

Synthesis and structural characterization of gallium and indium complexes obtained from redistribution reactions of mixed chalcogen-imidodiphosphinate ligands

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Received 16 February 2005; revised 22 March 2005; accepted 22 March 2005

Available online 5 May 2005

Abstract

The ionic complex $[\text{Ga}\{\text{N}(\text{SP}^i\text{Pr}_2)(\text{SeP}^i\text{Pr}_2)\text{-S, Se}\}_2]^+[\text{GaCl}_4]^-$ (**5**) was prepared by a ligand redistribution process from the mono-chelate $[\text{Cl}_2\text{Ga}\{\text{N}(\text{SP}^i\text{Pr}_2)(\text{SeP}^i\text{Pr}_2)\text{-S, Se}\}]$ (**3**) complex in benzene. A similar phenomenon was observed for the heavier indium homologues, where the neutral complexes $[\text{ClIn}\{\text{N}(\text{SP}^i\text{Pr}_2)(\text{SeP}^i\text{Pr}_2)\text{-S, Se}\}_2]$ (**7**) and $[\text{ClIn}\{\text{N}(\text{OP}^i\text{Pr}_2)(\text{SP}^i\text{Pr}_2)\text{-O, S}\}_2]$ (**8**) were isolated along with InCl_3 as the main reaction by-product. Complexes **5**, **7** and **8** were characterized by single-crystal X-ray structural analysis.

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Keywords: Indium; Gallium; Cations; Chalcogens

1. Introduction

Halogen-based gallium and indium complexes are important due to their Lewis acid properties, these compounds generally dissolve in polar solvents with a pronounced tendency to ionize, generally existing as high coordinated species [1]. Moreover, the formation of donor/acceptor complexes of GaCl_3 and InCl_3 is largely limited to adduct formation with ligands containing hard donor atoms such as O or N (crown

ether, DMSO, HMPA, pyridine, etc.) [2–4]. Although examples of gallium and indium tris-chelate complexes comprising symmetric and asymmetric imidodichalcogenodiphosphinate backbones are known [5,6], there are only a few examples of mono-chelate complexes bearing such types of ligands, and even less with asymmetric ligands [7,8]. Taking these facts into account, reactions were performed in order to study the coordinative ability of indium and gallium chlorides with imidodichalcogenodiphosphinate ligands comprising mixed chalcogen donor atoms. Herein, we report the first structurally characterized tetracoordinated Ga(III) cationic complex supported by mixed chalcogen atoms, along with the pentacoordinated neutral indium complexes achieved through the same type of ligand redistribution process.

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2. Results and discussion

2.1. Gallium complexes

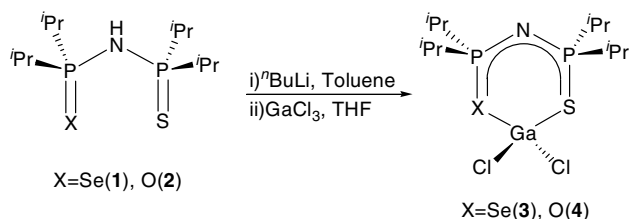
Reaction of the lithium salts of $\text{HN}(\text{SP}^i\text{Pr}_2)(\text{SeP}^i\text{Pr}_2)$ (**1**) and $\text{HN}(\text{OP}^i\text{Pr}_2)(\text{SP}^i\text{Pr}_2)$ (**2**) with GaCl_3 in dry toluene afforded the corresponding dichloro-complexes $\text{Cl}_2\text{Ga}\{\text{N}(\text{SP}^i\text{Pr}_2)(\text{SeP}^i\text{Pr}_2)\text{-S, Se}\}$ (**3**) and $\text{Cl}_2\text{Ga}\{\text{N}(\text{SP}^i\text{Pr}_2)(\text{OP}^i\text{Pr}_2)\text{-O, S}\}$ (**4**), respectively (Scheme 1). These complexes are moisture and air-sensitive, soluble in benzene, toluene and CH_2Cl_2 , but poorly soluble in hexane.

Compounds **3** and **4** were fully characterized by elemental analyses, IR, ^1H and ^{31}P NMR spectroscopy and EI-MS spectrometry. Compounds **3** and **4** exhibit the $\tilde{\nu}(\text{P-N-P})$ vibrations at 1241 and 1237 cm^{-1} , respectively; thus confirming the absence of the NH proton of the free ligands in their solid lattice. The EI-MS spectra for $^{35}\text{Cl}_2^{69}\text{Ga}\{\text{N}(\text{SP}^i\text{Pr}_2)(^{80}\text{SeP}^i\text{Pr}_2)\text{-S, Se}\}$ (**3**) and $^{35}\text{Cl}_2^{69}\text{Ga}\{\text{N}(\text{OP}^i\text{Pr}_2)(\text{SP}^i\text{Pr}_2)\text{-O, S}\}$ (**4**) display the corresponding molecular ions, albeit with low intensity at m/z 501 and 437, respectively. The ^1H NMR spectra of these compounds show the typical patterns for the deprotonated ligands, whilst, the ^{31}P NMR spectra exhibit two doublets at δ 67.6 ($P\text{-S}$) and 60.4 ($P\text{-Se}$) ppm ($^2J_{\text{P-P}} = 37$ Hz) for **3**, and δ 65.3 ($P\text{-S}$) and 54.6 ($P\text{-O}$) ppm, ($^2J_{\text{P-P}} = 31$ Hz) for **4**.

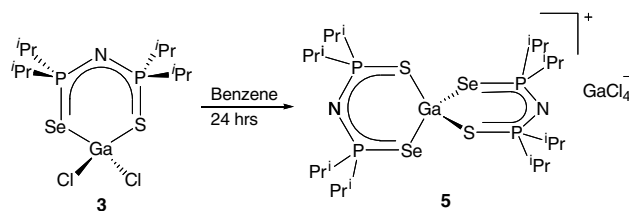
Attempts to grow single crystals of **3** in benzene resulted within 24 h in a rearrangement into an unusual salt-like complex $[\text{Ga}\{\text{N}(\text{SP}^i\text{Pr}_2)(\text{SeP}^i\text{Pr}_2)\text{-S, Se}\}_2]^+ [\text{GaCl}_4]^-$ (**5**), which was isolated as colorless crystals in 75% yield (Scheme 2). Attempts to obtain the corresponding rearrangement from **4** failed.

The moisture and air-sensitive compound **5** is insoluble in hydrocarbons but soluble in THF. The IR spectrum of **5** reveals a sharp absorption band at 1241 cm^{-1} owing to the $\tilde{\nu}(\text{P-N-P})$ vibration. The EI-MS spectrum of **5** shows the highest and most intense peak at m/z 789, corresponding to the cation $[\text{Ga}\{\text{N}(\text{SP}^i\text{Pr}_2)(^{80}\text{SeP}^i\text{Pr}_2)\text{-S, Se}\}_2]^+$. The ^{31}P NMR spectrum of **5** displays the same resonance signals as those observed in **3**, yet its $^2J_{\text{P-P}}$ (34 Hz) is smaller than that observed for **3** (37 Hz).

The structural features of **5** give an indication about the nature of the intermediate gallium complex in the transformation of **3**–**5**. We believe, that the plausible precursor for **5** should be the molecular compound



Scheme 1.



Scheme 2.

$[\text{ClGa}\{\text{N}(\text{SP}^i\text{Pr}_2)(\text{SeP}^i\text{Pr}_2)\text{-S, Se}\}_2]$, which through a donor/acceptor reaction with GaCl_3 yields the discrete ion pair $[\text{Ga}\{\text{N}(\text{SP}^i\text{Pr}_2)(\text{SeP}^i\text{Pr}_2)\text{-S, Se}\}_2]^+ [\text{GaCl}_4]^-$.

Single crystals of **5** suitable for X-ray structural analysis were obtained by keeping a saturated solution of **3** in benzene at ambient temperature for one day. Compound **5** crystallized in the tetragonal space group $P4_2/nbc$, with one quarter of the molecule in the asymmetric unit. The solid state structure of **5** reveals a discrete ion pair formed by the cationic bis-chelate species $[\text{Ga}\{\text{N}(\text{SP}^i\text{Pr}_2)(\text{SeP}^i\text{Pr}_2)\text{-S, Se}\}_2]^+$ containing a tetracoordinated Ga(III) center surrounded by four chalcogen donor atoms in a tetrahedral environment and the $[\text{GaCl}_4]^-$ anion. The central Ga(2) atom in the $[\text{GaCl}_4]^-$ anion has a distorted tetrahedral coordination sphere with common features to similar anions [9,10]. The chlorine atoms are disordered over two positions and due to the high symmetry of the molecule, the sulfur and selenium atoms are sharing the same position with an occupancy factor of 0.5 (Fig. 1).

The cationic Ga–Se bond length [2.417(8) Å] is significantly shorter than those in the related complexes $[\text{Me}_2\text{Ga}\{\text{N}(\text{SeP}^i\text{Pr}_2)_2\text{-Se, Se'}\}]$ [11] (av. 2.497(1) Å) and $[\text{Et}_2\text{Ga}\{\text{N}(\text{SePPh}_2)_2\text{-Se, Se'}\}]$ [7] (av. 2.524(2) Å), but is

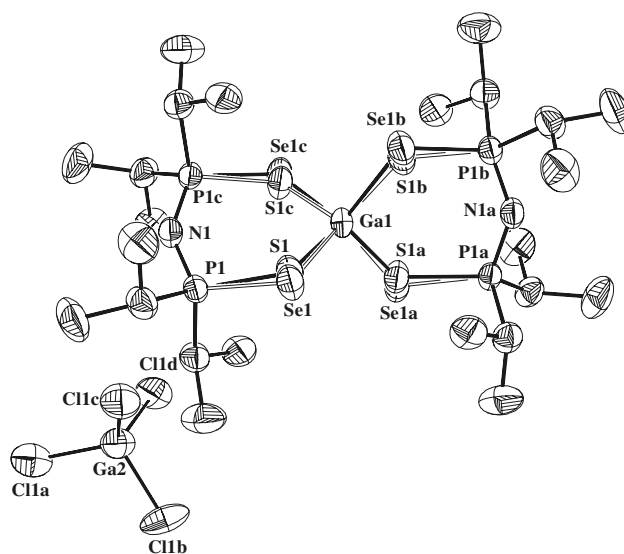
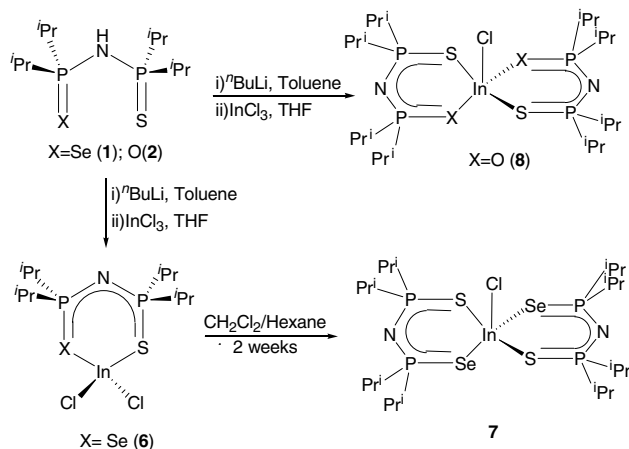


Fig. 1. ORTEP projection of **5**. Thermal ellipsoids at 50% probability. All H atoms and second position of the disordered chlorine atoms have been omitted for clarity.

in good agreement with the homoleptic complex $[\text{Ga}\{\text{N}(\text{SePPh}_2)_2\text{-Se, Se}\}_2][\text{GaCl}_4]^-$ (av. 2.406(1) Å) [12]. The Ga–S bond length (2.28(2) Å) is within the range of those found in the ion pair $[\text{Cl}_2\text{Ga}(\mu\text{-S})_2\text{Pt}_2(\text{PPh}_3)_4][\text{GaCl}_4]^-$ (av. 2.294(2) Å) [13] and in the molecular complexes $\text{Cl}_2\text{Ga}\{\text{N}(\text{SPPH}_2)(\text{SPMe}_2)\text{-S, S'}\}$ (2.273(2) Å) and $\text{Cl}_2\text{Ga}\{\text{N}(\text{SPPH}_2)_2\text{-S, S'}\}$ (2.263(2) Å) [12]. This shortening of the Ga–Se bond length suggests that the heterolytic Ga–Cl cleavage enhances the chalcogen $\text{X} \rightarrow \text{Ga}$ donation. However, such a conclusion cannot be borne out solely by the Ga–S or Ga–Se bond lengths due to the positional disorder of the chalcogens. Nonetheless, these structural observations are supported by the IR and ^{31}P NMR data of **5**. To the best of our knowledge, **5** is the first structurally characterized Ga(III) cation comprising both sulfur and selenium donor atoms.

2.2. Indium complexes

Reaction of the lithium salt of **1** with anhydrous InCl_3 in dry toluene afforded the corresponding dichloro-complex $\text{Cl}_2\text{In}\{\text{N}(\text{SP}^i\text{Pr}_2)(\text{SeP}^i\text{Pr}_2)\text{-S, Se}\}$ (**6**) in a good yield. Yet attempts to grow single crystals of **6** in a 1:1 dichloromethane/hexane mixture produced $[\text{ClIn}\{\text{N}(\text{SP}^i\text{Pr}_2)(\text{SeP}^i\text{Pr}_2)\text{-S, Se}\}_2]$ (**7**) and InCl_3 within two weeks time. In contrast, the reaction of the lithium salt of **2** with anhydrous InCl_3 in toluene in a 1:1 ratio yielded rather the bis-chelate complex $\text{ClIn}\{\text{N}(\text{OP}^i\text{Pr}_2)(\text{SP}^i\text{Pr}_2)\text{-O, S}\}_2$ (**8**) (84%) than the expected dichloro mono-chelate complex (Scheme 3). Compound **6** is poorly soluble in hydrocarbons but soluble in CH_2Cl_2 and THF, and is moisture and air-sensitive, whereas compounds **7** and **8** are soluble in CH_2Cl_2 , THF and diethylether, but insoluble in hexane and show no decomposition upon exposure to air.



The preparation of indium bis-chelates using symmetric imidodichalcogenodiphosphinate ligands has been reported, yet in this case a 2:1 ratio of the ligand and metal were used to achieve these structures [14]. The fact that InCl_3 was the only by-product isolated from the reaction mixtures of **7** and **8**, strongly suggests that the same ligand redistribution process as in **5** is involved in the formation of these bis-chelates. Moreover, certain types of heteroleptic gallium and indium complexes, particularly organometallic complexes are known to undergo ligand redistribution reactions to form homoleptic products [15–17].

Compounds **6–8** were fully characterized by elemental analyses, IR, ^1H and ^{31}P NMR spectroscopy, EI-MS spectrometry; and **7** and **8** were also characterized by X-ray diffraction studies. Compound **6** exhibits the characteristic $\tilde{\nu}(\text{P-N-P})$ vibration at 1234 cm^{-1} , while **7** and **8** exhibit very strong vibrations at $\tilde{\nu}$ 1235 and 1228 cm^{-1} , respectively. The ^{31}P NMR spectra for **6** and **7** exhibit only two doublets each, for all four phosphorus atoms (δ 67.3 (P–S) and 58.0 (P–Se), $^2J_{\text{P-P}} = 30\text{ Hz}$ for **6**; δ 67.3 (P–S) and 58.0 (P–Se), $^2J_{\text{P-P}} = 26\text{ Hz}$ for **7**); this pattern remains unchanged even at $-40\text{ }^\circ\text{C}$. As can be seen, the ^{31}P NMR spectrum of **7** displays the same resonance shifts as those observed

Table 1
Selected bond lengths (Å) and angles ($^\circ$) for compounds **7** and **8**

Compound 5			
Ga(1)–Se(1)	2.417(8)	S(1)–Ga(1)–Se(1A)	115.7(3)
Ga(1)–S(1)	2.28(2)	S(1)–Ga(1)–Se(1B)	96.8(4)
Ga(2)–Cl(av.)	2.173(7)	S(1)–Ga(1)–Se(1C)	116.5(4)
P(1)–Se(1)	2.158(9)	S(1)–Ga(1)–S(1A)	119(1)
P(1)–S(1)	2.15(2)	S(1)–Ga(1)–S(1B)	95(1)
N(1)–P(1)	1.570(1)	Se(1)–Ga(1)–Se(1A)	111.9(4)
		Se(1)–Ga(1)–Se(1B)	98.6(4)
		P(1)–N(1)–P(1C)	144.5(2)
Compound 7			
In(1)–Se(1)	2.618(1)	Se(1)–In(1)–Se(1A)	132.6(1)
In(1)–S(1)	2.657(1)	S(1)–In(1)–S(1A)	179.5(1)
In(1)–Cl(1)	2.404(2)	Se(1)–In(1)–S(1A)	100.2(1)
P(1)–Se(1)	2.187(1)	Se(1)–In(1)–S(1)	80.0(1)
N(1)–P(1)	1.592(4)	Se(1A)–In(1)–Cl(1)	113.7(1)
N(1)–P(2)	1.583(4)	S(1)–In(1)–Cl(1)	89.7(1)
P(2)–S(1)	2.048(2)	Se(1A)–In(1)–S(1)	100.2(1)
		P(1)–N(1)–P(2A)	138.7(3)
Compound 8			
In(1)–S(1)	2.488(1)	S(2)–In(1)–O(1)	100.2(1)
In(1)–S(2)	2.498(1)	S(2)–In(1)–O(2)	82.1(1)
In(1)–Cl(1)	2.369(1)	S(1)–In(1)–S(2)	125.5(3)
In(1)–O(1)	2.158(2)	O(1)–In(1)–O(2)	175.8(1)
In(1)–O(2)	2.151(2)	S(1)–In(1)–O(1)	94.6(1)
P(1)–S(1)	2.053(1)	S(1)–In(1)–O(2)	84.4(1)
P(3)–S(2)	2.042(1)	S(2)–In(1)–Cl(1)	114.5(1)
P(2)–O(1)	1.517(2)	S(1)–In(1)–Cl(1)	119.9(1)
P(4)–O(2)	1.519(2)	O(2)–In(1)–Cl(1)	91.2(2)
P(1)–N(1)	1.570(2)	O(1)–In(1)–Cl(1)	92.8(2)
P(2)–N(1)	1.593(2)	P(1)–N(1)–P(2)	135.0(2)
		P(3)–N(2)–P(4)	135.3(2)

in **6**, yet the magnitude of the $^2J_{P-P}$ in **6** (30 Hz) is significantly larger than that of **7** (26 Hz). The ^{31}P NMR spectrum of **8** reveals two doublets at δ 60.0 (P–S) and 53.5 (P–O) ppm, with a $^2J_{P-P}$ of 21 Hz.

The EI-MS spectrum of $^{35}Cl^{115}In\{N(SP^iPr_2)(^{80}SeP^iPr_2)-S, Se\}$ (**6**) displays a molecular ion at m/z 545 with the proper isotopic pattern, although with low intensity. The initial recognition of the bis-chelate nature of **7** stemmed from the observation of its EI-MS spectrum, where the highest peak at m/z 835 corresponds to the fragment $[M-Cl]^+$ ($^{115}In\{N(SP^iPr_2)(^{80}SeP^iPr_2)-S, Se\}$), while its molecular ion is silent. On the other hand, compound $^{35}Cl^{115}In\{N(OP^iPr_2)(SP^iPr_2)-O, S\}$ (**8**) revealed its bis-chelate nature by displaying a molecular ion at m/z 743. Nonetheless, the unambiguous molecular structures of **7** and **8** were determined by X-ray diffraction studies. Crystal data, data collection and refinement parameters are summarized in Table 1, and selected geometrical parameters are summarized in Table 2.

Compound **7** crystallized in a monoclinic space group $C2/c$, with one half of the molecule in the asymmetric unit (Fig. 2). The coordination environment around the indium atom reveals a distorted trigonal bipyramid (TBP), where Se(1), Se(1A) and the chlorine atom are

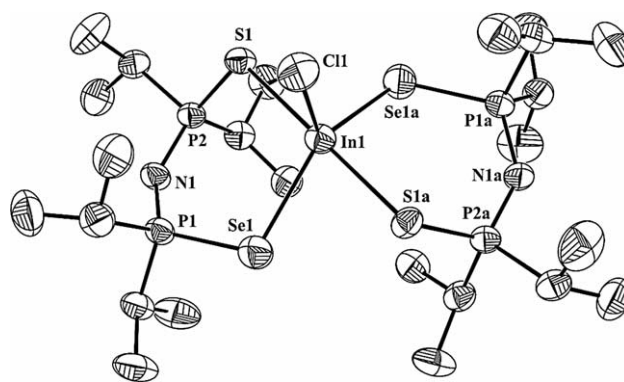


Fig. 2. ORTEP projection of **7**. Thermal ellipsoids at 50% probability. All H atoms have been omitted for clarity.

equatorially positioned, while S(1) and S(1A) occupy the axial positions.

The diaxial angle is $179.5(1)^\circ$, while the equatorial angles correspond to $132.6(1)^\circ$ and $113.7(2)^\circ$ for S(1A)–In(1)–Se(1) and Se(1)–In(1)–Cl(1), respectively. The endocyclic S(1)–In(1)–Se(1) angle ($100.2(3)^\circ$) results in an endocyclic S···Se distance of $4.047(3)$ Å. The axial In–S bond length ($2.657(1)$ Å) is larger than that of

Table 2
Crystal data and structural refinement for compounds **5**, **7** and **8**

	Compound 5	Compound 7	Compound 8
Formula	$C_{24}H_{56}Cl_4Ga_2N_2P_4S_2Se_2$	$C_{24}H_{56}ClInN_2P_4S_2Se_2$	$C_{24}H_{56}ClInN_2O_2P_4S_2$
Formula weight	999.91	868.90	742.98
Crystal system	Tetragonal	Monoclinic	Monoclinic
Space group	$P4_2/nbc$	$C2/c$	$P2_1/n$
Temperature, K	291(2)	293(2)	293(2)
λ , Å	0.71073	0.71073	0.71073
a , Å	15.382(1)	19.235(1)	9.343(1)
b , Å	15.382(1)	13.680(1)	14.606(1)
c , Å	18.307(1)	14.744(1)	26.629(1)
α , deg	90	90	90
β , deg	90	107.08(1)	90.12(1)
γ , deg	90	90	90
V , Å ³	4332(1)	3709(1)	3634(1)
Z	4	4	4
ρ_{calc} , g/cm ³	1.533	1.556	1.358
μ , mm ⁻¹	3.434	2.975	1.038
$F(000)$	2016	1760	1552
Crystal size, mm ³	$0.34 \times 0.26 \times 0.24$	$0.222 \times 0.160 \times 0.108$	$0.456 \times 0.238 \times 0.168$
θ range (deg)	1.87 to 25.03	1.86 to 32.54	2.07 to 32.49
Index ranges	$-18 \leq h \leq 18$, $-18 \leq k \leq 18$, $-21 \leq l \leq 21$	$-29 \leq h \leq 29$, $-20 \leq k \leq 20$, $-22 \leq l \leq 22$	$-14 \leq h \leq 14$, $-21 \leq k \leq 22$, $-39 \leq l \leq 40$
Number of reflections collected	32409	25410	49448
Number of independent reflection (R_{int})	1913 (0.0861)	6717 (0.0501)	13089 (0.0679)
Number of data/restraints/parameters	1913/99/140	6717/0/172	13089/0/341
Goodness-of-fit on F^2	0.920	0.984	1.002
R_1^a , wR_2^b ($I > 2(\sigma)$)	0.0323, 0.0776	0.0520, 0.1426	0.0593, 0.0841
R_1^a , wR_2^b (all data)	0.0434, 0.0804	0.0938, 0.1513	0.1166, 0.0958
Largest differential peak/hole (e Å ⁻³)	0.459/–0.231	1.458/–1.358	1.594/–0.772

^a $R = \sum |F_o| - |F_c| / \sum |F_o|$.

^b $wR_2 = \left[\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2) \right]^{1/2}$.

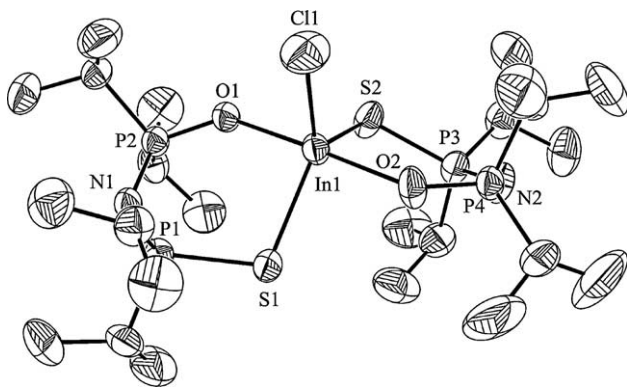


Fig. 3. ORTEP projection of **8**. Thermal ellipsoids at 50% probability. All H atoms have been omitted for clarity.

the equatorial In–Se bond (2.618(1) Å). These values are consistent with the characteristic larger bond lengths for the axial atoms in a TBP geometry, and are comparable with those found in $\text{ClIn}[\text{N}(\text{SPPH}_2)(\text{SePPH}_2)]_2$ (av. 2.576(2) Å for In–S and 2.667(2) Å for In–Se) [6], $\text{ClIn}[\text{N}(\text{SeP}^i\text{Pr}_2)_2]$ (2.645(3) Å) and $\text{ClIn}[\text{N}(\text{SP}^i\text{Pr}_2)_2]$ (2.616(1) Å) [6,14]. Likewise, the In–Cl bond length (2.404(2) Å) is in an agreement with the related complexes $[\text{ClIn}\{\text{N}(\text{XP}^i\text{Pr}_2)_2\}_2]$ (X = S, 2.410(2) Å; X = Se, 2.428(1) Å) [14], and $[\text{ClIn}\{\text{N}(\text{SPPH}_2)(\text{SePPH}_2)\}_2]$ (2.422(3) Å) [6].

Compound **8** crystallized in a monoclinic space group $P2_1/n$ and its molecular structure is illustrated in Fig. 3. The InO_2S_2 core exhibits a ψ -TPB geometry with an equatorial S(1)–In–S(2) angle of 125.5(3)° and an axial O(1)–In–O(2) angle corresponding to 175.8(1)°. The In–S and In–O bond lengths (av. 2.493(1) and 2.154(1) Å) are shorter than those corresponding to the tris-chelate $[\text{In}\{\text{N}(\text{SPPH}_2)(\text{OPPH}_2)\}_3]$ (av. 2.599(1) and 2.130(4) Å) [7]. Whereas, the endocyclic O–In–S angles (av. 91.2(1)°) and endocyclic O···S distances (av. 3.431(2) Å) are in good agreement with those in $[\text{In}\{\text{N}(\text{SPPH}_2)(\text{OPPH}_2)\}_3]$ [7].

Finally, the P–N–P angles for **7** (138.7(3)°) and **8** (135.2(2)°) are larger than those corresponding to the related complexes $[\text{ClIn}\{\text{N}(\text{SPPH}_2)(\text{SePPH}_2)\}_2]$ (129.3(3)°) and $[\text{In}\{\text{N}(\text{SPPH}_2)(\text{OPPH}_2)\}_3]$ (av. 130.4(4)°) [6].

3. Conclusion

Overall, we have identified a specific behavior for asymmetrically-substituted dichalcogen imido-diphosphate ligands with the heavier group 13 metals. In this process, the existence of a halogen-bound metal center seems to be determinant, since organometallic mono-chelate gallium complexes comprising XPNPY backbones have proven to be stable. Moreover, the structural outcome of this halide redistribution process seems to be governed by factors such as the electropos-

itive character and size of metal, the strength of M–Cl bond in the MCl_4^- anion, etc. [18]. Further research is currently underway to clarify the importance of these factors in determining the nature of the final products.

4. Experimental

4.1. Materials and measurements

All reactions were performed under an atmosphere of dry argon using standard Schlenk techniques. Solvents were properly dried and distilled prior to use. Elemental analyses were performed by Galbraith Laboratories (Knoxville, TN). ^1H (300 MHz) and ^{31}P (121.5 MHz) NMR spectra were recorded on a JEOL X300 spectrometer. Chemical shifts are reported in ppm with reference to TMS (internal) and H_2PO_3 85% (external). IR spectra were recorded on a Nicolet FT-IR Magna 750 in the range 4000–400 cm^{-1} as KBr pellets and in the range 4000–600 cm^{-1} as Nujol mulls. EI-MS data were obtained on a JEOL JMS-AX505HA (70 eV) utility. Melting points were measured in sealed and opened glass tubes on a Melt Temp II apparatus and are uncorrected. GaCl_3 and InCl_3 were obtained from commercial sources and used without further purification, $\text{HN}(\text{SP}^i\text{Pr}_2)(\text{SeP}^i\text{Pr}_2)$ (**1**) and $\text{HN}(\text{OP}^i\text{Pr}_2)(\text{SP}^i\text{Pr}_2)$ (**2**) were prepared according to the literature procedures [19]. Crystallographic data for all the structures were collected on a Bruker three-circle diffractometer equipped with a SMART Apex CCD detector using Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073$ Å). All structures were solved by direct methods [20] and refined against F^2 using SHELXL-97 [21].

4.2. Synthesis of $[\text{Cl}_2\text{Ga}\{\text{N}(\text{SP}^i\text{Pr}_2)(\text{SeP}^i\text{Pr}_2)\text{-S,Se}\}]$ (**3**)

A solution of $\text{HN}(\text{SP}^i\text{Pr}_2)(\text{SeP}^i\text{Pr}_2)$ (**1**) (0.50 g, 1.4 mmol) in toluene (15 ml) was cooled to 0 °C and a 1.6 M solution of $n\text{-BuLi}$ (0.9 ml, 1.5 mmol) in hexanes was added dropwise. The solution was stirred for 30 min at ambient temperature and slowly added to a solution of GaCl_3 (0.25 g, 1.4 mmol) in toluene (10 ml). The reaction mixture was stirred for additional 2 h and filtered to eliminate the precipitate. All the volatiles were removed under vacuum leaving a pale yellow solid. Yield: 0.61 g (87%), m.p. 123–124 °C. IR (nujol mull): 2926(s), 2855(s), 1461(m), 1241(w) cm^{-1} . ^1H NMR (C_6D_6 , 25 °C) δ 1.11–1.19 [br m, 24H, $\text{CH}(\text{CH}_3)_2$], 1.34 [sept, 4H, $\text{CH}(\text{CH}_3)_2$]; $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 25 °C) δ 67.6 (d, $^2J_{\text{P-P}} = 37$ Hz, P–S), 60.4 (d, $^2J_{\text{P-P}} = 37$ Hz, P–Se). EI-MS (70 eV), m/z (%): 501(2) [M^+ ; $\text{C}_{12}\text{H}_{28}^{35,37}\text{Cl}_2^{69}\text{GaNP}_2\text{S}^{80}\text{Se}$], 464(2) [$M^+ - ^{35}\text{Cl}$], 458(4) [$M^+ - \text{CH}(\text{CH}_3)_2$], 360(100) $M^+ - ^{69}\text{Ga}^{35}\text{Cl}_2$. Anal. Calc. for

$C_{12}H_{28}Cl_2GaNP_2SSe$: (499.95) C, 28.86; H, 5.66; N, 2.80. Found: C, 28.39; H, 5.59; N, 2.73%.

4.3. Synthesis of $[Cl_2Ga\{N(OP^iPr_2)(SP^iPr_2)-O,S\}]$ (4)

A similar procedure as that for **3** was used starting from **2** (0.36 g, 1.2 mmol), 1.6 M solution of $nBuLi$ in hexanes (0.8 ml, 1.3 mmol) and $GaCl_3$ (0.21 g, 1.2 mmol). Yield: 0.39 g (74%) semisolid; 1H NMR (C_6D_6 , 25 °C) δ 0.95–0.99 (br m, 24H, $CH(CH_3)_2$), 1.69 (m, 2H, $P(S)CH(CH_3)_2$), 1.87 (m, 2H, $P(O)CH(CH_3)_2$). ^{31}P NMR (C_6D_6 , 25 °C): δ 65.3 (d, $^2J_{P-P} = 31$ Hz, $P-S$), 54.6 (d, $^2J_{P-P} = 31$ Hz, $P-O$). EI-MS (70 eV), m/z (%): 437(3) [M^+ ; $C_{12}H_{28}^{35,37}Cl_2^{69}GaNP_2OS$], 296(100) [$M^+ - ^{69}Ga^{37}Cl_2$]. Anal. Calc. for $C_{12}H_{28}Cl_2GaNP_2OS$: (436.99) C, 32.98; H, 6.46; N, 3.21. Found: C, 33.09; H, 6.59; N, 3.33%.

4.4. Preparation of $[Ga\{N(SP^iPr_2)(SeP^iPr_2)-S,Se\}_2]^+ [GaCl_4]^-$ (5)

Compound **3** (0.20 g, 0.4 mmol) was dissolved in dry benzene and kept for 24 h under an atmosphere of argon. Colorless crystals of **5** were obtained in a 75% yield (0.15 g), m.p. 180 °C decomp. IR (KBr pellet): 2975(m), 2878(w), 1459(m), 1240(s) cm^{-1} . 1H NMR (C_6D_6 , 25 °C): δ 1.07 (m, 24H, $CH(CH_3)_2$), 1.91, 1.87 (sept, 4H, $CH(CH_3)_2$). $^{31}P\{^1H\}$ NMR (C_6D_6 , 25 °C) δ 67.7 (d, $^2J_{P-P} = 34$ Hz, $P-S$), 60.4 (d, $^2J_{P-P} = 34$ Hz, $P-Se$). EI-MS (70 eV), m/z (%): 788(100) [M^+ ; $C_{24}H_{56}^{69}GaNP_4S_2^{80}Se_2$], 703(25) [$M^+ - 2\{CH(CH_3)_2\}$], 464(40) [$C_{12}H_{28}^{35}Cl^{69}GaNP_2S^{80}Se$]. Anal. Calc. for $C_{24}H_{56}Cl_4Ga_2N_2P_4S_2Se_2$: (937.96) C, 30.77; H, 6.03; N, 2.99. Found: C, 30.29; H, 5.78, N, 2.87%.

4.5. Synthesis of $[Cl_2In\{N(SP^iPr_2)(SeP^iPr_2)-S,Se\}]$ (6)

A solution of **1** (0.50 g, 1.4 mmol) in toluene (15 ml) was cooled to 0 °C and a 1.6 M solution of $nBuLi$ (0.9 ml, 1.5 mmol) in hexanes was added dropwise. The solution was stirred for 30 min at ambient temperature and slowly added to a solution of $InCl_3$ (0.31 g, 1.4 mmol) in toluene (10 ml). The reaction mixture was stirred for additional 2 h and filtered to eliminate the precipitated $LiCl$. Subsequently, all the volatiles were removed under vacuum leaving a white solid. Yield: 0.60 g (79%), m.p. 138–140 °C. IR (Nujol mull): 2926(s), 2855(s), 1462(m), 1234(m) cm^{-1} . 1H NMR (C_6D_6 , 25 °C) δ 1.19 (br m, 24H, $CH(CH_3)_2$), 1.49 (br m, 4H, $CH(CH_3)_2$) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6 , 25 °C) δ 67.3 (d, $^2J_{P-P} = 30$ Hz, $P-S$), 58.0 (d, $^2J_{P-P} = 30$ Hz, $P-Se$) ppm. EI-MS (70 eV), m/z (%): 545(2) [M^+ ; $C_{12}H_{28}^{35}Cl_2^{115}InNP_2S^{80}Se$], 360(100) [$M^+ - ^{115}In^{35}Cl_2$]. Anal. Calc. for $C_{12}H_{28}Cl_2GaNP_2OS$: (545.05) C,

26.44; H, 5.18; N 2.57. Found: C, 26.09; H, 5.02; N 2.49%.

4.6. Synthesis of $[ClIn\{N(SP^iPr_2)(SeP^iPr_2)-S,Se\}_2]$ (7)

Method a. Compound **6** (0.220 g, 0.40 mmol) was dissolved in a 1:2 mixture of CH_2Cl_2 /hexane and kept under argon for two weeks. During this period white colorless crystals were formed. Yield: 0.17 g (98%).

Method b. Solution of **1** (0.50 g, 1.3 mmol) in toluene (15 ml) was cooled to 0 °C and a 1.6 M solution of $nBuLi$ (0.90 ml, 1.4 mmol) in hexanes was added dropwise. The solution was stirred for 30 min at room temperature and slowly added to a solution of $InCl_3$ (0.14 g, 0.65 mmol) in THF (10 ml). The reaction mixture was stirred for additional 2 h and filtered to eliminate the precipitate. All the volatiles were removed under vacuum leaving a white solid, which was recrystallized from CH_2Cl_2 /hexane mixture. The solution from the clear solution was then removed under vacuum to give a white hygroscopic solid that decomposed under air (presumably $InCl_3$). Yield: 0.42 g (74%), m.p. 180–182 °C. IR (KBr pellet) 2968(m), 2872(m), 1458(m), 1235(s) cm^{-1} . 1H NMR ($CDCl_3$, 25 °C): δ 1.24 [br m, 24H, $CH(CH_3)_2$], 2.29 [br m, 4H, $CH(CH_3)_2$] ppm; $^{31}P\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ 67.3 (d, $^2J_{P-P} = 26$ Hz, $P-S$), 58.0 (d, $^2J_{P-P} = 26$ Hz, $P-Se$) ppm. EI-MS m/z (%): 835(100) [$M^+ - ^{35}Cl$; $^{115}In\{N(SP^iPr_2)(^{80}SeP^iPr_2)\}_2$], 510(10) [$M^+ - L$]. Anal. Calc. for $C_{24}H_{56}ClInN_2O_2P_4S_2Se_2$: (868.93) C, 33.17; H, 6.50; N, 3.22. Found: C, 32.95; H, 6.20; N, 3.02%.

4.7. Synthesis of $[ClIn\{N(OP^iPr_2)(SP^iPr_2)-O,S\}_2]$ (8)

A solution of **2** (0.38 g, 1.3 mmol) in toluene (15 ml) was cooled to 0 °C and a 1.6 M solution of $nBuLi$ (0.90 ml, 1.4 mmol) in hexane was added dropwise. The solution was stirred for 30 min at room temperature and slowly added to a solution of $InCl_3$ (0.28 g, 1.3 mmol) in THF (10 ml). The reaction mixture was stirred for additional 2 h and filtered to eliminate the precipitate and concentrated to 5 ml, which upon standing yielded colorless crystals. The solvent from the solution was then removed under vacuum giving a white hygroscopic solid that decomposed under air (presumably $InCl_3$). Yield: 0.49 g (84%), m.p. 112–114 °C. IR (KBr pellet): 2967(m), 2875(m), 1461(m), 1228(s), 1069(s) cm^{-1} . 1H NMR ($CDCl_3$, 25 °C) δ 1.17, 1.30 (br m, 24H, $CH(CH_3)_2$), 2.26 (sept, 2H, $P(O)CH(CH_3)_2$) 1.91 (sept, 2H, $P(S)CH(CH_3)_2$) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 25 °C) δ 60.0 (d, $^2J_{P-P} = 21$ Hz, $P-S$) 53.5 (d, $^2J_{P-P} = 21$ Hz, $P-O$) ppm. EI-MS (70 eV), m/z (%): 742(5) [M^+ , $^{35}Cl^{115}In\{N(OP^iPr_2)(SP^iPr_2)\}_2$], 699(100) [$M^+ - CH(CH_3)_2$]. Anal. Calc. for $C_{24}H_{56}ClInN_2O_2P_4S_2$:

(743.01) C, 38.81; H, 7.60; N, 3.77. Found: C, 37.56; H, 7.23; N, 3.79%.

5. Supporting material

Crystallographic data for the compounds **5**, **7** and **8** have been deposited with the Cambridge Crystallographic Data Centre; CCDC Nos. 258004 for **5**, 258005 for **7**, and 262702 for **8**. Copies of this information maybe obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 IEZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk).

Acknowledgments

We are grateful to the DGAPA-UNAM (PAPIIT grant IN105203) for financial support on this work.

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