- $(OiPr)_2$  groups  $[Fp = Cp(CO)_2Fe]$ . These compounds are the one-electron oxidation products of secondary phosphite sele-

# Introduction

H-Phosphonoselenoates (secondary phosphite selenides) are a largely unexplored class of phosphorus compounds and are potentially useful synthetic intermediates. Although they have been known for a long time, they remain rare and synthetically hardly accessible.<sup>[1]</sup> In general, the known routes to H-phosphonoselenoates suffer from the use of highly toxic H<sub>2</sub>Se and aggressive dialkylphosphoro chlorides or are achievable by particular condensing agents.<sup>[2]</sup> At the same time, H-phosphonoselenoates have been successfully used for oxidative phosphorylation of 3'-O-(tert-butyldimethylsilyl)thymidine to produce dinucleoside phosphoroselenoates with a modified 3'-5' internucleotide linkage.<sup>[3]</sup> Some oxidative transformations of dinucleoside Hphosphonoselenoate were studied by Stawinski.<sup>[4]</sup> However, transformation of the P=Se moiety (in which the oxidation state of the P atom is +3) was either not touched upon or almost neglected owing to the unstable nature of H-phosphonoselenoates with respect to disproportionation. Owing to the potential applications of H-phosphonoselenoates as precursors to various biologically important phosphate esters and their analogs in selenium biomedicine,<sup>[5]</sup> we have

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nide **1** by group 13 (Ga, In) trichlorides. On the other hand, the reaction of GaCl<sub>3</sub> with  $(iPrO)_2PSe_2^-$  (dsep) yields only the Lewis adduct tris(*O*,*O*-diisopropyldiselenophosphate)gallium (**6**). The <sup>31</sup>P NMR spectrum of **6** at 183 K reveals that the gallium(III) center is surrounded by one chelating and two pendant dsep ligands, which is in line with the obtained X-ray structure. In addition, the two-electron oxidation of **1** leads to phosphite [Cp(CO)<sub>2</sub>FeP(O)(*Oi*Pr)<sub>2</sub>] formation.

undertaken systematic studies on this class of compounds. We discovered that the stable phosphonoselenoate reagent  $FpP(Se)(OiPr)_2$  (1), a conjugated base of a secondary phosphite selenide, can be readily prepared from dsep and Fp dimer.<sup>[6]</sup> The latter is a high-potential precursor for the fabrication of new Lewis adducts (in reactions with soft Lewis acids such as Cu<sup>I</sup>, Ag<sup>I</sup>, Cd<sup>II</sup>, and Hg<sup>II</sup> cations),<sup>[6,7]</sup> charge-transfer adducts (with iodine)<sup>[6b]</sup> or *Se*-methylated products (with Meerwein's reagent).<sup>[6b]</sup>

To gain further insights into the factors that govern the coordination chemistry of phosphite selenides and to explore this chemistry in more detail, we have initiated a study of 1 with borderline Lewis acids (LAs) of group 13 (Ga, In) trichlorides.<sup>[8]</sup> InCl<sub>3</sub> can complex such soft Lewis bases (LBs) as  $(RO)_2PSe_2^-$  or  $R_2PSe_2^{-}$ ,<sup>[9]</sup> in which the P atom has a +5 oxidation state. Also, O'Brien et al. prepared Lewis acid-base adducts, M(iPr<sub>2</sub>PSe<sub>2</sub>)<sub>3</sub>, from both GaCl<sub>3</sub> and InCl<sub>3</sub> with soft LBs, (R<sub>2</sub>PSe)<sub>2</sub>Se.<sup>[10]</sup> Notably, the [(SePPh<sub>2</sub>)<sub>2</sub>N]<sup>-</sup> anion has also formed stable tris-chelates with InCl<sub>3</sub>.<sup>[11]</sup> In addition, dsep can be oxidized by some borderline LAs (FeCl<sub>3</sub>, VCl<sub>3</sub>, VOSO<sub>4</sub>)<sup>[12]</sup> to form  $[{(RO)_2PSe}_2Se_n]$  products, which suggests that there is a significant energy difference in the frontier orbitals of the reactants. Thus, the differences in the electron-cloud distribution and the size of the energy gap between selenophosphoryl compounds and various LAs can yield different types of HOMO-LUMO interactions: (a) Lewis adducts in the case of sufficiently soft LAs, (b) oxidation products for borderline LAs as a result of the mismatched Lewis pair. This is due to the lower softness and high reduction potential  $(E_0^{r})^{[13]}$  values for these LAs. On the basis of these fun-



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damental facts, it could be anticipated that 1 would react with GaCl<sub>3</sub> and InCl<sub>3</sub> to yield Lewis adducts; however, some electronic arguments make these facts implausible (vide infra). Thus, oxidation products of the type [{Cp- $(CO)_2 FeP(OiPr)_2 {}_2 Se_n {}^{2+}$  that contain a catenated selenium chain are formed. To the best of our knowledge, until now there have been no reports of iron-containing selenophosphoryl compounds with an  $Fe-P-(Se)_n-P-Fe$  linkage. Although oxidative couplings of some seleno-organic compounds with different LAs have been reported in the literature,<sup>[14]</sup> condensation reactions of P<sup>III</sup>=Se fragments are not well known. The most commonly encountered P-Se<sub>n</sub>-P linkages in organoselenophosphorus chemistry connect neutral phosphorus(V)<sup>[2a,15]</sup> atoms or are generated by oneelectron oxidation of diselenophosph(in)ates<sup>[16]</sup> as uninegatively charged ligands. In the literature, there are only a few examples of oxidation reactions of the P=Se fragment in (Me<sub>2</sub>N)<sub>3</sub>P=Se and 1,1'-bis(di-tert-butylphosphoroselenoyl)ferrocene {Fc-1,1'-[PSe(tBu)<sub>2</sub>]<sub>2</sub>} by a strong LA (BiCl<sub>3</sub>) or acidic metallocene (acetylferrocenium tetrafluoroborate)<sup>[17]</sup> to form dicationic [P-Se-Se-P]<sup>2+</sup> moieties, which were confirmed by X-ray analyses.<sup>[18]</sup> Nevertheless, the P atom in these two compounds is pentavalent. No one has succeeded in the one-electron oxidation of secondary phosphite selenides or their conjugate bases on Se=P<sup>III</sup>.

### **Results and Discussion**

Two gallium(III) complexes,  $[{FpP(O_iPr)_2}_2Se_n][GaCl_4]_2$ [n = 2 (2), 3 (3)], and two indium(III) complexes,  $[{\text{FpP}(\text{O}i\text{Pr})_2}_2\text{Se}_n]_2[\text{InCl}_4]_2 [n = 2 (4), 3 (5)], \text{ were obtained}$ by the reactions of 2 equiv. of LA with 1 in dichloromethane (DCM) at -30 °C and 5 °C, respectively (Scheme 1). In all cases, compounds 2, 3 and 4, 5 were obtained as inseparable mixtures in 71 and 77% yields, respectively. The presence of catenated selenium chains with different numbers of selenium atoms (Se<sub>2</sub> for 2 and 4 and Se<sub>3</sub> for 3 and 5) was authenticated by X-ray crystallographic (for 3 and 4, Figures 1 and 2) and chemical investigations (for a mixture of 2 and 3, vide infra). Interestingly, the oxidation does not stop in the coupling process but proceeds with dismutation and gives mixtures of catenates. However, separation of both catenates was not feasible by virtue of their similar solubility in organic solvents and exceptional sensitivity to

air moisture. This feature is particular for the similar compounds.<sup>[19]</sup> There appears to be no literature reports to date on the oxidation of phosphonoselenoates by any LAs except BiCl<sub>3</sub>.<sup>[18a]</sup>



Figure 1. Perspective view of the dicationic complex in **3** with H atoms omitted for clarity. Selected bond lengths [Å] and angles [°]: Se(1)–P(1) 2.2580(15), Se(1)–Se(3) 2.3349(10), Se(2)–Se(3) 2.3154(9), Se(2)–P(2) 2.2688(13), Fe(1)–P(1) 2.1730(16), Fe(2)–P(2) 2.1661(14); Se(2)–Se(3)–Se(1) 107.09(4), P(1)–Se(1)–Se(3) 104.16(5), P(2)–Se(2)–Se(3) 101.50(4), Fe(2)–P(2)–Se(2) 119.71(6), Fe(1)–P(1)–Se(1) 108.68(7); P(1)–Se(1)–Se(3)–Se(2) 96.14, P(2)–Se(2)–Se(3)–Se(1) 85.97.



Figure 2. Perspective view of the dicationic complex in **4** with H atoms omitted for clarity. Selected bond lengths [Å] and angles [°]: Se(1)–P(1) 2.2565(18), Se(1)–Se(1A) 2.3490(13), Fe(1)–P(1) 2.1732(17); P(1)–Se(1)–Se(1A) 103.05(5), Fe(1)–P(1)–Se(1) 109.65(7); P(1)–Se(1)–Se(1A)–P(1A) 120.15, Fe(1)–P(1)–Se(1)–Se(1)–Se(1)–171.82.



Scheme 1. Reactivities of GaCl<sub>3</sub> and InCl<sub>3</sub> toward 1.



GaCl<sub>3</sub> and InCl<sub>3</sub><sup>[9b]</sup> react with ammonium diisopropyl diselenophosphate in methanol at 0 °C to yield the gallium(III) tris(diselenophosphate) **6** and the indium(III) tris-(diselenophosphate) **7** in 85 and 70% yields, respectively (Scheme 2).

 $\overset{\textcircled{b}}{\underset{NH_{4}}{\overset{\bigcirc}{\rightarrow}}} \overset{Se}{\underset{NH_{4}}{\overset{\bigcirc}{\rightarrow}}} P(OiPr)_{2} + MCl_{3} \xrightarrow{MeOH} M[Se_{2}P(OiPr)_{2}]_{3}$  M = Ga (6), ln (7)



Apparently, the energies of the highest occupied molecular orbital (HOMO) in (RO)<sub>2</sub>PSe<sub>2</sub><sup>-</sup> and the lowest unoccupied molecular orbitals (LUMOs) in GaCl<sub>3</sub> and InCl<sub>3</sub> match well with each other. They are in sharp contrast to those of the neutral species 1 owing to the considerably larger energy differences between the HOMO of 1 and the LUMOs of the LAs.<sup>[20]</sup> In accordance with the Klopman equation,<sup>[21]</sup> the difference postulates that no adducts can be formed, but only transfer of electrons from Se in 1 to LAs can take place. Notably, rather hard FeCl<sub>3</sub> reacts with 1 or dsep to give oxidized products owing to its lower softness (softness parameter  $E_n^{\neq} = -0.73 \text{ eV}$  in DCM) and higher  $E_0^r$  in comparison with those of Ga<sup>3+</sup> and In<sup>3+</sup>.<sup>[13]</sup> In contrast, the reactions of AlCl<sub>3</sub> (hard LA) with both 1 and dsep did not lead to either oxidized products or the Lewis adducts, and this fact correlates well with the hard and soft acids and bases (HSAB) concept. Notably, the softer Te atom of the [TePR<sub>2</sub>]<sub>2</sub>N<sup>-</sup> anion reacted with GaCl<sub>3</sub> in a nonpolar solvent such as toluene at -78 °C to yield at first an unstable adduct, Ga[(TePR<sub>2</sub>)<sub>2</sub>N]<sub>3</sub>, which then underwent an internal redox process followed by consecutive rearrangement and dimerization.<sup>[22]</sup> On this account GaCl<sub>3</sub> is believed to be a borderline Lewis acid, and its very low  $E_0^r$  allows for the formation of a Lewis adduct with dsep without any further redox reactions. In other words, the course of the reaction depends on reduction potentials, relative softness in a given solvent, and the energy gap between the frontier orbitals of the reactants. Thus, as the oxidation potentials for 1 and dsep are so different, 0.81 and 0.24 V, respectively,<sup>[7a,23]</sup> it is not surprising that 1 is easily oxidized in the reaction with borderline LAs (GaCl<sub>3</sub> and InCl<sub>3</sub>), whereas dsep gives Lewis acid–base adducts.<sup>[9b]</sup>

Two-electron oxidations of chalcogenophosphorus compounds proceed by means of powerful oxidants. A standard oxidation method for the conversion of thio- and selenophosphoryl compounds to oxophosphoryl ones by using Oxone has been reported.<sup>[24]</sup> Thus, phosphonoselenoates were treated with 2 equiv. of Oxone (0.1 M aq. solution) in an MeOH/THF mixture (1:1) to cleanly produce phosphite **8** in 90% yield (Scheme 3).

All the compounds have been characterized by spectroscopy (multinuclear NMR, IR) and microanalyses. Compounds 2–5 are soluble in common polar organic solvents and were crystallized by the slow diffusion of hexane into DCM solutions to yield transparent colorless crystals. Fortunately, we have succeeded in obtaining single crystals of



Scheme 3. Two-electron oxidation of 1.

3 and 4 suitable for X-ray diffraction studies, which allowed us to solve their molecular structures. Previously, it has been reported that similar selenophosphorus compounds are rather unstable and decompose rapidly when the solution is exposed to air or moisture.<sup>[25]</sup> We have found these complexes seem to be stable at -20 °C for several days under dry nitrogen. The complexes in solution gradually decompose at room temperature under daylight. However, separation of these catenates was not feasible by virtue of their similar solubility in organic solvents and exceptional sensitivity to air moisture. The X-ray structures of 3 and 4 (Figures 1 and 2) confirm the presence of the  $P-(Se)_n-P$ linkage (n = 2 or 3). The gallium(III) diselenophosphate 6 is more stable than 2-5. The structure consists of one chelating and two pendant dsep ligands in a distorted tetrahedral geometry around the gallium center (Figure 3). It is isostructural with its diselenophosphinate analogue,  $[Ga{Se_2P(iPr)_2}_3]$ .<sup>[10]</sup> Compound **8** is an oily product and is highly soluble in common organic solvents. The presence of the phosphito moiety was primarily ascertained by <sup>31</sup>P NMR and IR spectroscopy, and the composition of 8 was fully confirmed by MALDI-TOF mass spectrometry (vide infra).



Figure 3. Perspective view of **6**. Selected bond lengths [Å] and angles [°]: Ga(1)–Se(1) 2.4496(12), Ga(1)–Se(2) 2.4450(12), Ga(1)–Se(3) 2.3600(13), Ga(1)–Se(5) 2.3690(12), Se(1)–P(1) 2.173(2), Se(2)–P(1) 2.174(2), Se(3)–P(2) 2.221(2), Se(4)–P(2) 2.079(3), Se(5)–P(3) 2.187(2), Se(6)–P(3) 2.088(2); Se(2)–Ga(1)–Se(1) 89.82(4), Se(3)–Ga(1)–Se(5) 119.47(5), Se(1)–P(1)–Se(2) 105.28(8), Se(4)–P(2)–Se(3) 115.80(11), Se(6)–P(3)–Se(5) 115.52(11).

#### **Compound 3**

Compound **3** crystallizes in the orthorhombic space group  $Pna2_1$  with four molecules per unit cell. X-ray analy-



sis revealed that the dicationic salt comprises an Se<sub>3</sub> chain that bridges two (iPrO)<sub>2</sub>PFp groups. The P-Se distances in 3 [mean 2.263(2) Å] are significantly longer than the corresponding distance in 1 [2.128(1) Å], which suggests that a P-Se single bond exists in the former. They are similar to the average P-Se bond length found in [(Me<sub>2</sub>N)<sub>3</sub>PSe-]<sub>2</sub>- $[Bi_2Cl_8]$  (2.230 Å)<sup>[18a]</sup> and [dtbpfSe<sub>2</sub>][BF<sub>4</sub>]<sub>2</sub> [2.275 Å, dtbpf = 1,1'-bis(di-*tert*-butylphosphanyl)ferrocene].<sup>[18b]</sup> Within the Se<sub>3</sub> chain, the Se–Se bond lengths are unequal [Se1–Se3 2.3349(10), Se2-Se3 2.3154(9) Å] and almost identical to those in the (Se)P-Se<sub>3</sub>-P(Se) moiety of [(EtO)<sub>2</sub>P(Se)]<sub>2</sub>Se<sub>3</sub> [2.3448(6) and 2.3439(6) Å].<sup>[12b]</sup> The torsion angles of 96.14 [P(1)-Se(1)-Se(3)-Se(2)] and  $85.97^{\circ}$  [P(2)-Se(2)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(3)-Se(Se(1)] indicate that these planes are nearly perpendicular and comparable to those in [dtbpfSe<sub>2</sub>][BF<sub>4</sub>]<sub>2</sub> (-96.19°) and [(EtO)<sub>2</sub>P(Se)]<sub>2</sub>Se<sub>3</sub> (-87.8°).<sup>[12b]</sup> The arrangement of three Se atoms looks like a spiral along the P-P axis. The Fe-P-P-Fe torsion angle is  $85.78^\circ$ . In addition, two FpP(O*i*Pr)<sub>2</sub> moieties lie at each side of the Se<sub>3</sub> plane. It should be noted that the torsion angles of Se–P–Fe– $X_{Cp}$  are inequivalent (49.51 and -60.21°); this difference can be explained by the presence of strong van der Waals contacts between two chloride atoms (Cl5 and Cl8) of the tetrachlorogallate with two neighboring Se atoms (Se2 and Se3). The Se3---Cl5 and Se2…Cl8 nonbonded distances of 3.542 and 3.557 Å, respectively, are slightly shorter than the sum of their van der Waals radii (3.65 Å).<sup>[26]</sup>

#### **Compound 4**

Compound 4 crystallizes in the monoclinic space group C2/c. X-ray analysis of 4 revealed that two FpP(O*i*Pr)<sub>2</sub> fragments are connected through an Se<sub>2</sub> bridge and that the structure consists of a discrete [Fp(OiPr)2PSe-]2 dication and two tetrachloroindate anions. In the Se<sub>2</sub> bridge, the Se-Se bond length is 2.349(1) Å, typical of an Se-Se single bond,<sup>[27]</sup> and the structure is centrosymmetric. The P-Se-Se-P torsion angle (120.15°) in 4 is significantly larger than those in [dtbpfSe<sub>2</sub>][BF<sub>4</sub>]<sub>2</sub> (-96.19°)<sup>[18b]</sup> and [(Me<sub>2</sub>N)<sub>3</sub>PSe-]<sub>2</sub>-[Bi<sub>2</sub>Cl<sub>8</sub>] (-112.4°).<sup>[18a]</sup> The Se-P-Fe-X<sub>Cp</sub> torsion angles  $(-58.56^{\circ})$  are comparable to those in the *n*-propyl derivative of 1.[6b] Contrary to the structure reported by Willey et al.,<sup>[18a]</sup> the counterion in [(Me<sub>2</sub>N)<sub>3</sub>PSe–]<sub>2</sub>[Bi<sub>2</sub>Cl<sub>8</sub>] exists as a polymeric anionic chain  $[(BiCl_4)_2]_n^{2n-}$ ; however, tetrachlorogallate and tetrachloroindate are discrete anions in 3 and 4, respectively.

#### **Compound 6**

Compound **6** crystallizes in the monoclinic space group C2/c with eight molecules per unit cell. The gallium atom is coordinated by two dsep ligands in a monodentate fashion and a chelating dsep ligand. Although the bidentate Ga–Se distances [2.4496(12) and 2.4450(12) Å] are almost the same as those reported in [ $(iPr_2PSe_2)_3Ga$ ], the monodentate Ga–Se distances [2.3600(13) and 2.3690(12) Å] are slightly shorter than those [2.385(5) and 2.396(4) Å] iden-

tified in  $[(iPr_2PSe_2)_3Ga]$ .<sup>[10]</sup> The angles around the Ga<sup>III</sup> center, in the range 89.82(4)–119.47(5)°, indicate pseudotetrahedral geometry. The four-membered Se–P–Se–Ga chelate is approximately planar. The structure is different to that of its heavier congener,  $[{(iPrO)_2PSe_2}_3In]$ , which has three chelating dsep ligands around the In<sup>III</sup> center in a distorted octahedral geometry.<sup>[9b]</sup>

#### Infrared Spectroscopy

The IR spectra of the dicationic complexes 2-5 showed no v(P=Se) absorption bands at 540–600 cm<sup>-1</sup> in contrast with their parent compound, 1. Instead, the P-Se stretching frequency was identified in the range 320–374 cm<sup>-1</sup>, and the Se-Se absorption bands were identified in the range 226-251 cm<sup>-1</sup> for 2–5. The Se–Se stretching of Cs<sub>4</sub>Th<sub>4</sub>P<sub>4</sub>Se<sub>26</sub> was observed at 252 cm<sup>-1</sup>.<sup>[16a]</sup> The IR spectra of 3 and 4 revealed the characteristic peaks for symmetric and antisymmetric stretching frequencies of two CO groups at 2014-2015 and 2057–2058 cm<sup>-1</sup>, respectively, which confirms the conservation of the iron oxidation state (+2) in both molecules. The v(CO) band is about  $20 \text{ cm}^{-1}$  higher in these compounds than that of their precursor 1. The IR spectrum of 8 shows typical v(CO) bands at 1985 and 2036 cm<sup>-1</sup>, a phosphoryl group v(P=O) band at 1142 cm<sup>-1</sup>, and aliphatic phosphate group v(POC) bands at 977 and 970 cm<sup>-1</sup>.

#### Mass Spectrometry

Unfortunately, molecular ion peaks were not detected in the positive MALDI-TOF mass spectrum for dication complexes 2–5. However, fragment peaks of 2 and 3 at m/z =429.81, 391.02, and 349.91 (428.94, 391.17, and 350.06 for 4 and 5), which corresponded to  $[{\rm FpP}({\rm OiPr})_2\}_2{\rm Se}_3 {\rm CO}]^{2+}$  (m/z = 430.55),  $[{\rm FpP}({\rm OiPr})_2\}_2{\rm Se}_2 - {\rm CO}]^{2+}$  (m/z =391.07), and  $[{\rm FpP}({\rm OiPr})_2\}_2{\rm Se}_2 - 4 {\rm CO}]^{2+}$  (m/z = 349.05), respectively, were observed. On the other hand, peaks corresponding to GaCl<sub>4</sub><sup>-</sup> and InCl<sub>4</sub><sup>-</sup> were identified in the negative-ion mass spectra. A positive MALDI-TOF mass spectrum of **8** displays the molecular ion peak at m/z = 343.04( $M_{\rm calcd.}$  342.20 [M + H]), which provides further evidence in support of the structural assignment for **8**.

#### **NMR Studies**

The <sup>31</sup>P NMR spectra of **2–5** at 223 K show only singlets flanked by a pair of <sup>77</sup>Se satellite peaks ( $J_{P,Se} = 511, 513$ , 525, and 523 Hz for **2**, **3**, **4**, and **5**, respectively). The decrease of the coupling constants in **2–5** with respect to that of the precursor **1** ( $J_{P,Se} = 713$  Hz) indicates that the P–Se bond order has decreased and is consistent with those for a typical P–Se single bond.<sup>[28]</sup> The <sup>31</sup>P chemical shift of the products is approximately 10 ppm downfield of that of their precursor **1**. Similar downfield shifts were also noted for the above-mentioned diselenium salts,  $[(Me_2N)_3PSe-]_2[Bi_2Cl_8]$ and  $[dtbpfSe_2][BF_4]_2$ . Interestingly, the GaCl<sub>4</sub><sup>-</sup> and InCl<sub>4</sub><sup>-</sup> counterions have little effect on the <sup>31</sup>P chemical shifts,



which is apparently due to the strong solvation of ions in the deuterated solvent. For InCl<sub>3</sub>, both complexes (4 and 5) have just one <sup>31</sup>P NMR resonance at room temperature ( $\delta$ = 176.3 ppm) and two overlapped resonances at 223 K (179.5 and 179.8 ppm), whereas the two <sup>31</sup>P NMR resonances for 2 and 3 remain well separated regardless of temperature (Figure 4). However, the  ${}^{1}J_{P,Se}$  values for gallates 2 and 3 are smaller than those of indates 4 and 5, which reflects the strong van der Waals contacts of two chloride atoms in the tetrachlorogallate (Cl5 and Cl8) with the two neighboring Se atoms (vide supra). Curiously, we were unable to detect a 77Se NMR resonance for any of the dicationic complexes over the temperature range 298-253 K, presumably because of line broadening resulting from fast relaxation of the selenium nuclei in these large and asymmetric molecules. Only at 223 K did the <sup>77</sup>Se NMR studies reveal two doublets at  $\delta = 212$  (<sup>1</sup> $J_{P,Se} = 508$  Hz, 2) and 186.9 ppm ( ${}^{1}J_{P,Se} = 512 \text{ Hz}, 3$ ) for the gallates and  $\delta = 127.6$  $({}^{1}J_{P,Se} = 503 \text{ Hz}, 4)$  and 150.4 ppm  $({}^{1}J_{P,Se} = 526 \text{ Hz}, 5)$  for the indates (Figure 4). The <sup>1</sup>H and <sup>13</sup>C NMR spectra of 2-5 only corroborate the presence of ligand molecules.



Figure 4. (a) <sup>31</sup>P NMR spectrum of 2 and 3 in  $[D_6]$ acetone at 223 K; (b) <sup>77</sup>Se NMR spectrum of 2 and 3 in  $[D_6]$ acetone at 223 K; (c) <sup>31</sup>P NMR spectrum of 4 and 5 in  $[D_6]$ acetone at 223 K; (d) <sup>77</sup>Se NMR spectrum of 4 and 5 in  $[D_6]$ acetone at 223 K.

<sup>31</sup>P NMR spectroscopic studies of **6** in CD<sub>2</sub>Cl<sub>2</sub> confirmed the formation of the tris(diselenophosphato)gallium(III) compound. Two chemical shifts are observed at ambient temperature: one sharp resonance at  $\delta = 63.0$  ppm with a set of selenium satellite peaks ( ${}^{1}J_{P,Se} = 617$  Hz) and a small, slightly broad resonance at  $\delta = 53.9$  ppm ( ${}^{1}J_{P,Se} =$ 584 Hz). As the temperature is lowered to 183 K, the sharp signal broadens and shifts ca. 1.5 ppm downfield. The second peak ( $\delta = 55.4$  ppm) sharpens, and its intensity increases dramatically. However, their integration ratio remains roughly the same (2:1, Figure S1). The sharp resonance at 183 K, which is broad at 293 K, is the chemical shift of the chelating dsep ligand, for which the chelating– dangling interchange is fast at 293 K but slow at 183 K. A similar exchange for dsep ligands in solution has been identified in its heavier congener,  $In(dsep)_3$ .<sup>[9b]</sup> As there are two pendant dsep ligands in the solid-state structure of **6** (vide supra), two sets of selenium satellite peaks instead of one are expected for the peak at  $\delta = 63.0$  ppm.

Presumably, intramolecular exchange involving simultaneous formation of the Ga1–Se6 (Ga1–Se4) bond and cleavage of the Ga1–Se5 (Ga1–Se3) bond is so fast at 293 K that the phosphorus nuclei do not experience any difference between the two Se atoms attached. Slower exchange at 183 K helps assign the broad resonance at  $\delta = 64.5$  ppm to two pendant dsep units. In contrast, the <sup>77</sup>Se NMR spectrum at ambient temperature shows two doublets at  $\delta =$ 252.4 (<sup>1</sup>J<sub>P,Se</sub> = 616 Hz) and 311.4 ppm (<sup>1</sup>J<sub>P,Se</sub> = 584 Hz), which strongly suggests that the Ga–Se bonds are labile. Overall, the variable-temperature (VT) <sup>31</sup>P NMR spectra clearly demonstrate that two distinct chemical environments are unequivocally observed in solution for the P atoms of the dsep ligands; this is in agreement with the solid-state structure obtained by X-ray analysis.

The absence of selenium in **8** is supported by the fact that no typical satellite peaks were observed for the singlet at  $\delta = 105.5$  ppm in the <sup>31</sup>P NMR spectrum. The <sup>1</sup>H NMR spectrum displays peaks at  $\delta = 1.24$  and 4.71 ppm for OCH(CH<sub>3</sub>)<sub>2</sub> groups and at  $\delta = 5.03$  ppm for the Cp group.

#### **Mechanistic Studies**

A plausible mechanism for the one-electron oxidation can be rationalized as follows: In the first step it is reasonable to propose that the LA (GaCl<sub>3</sub> or InCl<sub>3</sub>) contacts with the lone pair of electrons on the Se atom. This complex is unstable due to the mismatched Lewis pair and rapidly disproportionates followed by a redox process. For example, GaCl<sub>3</sub> exists as a dimer (a mixed salt of [GaCl<sub>2</sub>]GaCl<sub>4</sub>)<sup>[29]</sup> and readily accepts 2 e<sup>-</sup>, each from one Se atom of 1, to release stable tetrachlorogallate anions and selenophosphoryl radical cations (Scheme 4). Notably, a white solid formed during the reaction and appears to be Ga<sup>I</sup>-[Ga<sup>III</sup>Cl<sub>4</sub>].<sup>[30]</sup> Recently, Bertrand and co-workers showed that borylene-bis[cyclic(alkyl)(amino)carbene] adducts can readily undergo one-electron oxidation with GaCl<sub>3</sub> to give a stable radical cation stabilized by GaCl<sub>4</sub><sup>-.[31]</sup> Phosphane sulfides can reduce some borderline LAs such as Cu<sup>II</sup> and Au<sup>III</sup> ions to Cu<sup>I</sup> and Au<sup>I</sup>,<sup>[32]</sup> and, to some extent, Fe<sup>III</sup> to Fe<sup>II</sup>,<sup>[33]</sup> whereas phosphane sulfides easily lose 1 e<sup>-</sup> to yield a radical cation followed by a rapid coupling. This mechanism is in good agreement with the data obtained for the electrochemical and chemical oxidations of C=S,[34] P=S,<sup>[25b]</sup> and P=Se<sup>[18]</sup> species to form dications by coupling of the radical cations.

At the same time, it is known that some hard–soft Lewis adducts (for instance, dithiophosphato<sup>[9a,35]</sup> complexes of





Scheme 4. Tentative mechanism for the reaction of GaCl<sub>3</sub> with 1. Presumably, the reaction with InCl<sub>3</sub> follows the same mechanism.

Cu<sup>2+</sup>, Au<sup>3+</sup>, Tl<sup>3+</sup>, Co<sup>3+</sup>, Fe<sup>3+</sup>, and VO<sup>2+</sup> or a diselenophosphinate complex<sup>[36]</sup> of Cu<sup>2+</sup>) are so unstable that they undergo an internal redox process to form Cu<sup>+</sup>, Au<sup>+</sup>, Tl<sup>+</sup>, Co<sup>2+</sup>, Fe<sup>2+</sup>, and V<sup>3+</sup> complexes (soft–soft) and the corresponding polysulfides [(RO)<sub>2</sub>P(S)]<sub>2</sub>S<sub>n</sub> or [R<sub>2</sub>P(S)]<sub>2</sub>S<sub>n</sub> (n = 1-3). Apparently, the dichalcogenophosph(in)ates, which are evidently not very well suited for the stabilization of highoxidation-state metal (hard LA) complexes, behave as strong reducing agents owing to their high reduction potentials. Therefore, an appropriate combination of  $E_0$ , softness (in a given solvent), and energy differences in the frontier orbitals of the reactants dictates the direction of the reaction toward either oxidation or adduct formation.

To exclude the effect of trace oxygen in the one-electron oxidation process, we have attempted to carry out a direct oxidation of **1** by dry air (LA,  $CH_2Cl_2$ , -30 °C, overnight). However, the <sup>31</sup>P NMR spectrum of the solution remains the same as those performed in an inert atmosphere. Apparently, the oxygen in air does not have any influence on the result of oxidation, though trace oxygen can initiate reoxidation of the remaining salt (M<sup>2+</sup>) to a stable trivalent state (M<sup>3+</sup>), which continues the reaction. In the absence of LAs, no reactions occur between oxygen and **1**.

As GaCl<sub>3</sub> and InCl<sub>3</sub> are generally referred to as rather strong LAs,<sup>[8]</sup> oxidations are complicated by a follow-up dismutation process that proceeds even at low temperatures (-50 °C) and in which the molar ratio of Se<sub>2</sub>/Se<sub>3</sub> remains almost unchanged (ca. 2:1) in all cases. Barnard and Woodbridge<sup>[37]</sup> have proposed that such kind of diselenide can be unstable and disproportionates to the mono- and triselenide by intermolecular rearrangement. However, this mechanism is not suitable to explain our results. Our NMR investigations reveal that only traces of monoselenide form in the reaction (vide infra).

To authenticate that the solid-state structure of **3** is relevant to the signal at  $\delta = 173.6$  ppm (CDCl<sub>3</sub>) in the <sup>31</sup>P NMR spectrum, we attempted to reduce the mixture of selenides **2** and **3** (molar ratio as 2:1) with soft reducing agents.

The reaction of excess Ph<sub>3</sub>P with the mixture was monitored by <sup>31</sup>P NMR spectroscopy and revealed a consecutive reduction of both salts in 48 h. The signal at  $\delta = 173.6$  ppm (Se<sub>3</sub>) significantly decreases with respect to the signal at  $\delta$ = 172.3 ppm (Se<sub>2</sub>), and eventually an integration ratio of ca. 4:1 is reached (Figure S2c). There are new signals for both Ph<sub>3</sub>P=Se ( $\delta$  = 36.4 ppm) and 1 ( $\delta$  = 167.4 ppm, Scheme 5). After 3 d, the <sup>31</sup>P spectrum shows two main peaks corresponding to Ph<sub>3</sub>P=Se and 1 with two new small doublets. It is possible that both doublets belong to one intermediate, a dicationic unit [FpP(OiPr)2-Se-PPh3]<sup>2+</sup> (i), which is indicated by the similarity of their coupling constants ( $\delta$  = 160.9 ppm, <sup>2</sup>J<sub>P,P</sub> = 24.7 Hz and  $\delta$  = 31.6 ppm,  ${}^{2}J_{\rm PP}$  = 24.4 Hz, Figure S2d). This dicationic intermediate i can accept 1 e<sup>-</sup> from Ph<sub>3</sub>P=Se to give 1 and another unidentified species ( $\delta_p = 30.7 \text{ ppm}, J_{P,P} = 19.6 \text{ Hz}$ ), which can be attributed to a monoselenium triphenylphosphane gallate species.

Apparently, the released [GaCl<sub>4</sub>]<sup>-</sup> reacts with Ph<sub>3</sub>P to form a complex, [GaCl<sub>3</sub>(Ph<sub>3</sub>P)], which cannot be detected by <sup>31</sup>P NMR spectroscopy at ambient temperature.<sup>[38]</sup> The experiment indicates that the signal at  $\delta = 173.6$  ppm can be unambiguously assigned to the triselenide **3**, which should rapidly lose one Se atom to yield diselenide **2** ( $\delta =$ 172.3 ppm), which is then slowly reduced to the initial phosphonoselenoate **1**. The reaction of the mixture of **2** and **3** with secondary phosphane R'<sub>2</sub>PH<sup>[39]</sup> instantly leads to **1** and R'<sub>2</sub>P(Se)H ( $\delta_{\rm P} = 3.5$  ppm,  $J_{\rm PSe} = 712$  Hz, Figure S3).

At the same time, a new singlet ( $\delta = 53.8$  ppm) appears in the <sup>31</sup>P NMR spectrum and is assigned to the chlorophosphane–gallium chloride represented in Equation (1).

$$[\{FPP(O/Pr)_{2}\}_{2}Se_{3}] \cdot [GaCl_{4}]_{2} + 2HPR_{2} \longrightarrow$$

$$3 \qquad R' = (CH_{2})_{2}Ph$$

$$Se \qquad Se \qquad Hi = 1$$

$$\longrightarrow 2FpP(O/Pr)_{2} + H \cdot PR'_{2} + [PR'_{2} - CI] \cdot GaCl_{3} + HGaCl_{4} \qquad (1)$$



Scheme 5. Reduction of 3 by  $Ph_3P$ .



The new resonance at  $\delta = 53.8$  ppm lies in the range of the known chemical shifts of chlorophosphane–gallium chloride complexes.<sup>[40]</sup> These investigations confirm that the initial reaction mixture consists of only Se<sub>2</sub> and Se<sub>3</sub> derivatives, and only one form preferentially crystallizes.

To gain insight into the probable interactions between the mixtures of selenides (2 and 3) with  $Ph_3P$ , we carried out selenium exchange reactions between  $R'_{2}PH$  and 1. The results shown below demonstrated that the above-mentioned reactions (Scheme 5) would proceed through a monoselenide intermediate like i. Thus, the secondary phosphane slowly reduced 1 to form the key intermediate [FpP(OiPr)2-Se-PHR'2] based on a mechanism<sup>[41]</sup> involving reoxidation by selenophilic attack in a linear transition state. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of the intermediate  $[FpP(OiPr)_2-Se-PHR'_2]$  displays two doublets ( $\delta = 42.8$ and 187.9 ppm, Figure S4a) with identical  ${}^{2}J_{PP}$  coupling constants (82.4 Hz), which is a typical value for such systems.<sup>[42]</sup> The peak at  $\delta = 187.9$  ppm corresponds to the  $FpP(OiPr)_2$  unit, and the peak at  $\delta = 42.8$  ppm corresponds to the R'<sub>2</sub>PH moiety. These two doublets are each flanked by a set of selenium satellite peaks with unequal  ${}^{1}J_{PSe}$  coupling constants (670 and 542 Hz, respectively) presumably owing to different P-Se bond lengths (Figure S4b). Both coupling constants are smaller than those for 1 ( $J_{P,Se}$ 713 Hz) and secondary phosphane selenide  $(J_{P,Se} =$ 712 Hz). This indicates the decrease of the P-Se bond order in [FpP(OiPr)2-Se-PHR'2] and corresponds to a bond order of 1.5.<sup>[43]</sup> The presence of a proton on the R'<sub>2</sub>P moiety has been proved by the <sup>1</sup>H-coupled <sup>31</sup>P NMR spectrum, which displays a doublet of doublets with a  ${}^{1}J_{\rm PH}$  coupling constant of 366 Hz (Figure S4c). An increase in the latter with respect to that of the initial secondary phosphane  $({}^{1}J_{\rm PH} = 198 \,{\rm Hz})$  indicated that the phosphorus atom is combined with the Se atom from 1. In the  ${}^{31}P{}^{1}H{}^{-31}P{}^{1}H{}$ COSY spectrum there are two cross peaks between these doublet peaks, which confirms that these two resonances belong to one compound with two different phosphorus atoms (Figure S5). Meanwhile, it must be emphasized that Ph<sub>3</sub>P practically does not react with 1 at ambient temperature.

#### Conclusions

The study on the one-electron oxidation process of secondary phosphite selenide 1 by group 13 (Ga, In) trichlorides described here contributes to the understanding of the reactivities of phosphonoselenoates  $[RPSe(OR')_2]$  with strong LAs. They gave rise to  $[{Cp(CO)_2FeP(OiPr)_2}_2Se_n]$ - $[GaCl_4]_2$  and  $[{Cp(CO)_2FeP(OiPr)_2}_2Se_n][InCl_4]_2$ , which contain an Se<sub>3</sub> or Se<sub>2</sub> unit between two FpP(OiPr)<sub>2</sub> groups. These are rare examples of the one-electron oxidation of a selenophosphoryl moiety. Moreover, **3** and **4** are the first structurally characterized iron–selenophosphoryl dicationic salts with an Fe–P–Se<sub>n</sub>–P–Fe linkage. Evidence to support the Se<sub>2</sub> and Se<sub>3</sub> assignment in the <sup>31</sup>P NMR spectra has been obtained by the sequential deselenization by Ph<sub>3</sub>P to slowly form diselenide and then the initial compound, **1**. In contrast, the reaction of GaCl<sub>3</sub> with dsep anions cleanly gives the Lewis adduct [ ${(iPrO)_2PSe_2}_3Ga$ ] as colorless crystals in a high-yield (85%) process. The formation of [(*iPrO*)<sub>2</sub>-PSe<sub>2</sub>]<sub>3</sub>Ga can be easily understood on the basis of the small energy gap between the HOMO of dsep and the LUMO of GaCl<sub>3</sub>. On the other hand, strong oxidants such as oxone in reaction with FpP(Se)(O*i*Pr)<sub>2</sub> gave iron complexes of secondary phosphites. These results contribute to both fundamental and synthetic chemistry of selenophosphorus compounds. As the Se–Se bond is labile and can be broken easily, studies to apply these P–Se iron-containing diselenides as synthetic precursors are currently underway.

# **Experimental Section**

**Caution!** Selenium and its derivatives are toxic. These materials should be handled with great caution.

Materials and Measurements: All chemicals were purchased from commercial sources and used as received. Commercial GaCl<sub>3</sub> and InCl<sub>3</sub> were purchased as crystalline solids and stored in a glovebox. Solvents were purified by applying standard protocols.<sup>[44]</sup> All reactions were performed in oven-dried Schlenk glassware by using standard inert-gas techniques. Elemental analyses were carried out with a Perkin-Elmer 2400 CHN analyzer. NMR spectra were recorded with a Bruker Avance DPX300 FT-NMR spectrometer, which operates at 300 MHz for <sup>1</sup>H, 75.5 MHz for <sup>13</sup>C, 121.49 MHz for <sup>31</sup>P, and 57.24 MHz for <sup>77</sup>Se. <sup>31</sup>P{ $^{1}$ H} and <sup>77</sup>Se{ $^{1}$ H} NMR spectra were referenced externally against 85%  $H_3PO_4$  ( $\delta = 0$  ppm) and (PhSe)<sub>2</sub> ( $\delta$  = 463 ppm), respectively. Chemical shifts ( $\delta$ ) and coupling constants (J) are reported in ppm and Hz, respectively. CDCl<sub>3</sub> and (CD<sub>3</sub>)<sub>2</sub>CO NMR solvents were dried with 4 Å molecular sieves prior to use. IR spectra were recorded with a Bruker Optics FTIR TENSOR 27 spectrometer (180-4000 cm<sup>-1</sup>) at 20 °C with CsI plates. FpP(Se)(OiPr)2 (1) was prepared according to a reported method.<sup>[6]</sup> MALDI-TOF spectra were acquired with an Autoflex time-of-flight mass spectrometer (Bruker Daltonic, Bremen) equipped with a 337 nm nitrogen laser (10 Hz, 3 ns pulse width). Spectral data were obtained in the reflection mode with an acceleration voltage of 20 kV. A 0.5 µL aliquot of the sample solution was applied on the target plate and dried before MALDI-TOF MS analysis. Each mass spectrum was derived from 100 summed scans.

 $[{Cp(CO)_2FeP(OiPr)_2}_2Se_n][GaCl_4]_2$  (2, n = 2; 3, n = 3): In a glovebox, GaCl<sub>3</sub> (0.070 g, 0.40 mmol) was added to a 100 mL round-bottomed Schlenk flask and then dissolved in DCM (30 mL) and stirred at -30 °C for 10 min. After 1 (0.081 g, 0.20 mmol) had been added and the mixture stirred overnight at -30 °C, a yellowbrown solution formed, which was filtered, and the filtrate was concentrated to dryness under vacuum. It was then extracted with acetone (10 mL) to afford a yellow-brown solution, which on concentration formed yellow-brown oils. Yield 0.097 g (71%).  $(C_{26}H_{38}Cl_8Fe_2Ga_2O_8P_2Se_3)_{0.33}(C_{26}H_{38}Cl_8Fe_2Ga_2O_8P_2Se_2)_{0.66}$ 0.5C<sub>3</sub>H<sub>6</sub>O (1275.97): calcd. C 25.64, H 3.21; found C 26.01, H 3.13. <sup>1</sup>H NMR ([D<sub>6</sub>]acetone):  $\delta$  = 1.38 (d, <sup>3</sup>J<sub>H,H</sub> = 5 Hz, 24 H, CH<sub>3</sub>), 4.83 (m, 4 H, OCH), 5.32 (s, 10 H, Cp) ppm. <sup>13</sup>C NMR ([D<sub>6</sub>]acetone):  $\delta$  = 209.4 (d, <sup>2</sup>J<sub>P,C</sub> = 34 Hz, CO), 88.6 (Cp, 3), 88.7 (Cp, **2**), 77.3 (d,  ${}^{2}J_{PC}$  = 9.9 Hz, OCH), 23.4 (CH<sub>3</sub>, **2**), 23.8 (CH<sub>3</sub>, **3**) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR ([D<sub>6</sub>]acetone, room temp.):  $\delta = 174.9$  (s, <sup>1</sup>J<sub>P,Se</sub> = 511.7 Hz, **2**), 176.1 (s,  ${}^{1}J_{P,Se}$  = 513.0 Hz, **3**); 223 K:  $\delta$  = 177.4 (s,  ${}^{1}J_{P,Se} = 511.0 \text{ Hz}, 2$ ), 179.5 (s,  ${}^{1}J_{P,Se} = 513.0 \text{ Hz}, 3$ ) ppm; (CDCl<sub>3</sub>, room temp.):  $\delta$  = 172.3 (s, <sup>1</sup>J<sub>P,Se</sub> = 511.7 Hz, **2**), 173.6 (s, <sup>1</sup>J<sub>P,Se</sub> =



511.7 Hz, **3**) ppm; relative ratio ca. 2:1. <sup>77</sup>Se{<sup>1</sup>H} NMR ([D<sub>6</sub>]acetone, 223 K):  $\delta$  = 186.9 (d, <sup>1</sup>*J*<sub>P,Se</sub> = 512 Hz, **2**), 212.0 (d, <sup>1</sup>*J*<sub>P,Se</sub> = 507.8 Hz, **3**) ppm. IR (KBr):  $\tilde{v}$  = 251 [v(Se–Se)], 345, 374 [v(P–Se)], 963 [v(POC)], 2015, 2058 [v(CO)] cm<sup>-1</sup>.

 $[{Cp(CO)_2FeP(OiPr)_2}_2Se_n][InCl_4]_2$  (4, n = 2; 5, n = 3): The same procedure as that described for 2 was used. However, InCl<sub>3</sub> (0.076 g, 0.34 mmol) was used instead of GaCl<sub>3</sub>, and a 2:1 ratio of LA to initial precursor at 5 °C was maintained. Yield 0.096 g (77%).  $(C_{26}H_{38}Cl_8Fe_2In_2O_8P_2Se_2)_{0.33}(C_{26}H_{38}Cl_8Fe_2In_2O_8P_2Se_3)_{0.66}$ 1.5C3H6O (1449.39): calcd. C 25.06, H 3.24; found C 24.99, H 2.84. <sup>1</sup>H NMR ([D<sub>6</sub>]acetone):  $\delta$  = 1.46 (d, <sup>3</sup>J<sub>H,H</sub> = 3 Hz, 24 H, CH<sub>3</sub>), 4.97 (m, 4 H, OCH), 5.51 (s, 10 H, Cp) ppm. <sup>13</sup>C NMR ([D<sub>6</sub>]acetone):  $\delta$  = 209.3 (d, <sup>2</sup>J<sub>P,C</sub> = 32 Hz, CO), 89.3 (Cp), 77.4 (d, <sup>2</sup>J<sub>P,C</sub> = 10.9 Hz, OCH), 23.9 (CH<sub>3</sub>, 4), 24.0 (CH<sub>3</sub>, 5) ppm.  ${}^{31}P{}^{1}H{}$ NMR ([D<sub>6</sub>]acetone, room temp.):  $\delta = 176.3$  (s,  ${}^{1}J_{P,Se} = 531.0$  Hz): 223 K  $\delta$  = 179.5 (s, <sup>1</sup>J<sub>P,Se</sub> = 525.0 Hz), 179.8 (s, <sup>1</sup>J<sub>P,Se</sub> = 523.0 Hz) ppm. <sup>77</sup>Se{<sup>1</sup>H} NMR ([D<sub>6</sub>]acetone, 223 K):  $\delta = 127.6$  (d, <sup>1</sup>J<sub>Se,P</sub> = 502.5 Hz, **5**), 150.4 (d,  ${}^{1}J_{\text{Se,P}}$  = 525.9 Hz, **4**) ppm. IR (KBr):  $\tilde{v}$  = 226 [v(Se-Se)], 320, 330 [v(P-Se)], 955 [v(POC)], 2014, 2057 [v(CO)]  $cm^{-1}$ .

Reactions of 2 and 3 with a Tertiary (or Secondary) Phosphane: Treatment of a mixture of 2 and 3 (30 mg) with a slight excess of Ph<sub>3</sub>P in CDCl<sub>3</sub> (NMR tube under Ar) for 3 d resulted in the formation of 1 together with Ph<sub>3</sub>P=Se ( $\delta_P = 36.4 \text{ ppm}$ ,  $J_{P,Se} = 727 \text{ Hz}$ ) and a new intermediate cationic species (see NMR section). The formation of 1 and Ph<sub>3</sub>P=Se was monitored by <sup>31</sup>P NMR spectroscopy. With bis(2-phenethyl)phosphane (R'<sub>2</sub>PH),<sup>[39]</sup> 2 and 3 immediately and quantitatively produced 1, R'<sub>2</sub>P(Se)H, and an unknown R'<sub>2</sub>PCl–gallium(III) chloride complex. The reaction of 1 with R'<sub>2</sub>PH formed new cationic diphosphorus monoselenium species together with R'<sub>2</sub>P(Se)H (vide supra).

[{ $(iPrO)_2PSe_2$ }Ga] (6): NH<sub>4</sub>[Se<sub>2</sub>P(OiPr)<sub>2</sub>] (0.3 g, 1 mmol) was dissolved in MeOH (20 mL) in a 100 mL Schlenk flask, and GaCl<sub>3</sub> (0.06 g, 0.34 mmol) was added. The resulting mixture was stirred for 1 h (0 °C, N<sub>2</sub>). The solution was then concentrated to dryness under vacuum. The powder formed was redissolved in DCM

Table 1. Selected crystallographic data for 3, 4, and 6.

(30 mL) and the solution filtered. The colorless filtrate was concentrated to dryness under vacuum to obtain the product as a pale yellow powder of **6**. Yield 0.255 g (85%). M.p. 157 °C. C<sub>18</sub>H<sub>42</sub>Ga-O<sub>6</sub>P<sub>3</sub>Se<sub>6</sub> (990.93): calcd. C 21.82, H 4.27; found C 21.36, H 4.38. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta = 1.41$  (d,  ${}^{3}J_{\rm H,H} = 6.2$  Hz, 36 H, CH<sub>3</sub>), 4.96 (m, 6 H, OCH) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, room temp.):  $\delta = 63.0$  (s,  ${}^{1}J_{\rm P,Se} = 617$  Hz), 53.8 (br. s,  ${}^{1}J_{\rm P,Se} = 584$  Hz) ppm. <sup>77</sup>Se NMR (CDCl<sub>3</sub>, room temp.):  $\delta = 252.4$  (d,  ${}^{1}J_{\rm P,Se} = 616$  Hz), 311.4 (d,  ${}^{1}J_{\rm P,Se} = 584$  Hz) ppm.

**[Cp(CO)<sub>2</sub>FeP(O)(OiPr)<sub>2</sub>] (8):** To a vigorously stirred solution of 1 (0.708 g, 1.75 mmol) in THF/MeOH (1:1, v/v; 35 mL), a solution of Oxone (37 mL, 0.1 M) was added in one portion. The temperature of the reaction mixture increased to 40 °C, and the mixture was stirred for 30 min. Solid precipitates were removed by centrifuge, the filtrates were extracted with DCM ( $3 \times 20$  mL), and the combined organic phase was washed with water three times. The solution was dried with Na<sub>2</sub>SO<sub>4</sub>, and the solvent was removed from the filtrate to yield a yellow-brown oil. Yield 0.538 g (90%). C<sub>13</sub>H<sub>19</sub>FeO<sub>5</sub>P·THF (414.21): calcd. C 49.28, H 6.57; found C 49.33, H 6.71. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 1.24 (t, <sup>3</sup>J<sub>H,H</sub> = 9.7 Hz, 12 H, CH<sub>3</sub>), 4.71 (m, 2 H, OCH), 5.03 (s, 5 H, Cp) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  = 105.5 (s) ppm. IR (KBr):  $\tilde{v}$  = 970 and 977 [v(POC)], 1145 [v(P=O)], 1985, 2026 [v(CO)] cm<sup>-1</sup>. MS (MALDI-TOF): *m*/*z* (calcd.) = 343.0 (342.2).

**Crystal Structure Determinations:** Single crystals of **3**, **4**, and **6** suitable for X-ray crystallography were obtained by diffusing hexane into DCM solutions of the compounds. The crystals were mounted on the tips of glass fibers with epoxy resin, and the data were collected with an APEX II CCD diffractometer with graphite-mono-chromated Mo- $K_a$  radiation ( $\lambda = 0.71073$  Å). Data reduction was performed with SAINT,<sup>[45]</sup> which corrects for Lorentz and polarization effects. A multiscan absorption correction based on SAD-ABS was applied. Structures were solved by the use of direct methods, and the refinements were performed by the least-squares method on  $F^2$  with the SHELXL-97 package,<sup>[46]</sup> incorporated in SHELXTL/PC V5.10.<sup>[47]</sup> Crystallographic data are presented in

3 4 6 Empirical formula  $C_{26}H_{38}Cl_8Fe_2Ga_2O_8P_2Se_3\\$  $C_{26}H_{38}Cl_8Fe_2In_2O_8P_2Se_2$ C18H42GaO6P3Se6 1312.16 1323.29 990.91 Formula mass monoclinic Crystal system orthorhombic monoclinic  $Pna2_1$ C2/cSpace group C2/c30.363 (2) a [Å] 22.5285(8) 15.751(3)13.9131(5) b [Å] 13.084(3)13.7567 (9) c [Å] 15.3894(5) 20.6389 (14) 23.041(5) a [°] 90 90 90 90 95.024(5) 119.802 (2) β [°] γ [°] 90 90 90 4730.2(18) V [Å<sup>3</sup>] 4823.7(3) 7480.7 (9) Ζ 4 8 8  $\rho_{\rm calcd.} \, [\rm g\, cm^{-3}]$ 1.807 1.858 1.760  $\mu \,[{\rm mm}^{-1}]$ 4.506 3.660 6.729 T [K] 296(2) 296(2)296 Reflections collected 48598 31188 7366 10945 ( $R_{int} = 0.0654$ ) 5676 ( $R_{int} = 0.0424$ )  $4358(R_{\rm int} = 0.049)$ Independent reflections Final *R* indices  $[I \ge 2\sigma(I)]^{[a,b]}$ R1 = 0.0388R1 = 0.0510R1 = 0.0583wR2 = 0.1447wR2 = 0.1749wR2 = 0.0778R indices (all data)[a,b] R1 = 0.0850, R1 = 0.0880R1 = 0.1044wR2 = 0.0897wR2 = 0.1662wR2 = 0.1937Goodness of fit 0.994 1.040 1.093 Largest difference peak/hole [eÅ<sup>-3</sup>] 1.537/-0.739 0.427/-0.378 2.683/-1.170 [a]  $R1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$ . [b]  $wR2 = \{\Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2] \}^{1/2}$ .

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Table 1. CCDC-858704 (for **3**), -858705 (for **4**), and -858706 (for **6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data\_request/cif.

**Supporting Information** (see footnote on the first page of this article): <sup>31</sup>P NMR spectra (S1–S5).

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