

Inorganic rings with group 13 organometallics and iminodiphosphinechalcogenides

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Abstract

Herein we report the synthesis and characterization of the organometallic complexes $[R_2Al\{(SePPh_2)_2N\}]$ ($R = Me$ (**1**), Et (**2**), tBu (**3**)) and $[Et_2Ga\{(SePPh_2)_2N\}]$ (**4**) which were obtained through alkane elimination reactions. The compounds were characterized by physical (m.p.); chemical (C, H, analysis), and spectroscopic techniques (multinuclear NMR and IR). In addition, the crystal structure of **4** was obtained by single crystal X-ray diffraction. The molecular structure of **4** reveals a metallacycle with a diethylgallium fragment coordinated symmetrically to the imidophosphinoselenate ligand in a distorted tetrahedral environment. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Aluminum; Gallium; Iminodiphosphinates; Selenium; Alkane elimination

1. Introduction

The preparation of complexes that contain a variety of transition and main group elements with iminodiphosphinate ligands $[R_2P(E)NP(E')R_2]^-$ ($E, E' = NR_2, O, S$ or Se ; $R = Me, tPr$ or Ph) have recently received considerable attention (Fig. 1A) [1,2]. These ligands are the inorganic analogs of the ubiquitous acetylacetonate (acac) [3,4]. Contrary to the complexes formed with acac, the ones with iminodiphosphinates show a variety of conformations of the six-membered ring MEPNPE'. In addition to their fundamental interest, tris-chelate complexes with iminodiphosphinate ligands have been used to study the stereochemical consequences of the bismuth atom electron lone pair [5,6]. The possibility of the selective coordination of metallic centers with iminodiphosphinate ligands through the manipulation of the R groups and the donor atoms E and E' has been suggested [2]. This

potential property could make them superior to modified β -diketonates for the selective solvent extraction of metals (e.g. β -diketonates are efficient for the extraction of Al (III) and In (III)) [7]. The chemistry of the iminodiphosphinoselenates with group 13 elements is less well known by comparison to the chemistry with the related oxo and thio ligands. There are only two tris-chelates with In and Bi with the ligand $Ph_2P(Se)NHP(Se)Ph_2$ (**LH**) (Fig. 1B) [6].

The present report involves the synthesis and characterization of the organometallic complexes $[R_2Al\{(SePPh_2)_2N\}]$ ($R = Me$ (**1**), Et (**2**), tBu (**3**)) and $[Et_2Ga\{(SePPh_2)_2N\}]$ (**4**) which to our knowledge are the first organometallic compounds that contain group 13 elements with iminodiphosphinates.

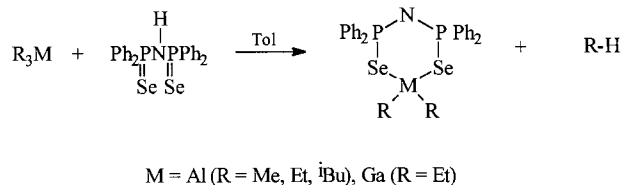
2. Results and discussion

The acidic nature of the imino hydrogen in the ligand $Ph_2P(Se)NHP(Se)Ph_2$ (**LH**) makes it a good candidate

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for alkane elimination reactions toward group 13 organometallics. This idea stimulated us to perform reactions of trialkylaluminum and gallium with LH. The reactions were carried out in a 1:1 stoichiometry in toluene at r.t. (Scheme 1). The products were isolated in yields of 75–80%. Compounds **1–3** are very susceptible to hydrolysis; on exposure to air they produce the metal hydroxide and the free ligand (demonstrated by $^1\text{H-NMR}$).

The first indication of complexation of LH through alkane elimination instead of adduct formation in **1–4** is offered by the absence of the characteristic free ligand IR absorption at 2623 cm^{-1} and the N–H resonance in $^1\text{H-NMR}$ at 4.27 ppm. It is worth to note that in **4** and in **1–3** the nitrogen atom which can be pictured to have lost hydrogen does not participate in bonding to the metal. When LH is in solution the hydrogen can be delocalized through the P(Se)NP(Se) fragment facilitating bond formation to the metal without nitrogen. Evidence can be found in the solid-state molecular structures of $\text{Ph}_2\text{P(E)NHP(E)Ph}_2$ (O, S, Se). The ligand with E=O is a tautomer with a linear P–N–P arrangement and an O–H bond. The sulfur and selenium ligands are isostructural with the P=E in *anti* positions and hydrogen bonding between P=E and NH groups responsible for dimer formation [2]. In addition the $^1\text{H-NMR}$ spectra show signals due to the carbon atom directly bonded to the metallic center at a distinct high field chemical shift of -0.13 to 0.90 ppm. The $^{31}\text{P}\{^1\text{H}\}$ -NMR spectra show a singlet of 92% intensity and the resonances of 8% intensity due to the AA'X spin system associated with the $\text{Ph}_2\text{P(Se)NHP}(^{77}\text{Se})\text{Ph}_2$ isotopomer. The chemical shifts and $^1J(\text{PSe})$ coupling constants for **1–3** (54 ppm and 802–804 Hz) are similar to those of the free ligand LH (53 ppm and 793 Hz). This can be interpreted as the result of weak Al–Se bonds in the complexes. On the contrary, **4** shows a high field chemical shift and a reduction in magnitude of the coupling constant (30 ppm and 534 Hz), the result of stronger Ga–Se bonds. For **1–3** the ^{27}Al -



Scheme 1. General synthesis of compounds **1–4**.

NMR spectra show one signal in the range of 115–156 ppm which suggests discrete monomeric molecules with a tetrahedral environment around the aluminum atom [8].

Stoichiometries of 1:2 and 1:3 were attempted with AlMe_3 and LH in toluene with the isolation of **1** as the exclusive product after removal of volatiles. In an effort to explore the reactivity of **1** and **4**, reactions with Ph_3SiOH and NH_4BPh_4 in THF were tried. In both cases the unreacted starting materials were isolated in high yields.

Suitable crystals of **4** for X-ray analysis were grown from a solution of hexanes at -35°C . A summary of crystallographic data is given in Table 1. Selected bond distances and angles are given in Table 2. The molecular structure and atom numbering scheme are shown in Fig. 2. The structure of **4** shows a metallacycle with a diethylgallium fragment coordinated symmetrically to

Table 1
Crystal data for **4**

Empirical formula	$\text{C}_{28}\text{H}_{30}\text{GaNP}_2\text{Se}_2$
Formula weight	670.14
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
<i>a</i> (Å)	10.0479(6)
<i>b</i> (Å)	10.6760(7)
<i>c</i> (Å)	13.6879(8)
α (°)	94.817(1)
β (°)	91.018(1)
γ (°)	96.706(1)
<i>V</i> (Å ³)	1452.6(2)
<i>Z</i>	2
<i>D</i> _{calc} (g cm ⁻³)	1.532
Crystal size (mm)	(0.4) ³
Radiation, <i>K</i> _α ; λ (Å)	Mo; 0.71073
Temperature (K)	298
2θ Range (°)	2.98–42
Scan type	2θ–θ
Scan speed (° min ⁻¹)	1–60
Scan range (°)	0.55
Reflections collected	5011
Independent reflections	3045 (<i>R</i> _{int} = 0.1197)
Observed reflections	3045 [<i>F</i> > 4.0σ(<i>F</i>)]
No. of parameters	307
<i>R</i>	0.0517
<i>R</i> _w	0.1258
Goodness-of-fit	1.039
Largest difference electron density (e Å ⁻³)	0.75 and -0.993

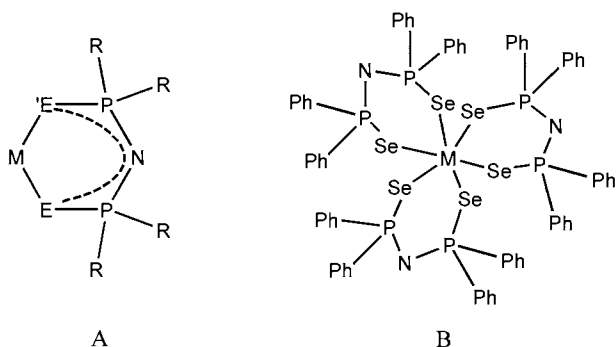


Fig. 1. (A) General depiction of complexes that contain transition and main group elements with imidodiphosphinate ligands [1,2]. (B) Tris-chelates with M = In and Bi, and the ligand $\text{Ph}_2\text{P(Se)NHP(Se)Ph}_2$ (LH) [6].

Table 2
Selected bond lengths (Å) and angles (°) for **4**

Ga(1)–C(1)	1.998(7)	C(3)–Ga(1)–C(1)	125.5(4)
Ga(1)–C(3)	1.977(7)	C(3)–Ga(1)–Se(1)	99.7(3)
Ga(1)–Se(1)	2.5347(10)	C(3)–Ga(1)–Se(2)	107.5(3)
Ga(1)–Se(2)	2.5139(10)	C(1)–Ga(1)–Se(2)	104.4(3)
P(1)–Se(1)	2.173(2)	Se(2)–Ga(1)–Se(1)	108.36(3)
P(2)–S(2)	2.168(2)	P(1)–Se(1)–Ga(1)	98.16(5)
P(1)–N(1)	1.591(5)	P(2)–Se(2)–Ga(1)	100.14(5)
P(2)–N(1)	1.594(5)	N(1)–P(1)–C(11)	105.9(3)
P(1)–C(5)	1.805(6)	N(1)–P(1)–C(5)	109.5(3)
P(1)–C(11)	1.808(6)	N(1)–P(1)–Se(1)	117.3(2)
P(2)–C(17)	1.812(6)	C(5)–P(1)–C(11)	105.5(2)
P(2)–C(23)	1.814(5)	C(5)–P(1)–Se(1)	109.8(2)
		N(1)–P(2)–C(17)	104.9(3)
		N(1)–P(2)–C(23)	111.3(3)
		N(1)–P(2)–Se(2)	117.4(2)
		P(1)–N(1)–P(2)	129.8(3)
		C(23)–P(2)–Se(2)	109.8(2)
		C(2)–C(1)–Ga(1)	119.5(7)
		C(10)–C(5)–P(1)	120.0(5)
		C(6)–C(5)–P(1)	121.1(5)

the imidophosphineselenate ligand in a distorted tetrahedral environment. The greater deviation from an ideal tetrahedral geometry is found in the Et₂Ga moiety with an angle of 125.5(4)°. The six-membered GaSe₂P₂N ring is puckered with a distorted boat conformation, the Se1 and P2 atoms are in the apices of the boat. This non-planar ring is a common feature with complexes formed with imidophosphinochalcogenide ligands. Replacing phosphorous for carbon atoms in the ring as in [Me₂Ga{HNC(CF₃)NC(CF₃)NH}] forms a planar six-membered ring [9]. The P–Se and P–N bond lengths are increased and decreased, respectively, as a consequence of deprotonation and

coordination relative to the free ligand (P–Se: 2.09–2.10 Å, P–N: 1.68–1.69 Å) [10]. The Ga–Se bonds are different in **4** (2.5139(10) and 2.5347(10) Å). These bonds are similar in magnitude to those found in the dimer [Me₃SiCH₂)₂Ga(μ-Se(CH₂SiMe₃))₂ (2.52–2.54 Å) [11]. Shorter Ga–Se single bonds have been reported for the dimeric [MesGa(μ-Se)·(μ-Me-pyridine)]₂ (2.38–2.39 Å), the monomeric Mes₂Ga(SeMes)·(μ-Me-pyridine) (2.44 Å) [11] and the cluster [Cp*Ga(μ₃-Se)]₄ (2.45–2.50 Å) [12]. The complex [Tp^{But}]₂GaSe supported by tris(3,5-di-*tert*-butylpyrazolyl)hydroborato ligation displays the shortest Ga–Se bond (2.214(1) Å) which is consistent with multiple bond character [13]. The crystal structure of the tris-chelate {[In{(SePPh₂)₂-N}]₃} shows a longer average metal–selenium bond of 2.75 (3) Å, as expected based on the larger size of indium [6]. The ligand ‘bite’ of **4** manifested in the Se–Ga–Se angle of 108.36(3)° is considerably greater than the bite observed in other tris-chelates M{(EPPH₂)₂N}₃, with M = In, Sb, Bi and E = O, S, Se (but not all the combinations). The E–M–E angle in these metallacycles is in the range 83.4 (1.0)–96.8(9)° [6]. The smaller ligand bite in the tris-chelates can be ascribed to the greater steric requirements of three ligands around a six-coordinate metal center by comparison to one that is four coordinate.

The structure of **4** and the spectroscopic and analytical data of **1–3** are consistent with Al–R and N–H cleavage during product formation. Condensation reactions of Me₃Al and ^{*i*}Bu₂AlH with the similar ligand Ph₂P(E)CH₂P(E)Ph₂ (E = O, S) are known [14,15]. The resulting products [Al(CH₃)](Ph₂P(O)CP(O)Ph₂)₂[Al(CH₃)₂]₂ and [Al^{*i*}Bu₂]₂(Ph₂P(S)CP(S)Ph₂)₂[Al^{*i*}Bu₂]₂ possess multimetallic bonding with the carbon atom of the ligand binding an aluminum center or two.

3. Experimental section

3.1. General considerations

All manipulations were conducted using Schlenk techniques in conjunction with an inert atmosphere glovebox. All solvents were rigorously dried prior to use. The ligand LH was synthesized from NH(PPh₂)₂ [16] and elemental selenium according to literature methods [10]. AlMe₃, AlEt₃, Al^{*i*}Bu₃ and GaEt₃ were used as received from commercial sources. NMR data were obtained at 295 K in benzene-*d*₆ solutions on JEOL-GSX-400 and -270 instruments operating at 270.17 or 399.78 (¹H), 108.9 or 161.33 (³¹P), 51.49 (Se⁷⁷) and 104.17 or 70.39 (Al²⁷) MHz. Chemical shifts in ppm are reported relative to Si(CH₃)₄, 85% H₃PO₄, Me₂Se and Al(H₂O)₆³⁺. Elemental analyses were obtained on a Perkin–Elmer 2400 analyzer. Infrared data

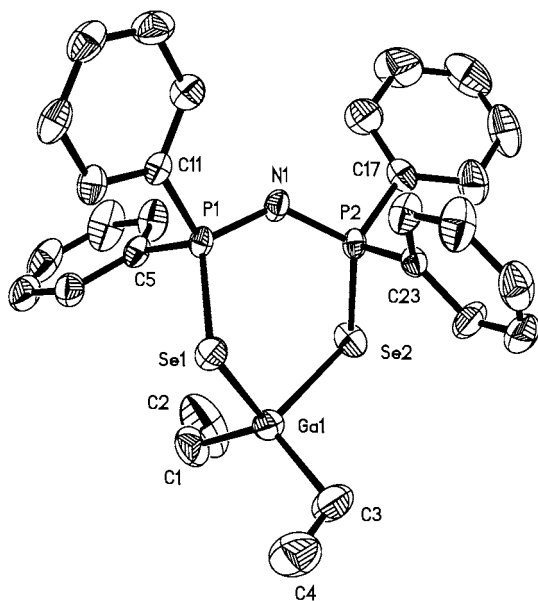


Fig. 2. Molecular structure and atom numbering scheme of **4**.

were recorded as KBr pellets on a Matheson Instruments 2020 Galaxy series spectrometer and are reported in cm^{-1} . X-ray data were collected on a Siemens CCD diffractometer using graphite monocromated Mo-K α (0.71073 Å) radiation. All calculations were performed on a PC using the Siemens software package, SHELXTL-Plus.

3.2. [$\text{Me}_2\text{Al}\{\text{SePPh}_2\}_2\text{N}\}$] (1)

A solution of trimethylaluminum (0.13 g, 1.84 mmol) in toluene (10 ml) was added to a stirred suspension of LH (1.0 g, 1.84 mmol) in toluene (30 ml) causing vigorous gas evolution and the formation of a colorless clear solution, which was stirred for 12 h. Removal of volatiles under reduced pressure produced a liquid which was treated with 20 ml of hexanes, resulting in precipitation of a white powder with stirring. Filtration and vacuum drying of the remaining solid afforded **1**. Yield 0.83 g, 75%, m.p. 133–135°C. $^1\text{H-NMR}$: δ –0.13 (s, 6H, AlCH_3), 6.93 (m, 12H, C_6H_5), 7.96 (m, 8H, C_6H_5). $^{31}\text{P}\{\text{H}\}\text{-NMR}$: δ 54.09 (m, AlSePPh_2 , $^1J(\text{PSe}) = -804$ Hz). $^{27}\text{Al}\{\text{H}\}\text{-NMR}$: δ 114.89 ($w_{1/2} = 8447$ Hz). IR (cm^{-1}): 3125 (w), 3054(w), 1435 (s), 1400 (s), 1181 (w), 1107 (s), 1019 (s), 1015 (s), 781 (m), 741 (s), 689 (s), 675 (m), 554 (m), 532 (w) 494 (m). Anal. Calc. for $\text{C}_{26}\text{H}_{26}\text{AlNP}_2\text{Se}_2$: C, 52.10; H, 4.37; N, 2.34. Found: C, 51.98; H, 4.35; N, 2.27.

3.3. [$\text{Et}_2\text{Al}\{\text{SePPh}_2\}_2\text{N}\}$] (2)

Compound **2** was prepared in a similar manner to **1** from LH (1.0 g, 1.84 mmol) in toluene (30 ml) and triethylaluminum (0.21 g, 1.84 mmol) affording **2** as a white solid. Yield 0.92 g, 80%, m.p. 130–133°C. $^1\text{H-NMR}$: δ 0.51 (q, 4H, AlCH_2CH_3), 1.35 (t, 6H, AlCH_2CH_3), 6.94 (m, 12H, C_6H_5), 7.92 (m, 8H, C_6H_5). $^{31}\text{P}\{\text{H}\}\text{-NMR}$: δ 54.04 (m, AlSePPh_2 , $^1J(\text{PSe}) = -802$ Hz). $^{27}\text{Al}\{\text{H}\}\text{-NMR}$: δ 155.74 ($w_{1/2} = 6737$ Hz). IR (cm^{-1}): 3049 (w), 2855(m), 1513 (w), 1437 (s), 1209 (s), 1182 (m), 1103 (s), 916 (m), 693 (s), 534 (s), 507 (m). Anal. Calc. for $\text{C}_{28}\text{H}_{30}\text{AlNP}_2\text{Se}_2$: C, 53.60; H, 4.82; N, 2.23. Found: C, 54.13; H, 4.77; N, 2.10.

3.4. [$\text{tBu}_2\text{Al}\{\text{SePPh}_2\}_2\text{N}\}$] (3)

Compound **3** was prepared in a similar manner to **1** from LH (1.0 g, 1.84 mmol) in toluene (30 ml) and triisobutylaluminum (0.36 g, 1.84 mmol) affording **3** as a white solid. Yield 0.96 g, 79%, m.p. 133–135°C. $^1\text{H-NMR}$: δ 0.67 (d, 4H, $\text{AlCH}_2\text{CH}(\text{CH}_3)_2$), 1.23 (d, 12H, $\text{AlCH}_2\text{CH}(\text{CH}_3)_2$), 2.22 (m, 2H, $\text{AlCH}_2\text{CH}(\text{CH}_3)_2$), 7.03 (m, 12H, C_6H_5), 7.99 (m, 8H, C_6H_5). $^{31}\text{P}\{\text{H}\}\text{-NMR}$: δ 54.04 (m, AlSePPh_2 , $^1J(\text{PSe}) = -804$ Hz). IR (cm^{-1}): 3057 (w), 2946(m), 2868 (m), 1586 (w), 1437 (s), 1323 (m), 1209 (s), 1198 (m), 1182 (m), 1101

(s), 918 (s), 801 (w), 687 (s), 534 (s), 507 (m). Anal. Calc. for $\text{C}_{32}\text{H}_{38}\text{AlNP}_2\text{Se}_2$: C, 56.23; H, 5.60; N, 2.05. Found: C, 56.21; H, 5.22; N, 2.15.

3.5. [$\text{Et}_2\text{Ga}\{\text{SePPh}_2\}_2\text{N}\}$] (4)

Compound **4** was prepared from LH (0.5 g, 0.92 mmol) in toluene (30 ml) and triethylgallium (0.14 g, 92 mmol) affording **4** as a white solid after removal of volatiles. The product was treated with 10 of hexanes and filtered. Storage of the filtrate at -35°C for 1 day afforded crystals suitable for X-ray analysis. Yield 0.47 g, 75%, m.p. 135–137°C. $^1\text{H-NMR}$: δ 0.90 (q, 4H, GaCH_2CH_3), 1.30 (t, 6H, GaCH_2CH_3), 6.93 (m, 12H, C_6H_5), 7.98 (m, 8H, C_6H_5). $^{31}\text{P}\{\text{H}\}\text{-NMR}$: δ 29.51 (m, GaSePPh_2 , $^1J(\text{PSe}) = -534$ Hz), $^{77}\text{Se}\{\text{H}\}\text{-NMR}$: δ –414.42 (d, GaSePPh_2 , $^1J(\text{PSe}) = -532$ Hz) IR (cm^{-1}): 3054 (w), 2982 (w), 2832 (w), 1480 (w), 1437 (m), 1208 (s), 1197 (m), 1101 (m), 997 (w), 801 (w), 716 (m), 694 (s), 683 (w), 532 (s), 527 (s), 505 (s). Anal. Calc. for $\text{C}_{28}\text{H}_{30}\text{GaNP}_2\text{Se}_2$: C, 50.08; H, 4.51; N, 2.09. Found: C, 49.86; H, 4.38; N, 2.07.

4. Supplementary material

Supplementary material contains for **4**: structure determination summary; heavy atom coordinates; bond lengths and bond angles; anisotropic parameters; hydrogen atom coordinates; observed and calculated structure factors; full-atom labeling figure; unit cell view.

Acknowledgements

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