FULL PAPER

Dalton
www.rsc.org/dalton

Dichloro and alkylchloro gallium derivatives of dichalcogenoimidodiphosphinate ligands: isolation of a spirogallium cation

Miguel-Ángel Muñoz-Hernández,*[a] Virginia Montiel-Palma,[a] Estefanía Huitrón-Rattinger,[a] Sara Cortés-Llamas,[a] Norma Tiempos-Flores,[a] Jean-Michel Grevy,[a] Cristian Silvestru[b] and Philip Power[c]

[a] *Centro de Investigaciones Químicas, Universidad Autónoma del Estado de Morelos, Av. Universidad 1001, Col. Chamilpa, Cuernavaca, Morelos, 62210, México. E-mail: mamund2@buzon.uaem.mx; Fax: (52) 777 3297997; Tel: (52) 777 3297997*

[b] *Facultatea de Chimie si Inginerie Chimica, Universitatea Babes-Bolyai, RO-3400, Cluj-Napoca, Romania*

[c] *Department of Chemistry, University of California, Davis, One Shields Ave., Davis, CA 95616, USA*

Received 20th August 2004, Accepted 29th October 2004
First published as an Advance Article on the web 17th November 2004

Dichloro and chloromethyl Ga(III) complexes of general formulae [XClGa-η^2-{$R_2P(E)NP(E')R'_2$-*E*,*E'*}] (X = Cl, R, R′ = Ph, E, E′ = O (**1**), S (**2**), Se (**3**); R = Ph, R′ = OEt, E = O, E′ = S (**4**); R = Me, R′ = Ph, E, E′ = S (**5**) and X = Me, E, E′ = O (**6**), S (**7**), Se (**8**)) were synthesised by either metathesis reactions between $GaCl_3$ and the potassium salt of the ligand (X = Cl) or by methane eliminations from *in situ* prepared $GaMe_2Cl$ and the protonated ligands LH (X = Me). Redistribution reaction of **3** in either $CDCl_3$ or THF afforded the solvent-free tetracoordinate gallium spirocycle cation [Ga-{η^2-{$Ph_2P(Se)NP(Se)Ph_2$-*Se*,*Se'*}$_2$}]$^+$ (**9**$^+$). The molecular structures of complexes **2**, **4**, **5**, **7** and **9**$^+$ show non-planar gallacycle rings.

Introduction

The development of highly reactive main group polymerization catalysts as lower-cost alternatives to transition metals has stimulated a considerable amount of work on group 13 complexes.[1] In particular, group 13 cationic complexes posses enhanced Lewis acidity and can act as activators or catalysts in reactions otherwise unaltered by the neutral species.[2–8] However, only a handful of these cations have been structurally and spectroscopically characterised. It is generally accepted that the catalytic activity of aluminium cations depends on their coordination number. Indeed, five- and six-coordinate compounds with Salen-type ligands have been demonstrated to be efficient catalysts for ring-opening polymerization and oligomerization of substrates that bear Lewis basic atoms.[5,9] On the other hand, two-, three- and four-coordinate aluminium compounds play a major role in the polymerization of olefins.[2,3,10,11] *Vis-à-vis* to their Al analogues, Ga cations are considerably less Lewis acidic and reactive and hence are particularly suitable for detailed studies. Indeed, Wehmschulte's two-coordinate bisterphenyl Ga(III) cation,[12] shows a Ga atom in an essentially undistorted linear array (175.7(1)°) by comparison with the bent two-coordinate alumenium cation Et_2Al^+ isolated by Reed and co-workers[13] with the use of carborane anions $CB_{11}H_6X_6$ (X = Cl, Br). The latter compounds exhibit weak Al···X interactions which decrease C–Al–C bond angles from the expected 180° to 136.6° (X = Cl) or 130.0° (X = Br).

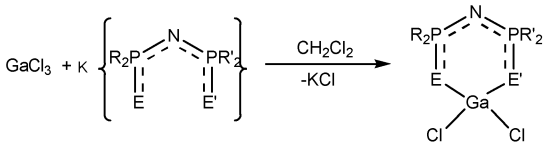
In our search for robust and stable ring backbones to stabilize Al and Ga ring heterocycles, we have been employing chelating dichalocogenoimidophosphinate (EPNPE′) ligands whose compounds may undergo substitution reactions without degradation of the original skeletal ring structure.[14,15] Furthermore, their wide bite angles (around 110°) help stabilise labile metal cations. In this regard Jordan and co-workers have demonstrated that the lability of three-coordinate aluminium complexes is greatly reduced with the use of large bite-angle ligands, as in the amidinate systems [{$RC(NR')_2$}AlMe]$^+$.[16]

Herein we report the synthesis, characterization and reactivity of dichloro and chloromethyl Ga species derived from EPNPE′ ligands. We show that in solution selenium dichloro derivatives undergo redistribution reactions to generate a solvent-free, four-coordinate Ga(III) spirocycle cation.

Results and discussion

Synthesis and spectroscopy of dichloro and chloromethyl gallium compounds

Metathesis reactions between equimolar amounts of $GaCl_3$ and KL salts (L = [$R_2P(E)NP(E')R'_2$]$^-$) in methylene dichloride resulted in the formation of the dichloro complexes [Cl_2Ga-η^2-{$R_2P(E)NP(E')R'_2$-*E*,*E'*}] (R, R′ = Ph, E, E′ = O (**1**), S (**2**), Se (**3**); R = Ph, R′ = OEt, E = O, E′ = S (**4**) and R = Me, R′ = Ph, E, E′ = S (**5**)) [eqn. (1)].



R, R' = Ph, E, E' = O (**1**)
R, R' = Ph, E, E' = S (**2**)
R, R' = Ph, E, E' = Se (**3**)
R = Ph, R' = OEt, E = O, E' = S (**4**)
R = Me, R' = Ph, E, E' = S (**5**)

(1)

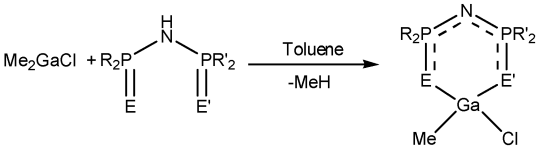
On the other hand, chloromethyl complexes [MeClGa-η^2-{$Ph_2P(E)NP(E')Ph_2$-*E*,*E'*}] (E, E′ = O (**6**), S (**7**), Se (**8**)), were synthesised by methane elimination reactions from *in situ* prepared $GaMe_2Cl$ and the protonated LH ligands {$R_2P(E)NHP(E')R'_2$}, [eqn. (2)].

DOI: 10.1039/b412874e

Table 1 Comparison of $^{31}P\{^{1}H\}$ NMR data in $CDCl_3$ of $[Cl_2GaL]$ complexes **1**–**5** and [ClMeGaL] complexes **6**–**8** with literature data of compounds of formulae $[Me_2GaL]$,[15] free acidic ligands LH and potassium salts KL

Complex of the type $[Cl_2GaL]$	Complex of the type [ClMeGaL]	Complex of the type $[Me_2GaL]$	Free acidic ligand LH	Potassium salt KL
1, 33.8 (s)	**6**, 29.9 (s)	26.4 (s)[15,a]	19.4 (s)[20,c]	10.5 (s)[21]
2, 38.2 (s)	**7**, 37.8 (s)	36.7 (s)[15,b]	55.7 (s)[22,c]	35.8 (s)[22]
3, 33.7 (s, $^{1}J_{PSe}$ 447 Hz)	**8**, 31.7 (s, $^{1}J_{PSe}$ 485 Hz)	29.3 (s, $^{1}J_{PSe}$ 534 Hz)[15,c]	53.2 (s, $^{1}J_{PSe}$ 786 Hz)[23,b]	28.5 (s, $^{1}J_{PSe}$ 687 Hz)[23,d]
4, 35.0 (d, $^{2}J_{PP}$ 24.4 Hz, PS); 2.9 (d, $^{2}J_{PP}$ 24.4 Hz, PO)			53.2 (d, $^{2}J_{PP}$ 8.2 Hz, PS); 1.3 (d, $^{2}J_{PP}$ 8.2 Hz, PO)[24,b]	KL·H_2O: 37.3 (d, $^{2}J_{PP}$ 20.6 Hz, PS); 5.3 (d, $^{2}J_{PP}$ 20.6 Hz, PO)[24,b]
5, 44.0 (br, PMe_2); 36.5 (d, $^{2}J_{PP}$ 14.1 Hz, PPh_2)			63.9 (d, $^{2}J_{PP}$ 22.8 Hz, PMe_2); 51.3 (d, $^{2}J_{PP}$ 22.8 Hz, PPh_2)[25,b]	44.2 (d, $^{2}J_{PP}$ 13.7 Hz, PMe_2), 38.0 (d, $^{2}J_{PP}$ 13.7 Hz, PPh_2)[26,d]

[a] C_6D_6. [b] $CDCl_3$. [c] $[D_6]$-THF. [d] CD_3OD.



E, E' = O (**6**)
E, E' = S (**7**)
E, E' = Se (**8**) (2)

A discrete number of dichloro[17] and chloromethyl[18] Ga complexes have been reported, nonetheless compounds **1**–**8** represent the first examples of Ga species bearing EPNPE′-type ligands apart from a handful of dialkyl gallium complexes.[14,15,19]

The characterization of the complexes was achieved by physical (mp), chemical (C, H and N analysis) and spectroscopic techniques (multinuclear NMR and IR spectroscopy) in conjunction with single crystal X-ray diffraction determinations of complexes **2**, **4**, **5** and **7**.

The ^{1}H, $^{13}C\{^{1}H\}$ and $^{31}P\{^{1}H\}$ NMR spectra of the products in $CDCl_3$ were consistent with coordination of the dichalcogenoimidodiphosphinate ligands to the Ga centres resulting in C_{2v} symmetric ring structures of compounds **1**–**3** and C_s in **4**–**8**. In the ^{1}H NMR spectra of chloromethyl complexes **6**–**8**, the Ga–methyl resonances appeared as singlets between 0.0 and 0.1 ppm. Due to metal coordination, the $^{31}P\{^{1}H\}$ NMR spectra of chloromethyl complexes **7** and **8** showed a highfield shift of the resonance signals with respect to the free protonated ligands LH[20] (Table 1). Along the series $[Cl_2GaL]$, [ClMeGaL] and $[Me_2GaL]$[14,15] the $^{31}P\{^{1}H\}$ signals also showed a small but consistent highfield shift. The values of the coupling constants $^{1}J_{PSe}$ of selenium derivatives **3** and **8** were significantly smaller than those in the corresponding potassium salts KL and in the free acidic ligands LH.

X-Ray crystallographic analysis of 2, 4, 5 and 7

Relevant crystal data for dichloro **2**, **4** and **5** and chloromethyl **7** complexes (Figs. 1–4) are summarised in Table 4 and important bond lengths and angles are contained in Table 2. In all cases, the X-ray study show non-planar six-membered gallacycles adopting different conformations. Non-planar rings are commonly

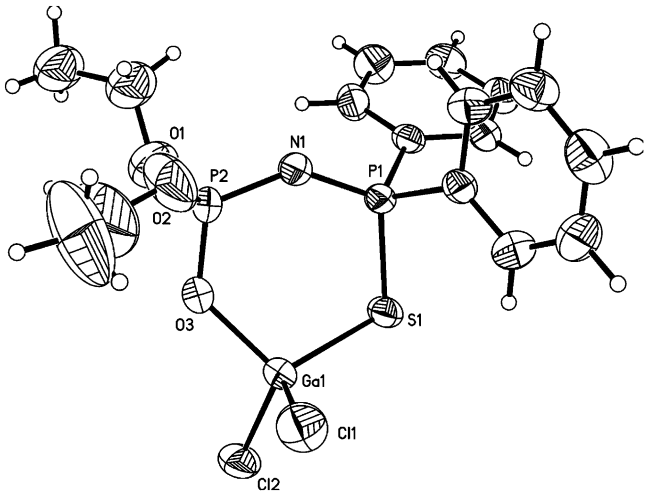


Fig. 2 Molecular structure of **4** with thermal ellipsoids shown at 30% probability level.

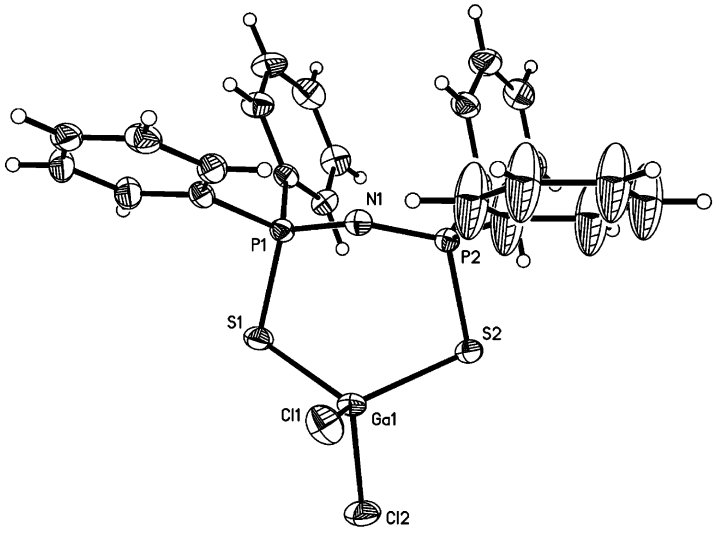


Fig. 1 Molecular structure of **2** with thermal ellipsoids shown at 50% probability level.

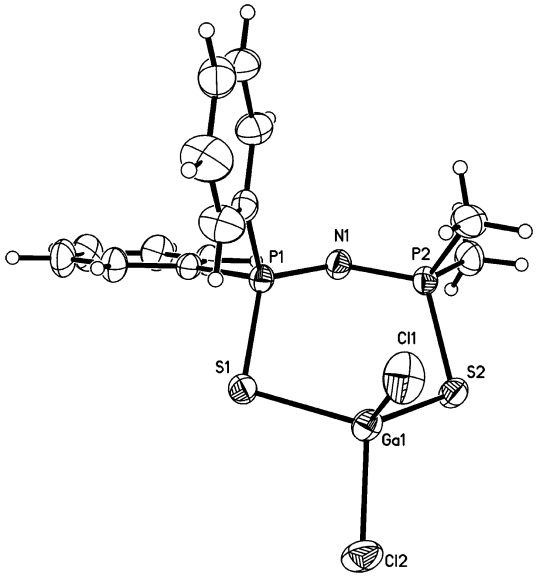


Fig. 3 Molecular structure of **5** with thermal ellipsoids shown at 50% probability level.

obtained in complexes derived from dichalcogenoimidodiphosphinate ligands as demonstrated by the variety of examples encountered in main group and transition metal chemistry.[20] The metallacycle ring in symmetrically substituted disulfur complex **2** adopts a boat conformation with the Ga and N(1) atoms at the apices of the boat. Unsymmetrically substituted disulfur complex **5** is a chair with apices Ga and N(1). Mixed oxygen–sulfur compound **4** is an envelope with Ga out of the plane and chloromethyl disulfur **7** is a boat with S(1) and P(2) at the apices. On this basis, no structural pattern for variation can be predicted, nor can it be found when compared to other EPNPE′ organogallium derivatives.[14,15,19]

Comparison of the P–E, P–E′ and P–N bond lengths in the complexes to those in the free acidic ligands suggests changes in bond orders. Indeed, the P–S bond distances 2.060(2) and 2.047(2) Å in **2**, 2.057(2) Å in **4**, 2.059(1) and 2.054(1) Å in **5**, and 2.034(2) and 2.027(2) Å in **7** are elongated with respect to uncomplexed P=S units (1.89–1.96 Å) and indicate a lower bond order.[27] On the contrary, the P–N bond distances range from 1.55 to 1.60 Å, shorter than in uncomplexed P–N units (1.63–1.69 Å) in which there is not P=N character.[20] These results are in agreement with the proposed structures.

The Ga–Cl bonds in **2**, **4** and **5** are somewhat elongated with respect to the corresponding ones in tetracoordinate $(GaMeCl_2)_2$[28] at 2.129(3) Å, $GaCl_2$(acac) (acac = 2,4-pentanedionato) at 2.115(6) Å and $GaCl_2$(tmhd) (2,2,6,6-tetramethylheptanedionato)[17] at 2.124(2) Å and are more similar to those in tricoordinate $(2,6\text{-}Mes_2C_6H_3)_2GaCl$ at 2.177 (5) Å.[29]

In particular, comparison of dichloro compound **2** with its dimethyl analogue $[Me_2Ga\text{-}\eta^2\text{-}\{Ph_2P(S)NP(S)Ph_2\text{-}S,S'\}]$[15] allows interesting deductions. The Ga–Cl distances are longer than the Ga–C distances (Table 3), as expected from the larger radius of Cl and the higher electronegativity and higher tendency of Cl to occupy Ga hybrid orbitals with higher p-character. Furthermore, the Ga–S distances are shorter in **2** than in the dimethyl species as a result of the greater δ+ charge on Ga due to Cl substitution. Other consequence of the replacement of CH_3 for Cl is reflected in a larger S–Ga–S bond angle in **2** (*ca.* 12°). Meanwhile, the Cl–Ga–Cl angle in **2** is narrowed by *ca.* 16° than the C–Ga–C angle. A similar effect has been noticed by Jordan and co-workers in dichloro and dialkyl amidinate Al complexes[30] and goes against a predicted larger Cl–Al–Cl angle compared to C–Al–C on the basis of the cone angles Al–Cl (56.3°) and Al–CH_3 (51°). Jordan explains this apparent discrepancy also in terms of Al–Cl bonding electron pair being smaller than the Al–CH_3 boding electron pair and on the higher p-character of Al orbitals used to bind more electronegative Cl atoms.

In general, the Cl–Ga–Cl angles in **2**, **4** and **5** show little distortion from the ideal tetrahedral geometry. Nevertheless, the Cl–Ga–Cl angles are smaller than in $GaCl_2$(acac) (116.1(3)°) and in $GaCl_2$(tmhd) (113.2(1)°)[17] as a result of a larger ligand cone angle. Interestingly, the Ga–Cl distances in the dimethyldiphenyl complex **5** (2.176(1) and 2.177(1) Å) are identical within experimental error while the equivalent distances in the tetraphenyl compound **2** (2.163(1) and 2.175(1) Å) show a bigger difference. This behaviour could perhaps be attributed to the adoption of different conformations of the metallacycle rings (*vide supra*).

In chloromethyl complex **7**, both the Ga–S bond distances and the Cl–Ga–C bond angles are of intermediate values between **2** and the dimethyl analogue (Table 3). Besides the Ga–Cl and Ga–C bond distances are smaller than in either the dichloro and dimethyl species.

Pure monomeric heavier group 13 element compounds with two or three different ligands are scarce due to ligand redistribution reactions amongst heteroleptic species.[17] Indeed,

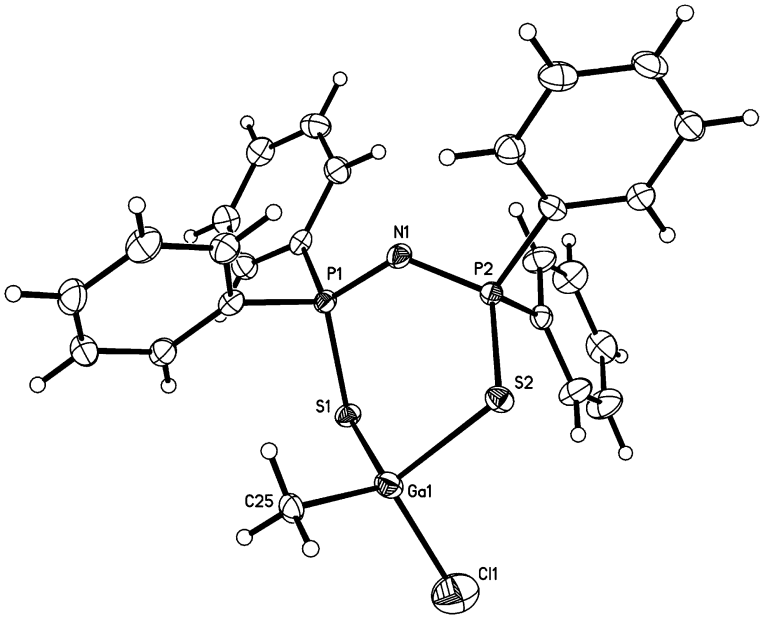


Fig. 4 Molecular structure of **7** with thermal ellipsoids shown at 50% probability level.

Table 2 Selected bond lengths (Å) and angles (°) for complexes **2**, **4**, **5**, **7** and **9**$^+$

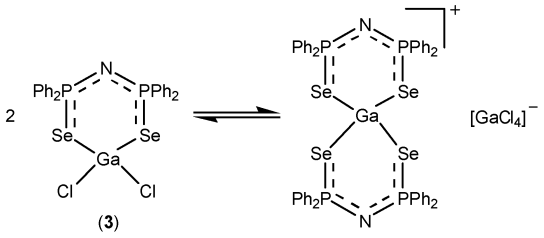
2			
Ga(1)–Cl(1)	2.1627(16)	Cl(2)–Ga(1)–Cl(1)	109.92(7)
Ga(1)–Cl(2)	2.1748(16)	Cl(1)–Ga(1)–S(1)	111.39(6)
Ga(1)–S(1)	2.2692(16)	Cl(2)–Ga(1)–S(1)	107.91(6)
Ga(1)–S(2)	2.2763(15)	Cl(1)–Ga(1)–S(2)	113.97(6)
S(1)–P(1)	2.0595(19)	Cl(2)–Ga(1)–S(2)	101.62(6)
S(2)–P(2)	2.0466(19)	S(1)–Ga(1)–S(2)	111.44(5)
P(1)–N(1)	1.590(5)	P(2)–N(1)–P(1)	132.4(3)
P(2)–N(1)	1.584(5)		
4			
Ga(1)–O(3)	1.867(3)	O(3)–Ga(1)–Cl(2)	107.62(11)
Ga(1)–Cl(2)	2.1446(14)	O(3)–Ga(1)–Cl(1)	106.99(13)
Ga(1)–Cl(1)	2.1494(15)	Cl(2)–Ga(1)–Cl(1)	111.82(7)
Ga(1)–S(1)	2.2525(12)	O(3)–Ga(1)–S(1)	106.95(11)
S(1)–P(1)	2.0563(15)	Cl(2)–Ga(1)–S(1)	108.39(6)
O(3)–P(2)	1.508(3)	Cl(1)–Ga(1)–S(1)	114.72(6)
P(1)–N(1)	1.567(4)	P(2)–N(1)–P(1)	137.3(3)
P(2)–N(1)	1.549(4)		
5			
Ga(1)–Cl(2)	2.1764(6)	Cl(2)–Ga(1)–Cl(1)	108.24(3)
Ga(1)–Cl(1)	2.1767(6)	Cl(2)–Ga(1)–S(2)	107.84(2)
Ga(1)–S(2)	2.2579(6)	Cl(1)–Ga(1)–S(2)	111.61 (3)
Ga(1)–S(1)	2.2691(6)	Cl(2)–Ga(1)–S(1)	104.04(2)
S(1)–P(1)	2.0592(7)	Cl(1)–Ga(1)–S(1)	111.83(3)
S(2)–P(2)	2.0536(7)	S(2)–Ga(1)–S(1)	112.83(2)
P(1)–N(1)	1.5809(16)	P(2)–N(1)–P(1)	135.79(11)
P(2)–N(1)	1.5789(17)		
7			
Ga(1)–C(25)	1.948(4)	C(25)–Ga(1)–Cl(1)	115.69(12)
Ga(1)–Cl(1)	2.1222(15)	C(25)–Ga(1)–S(1)	113.57(12)
Ga(1)–S(1)	2.3576(10)	Cl(1)–Ga(1)–S(1)	105.73 (5)
Ga(1)–S(2)	2.3618(11)	C(25)–Ga(1)–S(2)	110.07(12)
S(1)–P(1)	2.0339(13)	Cl(1)–Ga(1)–S(2)	103.31(5)
S(2)–P(2)	2.0266(13)	S(2)–Ga(1)–S(1)	107.71(4)
P(1)–N(1)	1.588(3)	P(2)–N(1)–P(1)	127.5(2)
P(2)–N(1)	1.596(3)		
9$^+$			
Ga(1)–Se(1)	2.4047(9)	Se(2)–Ga(1)–Se(1)	105.16(3)
Ga(1)–Se(2)	2.4070(7)	Se(4)–Ga(1)–Se(3)	112.77(3)
Se(1)–P(1)	2.1980(14)	Se(1)–Ga(1)–Se(3)	113.08(3)
Se(2)–P(2)	2.2078(14)	Se(1)–Ga(1)–Se(4)	108.17(3)
P(1)–N(1)	1.590(4)	Se(2)–Ga(1)–Se(3)	104.56(3)
P(2)–N(1)	1.599(4)	Se(2)–Ga(1)–Se(4)	112.90(3)
Ga(1)–Se(3)	2.3906(7)	P(2)–N(1)–P(1)	131.8(3)
Ga(1)–Se(4)	2.4071(8)	P(3)–N(2)–P(4)	127.3(3)
Se(3)–P(3)	2.2196(13)		
Se(4)–P(4)	2.1940(15)		
P(4)–N(2)	1.598(4)		
P(3)–N(2)	1.591(4)		

organogallium $R_{3-n}GaCp_n$ (R = Me,[31,32] Et;[32,33] n = 1, 2) undergo ligand redistribution reactions to form mixtures of GaR_3, R_2GaCp, $RGaCp_2$ and $GaCp_3$ when dissolved in donor solvents. Beachley *et al.*[17] have recently employed bidentate acac-type ligands to stabilise group 13 heteroleptic compounds with three different ligands. But while acac derivatives show enhanced stability, hfac (1,1,1,5,5,5-hexafluoro-2,4-pentanedionato) compounds redistribute to form Ga(hfac)$_3$ over days at room temperature. In a similar line, our monomeric Ga(III) compounds with two or three different ligands are obtained in high yield, thus evidencing the conferred stabilisation by EPNPE′-type ligands. The only exception to this behaviour is compound **3**, which undergoes redistribution reactions to render ionic species **9**$^+$[$GaCl_4$]$^-$ in THF (*vide infra*).

Synthesis and spectroscopy of cationic gallium compound 9$^+$

During the synthesis of **3** in CH_2Cl_2 a small new signal in the $^{31}P\{^1H\}$ NMR spectrum in $CDCl_3$ indicated the presence of a second species, later confirmed to be the cationic spirocycle [Ga(η^2-{$Ph_2P(Se)NP(Se)Ph_2$-*Se*,*Se*})$_2$]$^+$ (**9**$^+$) which balances its charge with $GaCl_4^-$. Thus, pure **3** was dissolved in $CDCl_3$, the NMR tube kept at room temperature and periodically monitored by $^{31}P\{^1H\}$ NMR spectroscopy. Under these conditions and over a period of several days, a gradual growth of the signal of **9**$^+$ at the expense of **3** was observed [eqn. (3)]. In order to favour the formation of **9**$^+$, the reaction between equimolar amounts of $GaCl_3$ and K[$Ph_2P(Se)NP(Se)Ph_2$] was conducted in THF. Again, **3** and **9**$^+$ were detected, but even from early monitoring times **9**$^+$ was majority (ratio 7 : 3, respectively).

In contrast, only very small amounts of an analogous species, presumably the corresponding sulfur spirocycle cation, were detected in the $^{31}P\{^1H\}$ NMR spectrum of **2** in $CDCl_3$ or even when the reaction was performed and monitored in THF. Further, no spectroscopically detectable side products were observed during the synthesis of **1** in THF. Thus, it appears the less electronegative the chalcogen bound to gallium, the more favourable the disproportionation reaction leading to the formation of the tetrachloride anion becomes.



(3)

Crystal structure of [9$^+$$GaCl_4^-$]

9$^+$$GaCl_4^-$ crystallizes in the triclinic $P\bar{1}$ space group with two crystallographically independent ions **9**$^+$ with no statistically significant differences in either bond lengths or angles.† The molecular structure of **9**$^+$ (Fig. 5) shows the Ga centre in an approximately tetrahedral arrangement forming part of two fused metallacycle rings almost perpendicular to each other (the angle between the planes defined by Se(1)Ga(1)Se(2) and Se(3)Ga(1)Se(4) is 85.2°). One of the rings shows a boat conformation with N(1) and Ga on the apices and the second ring is a distorted boat with P(4) and Se(3) on the apices.

† The crystal data for **9** is contained in Table 4 and one of the **9**$^+$ ions is shown in Fig. 5 with its relevant bond lengths and angles presented in Table 2.

Table 3 Selected bond distances and angles of compounds **2** and **7** for comparison with their dimethyl Me_2GaL[15] analogue

Complex	Ga–S/Å	Ga–Cl/Å	Ga–CH_3/Å	S–Ga–S/°	X–Ga–X′/°
[Cl_2GaL], **2**	2.269(2), 2.276(2)	2.163(2), 2.175(2)		111.4(1)	109.9(1) (X, X′ = Cl)
[MeClGaL], **7**	2.358(1), 2.362(1)	2.122(2)	1.948(4)	107.7(1)	115.7(1) (X, X′ = Cl, CH_3)
[Me_2GaL][15]	2.416(2), 2.380(1)		1.978(5), 1.958(5)	99.2(1)	126.1(2) (X, X′ = CH_3)

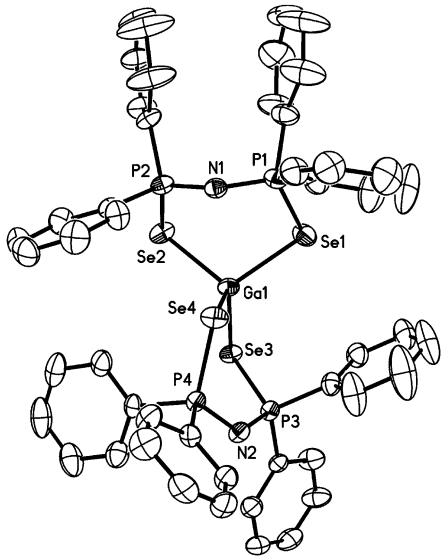


Fig. 5 Molecular structure of one $\mathbf{9}^{+}$ ion with thermal ellipsoids shown at 50% probability level. Hydrogen atoms have been omitted for clarity.

The Ga–Se bond distances in $\mathbf{9}^{+}$ are significantly shorter (average 2.403 Å) than in Et_2Ga-η²-{$Ph_2P(Se)NP(Se)Ph_2$-*Se*,*Se*′} (average 2.524 Å)[14] as a result of the positive charge on the Ga centre.

Though a number of Ga spirocycles have been structurally characterised, most of them include N or C in their fused rings. To date no other Se containing Ga spirocycle has been reported. β-Diketonate stabilized GaClMe(bdk) and $GaCl_2$(bdk) (bdk = β-diketonate) both react with THF yielding ionic $[Ga(bdk)_2(THF)_2]^{+}[GaCl_4]^{-}$.[17] In the latter cases, small steric hindrance allows THF to coordinate to the metal centre. Presumably, it is the steric bulk which prevents the solvent to behave similarly in $\mathbf{9}^{+}$.

Concluding remarks

The synthesis of dichloro and chloromethyl Ga(III) dichalcogenimidodiphoshinato complexes proceeds cleanly and in a facile manner. Their robust ligand skeleton and wide bite angles are advantages that will be later used to generate cationic gallium species having as a precedent the isolation of the four-coordinate Ga spirocycle cation $\mathbf{9}^{+}$. Further work concerning the isolation of these cationic species and their mechanisms of formation is currently in progress.

Experimental

General

All syntheses and manipulations of the air sensitive compounds were carried out under argon using standard Schlenk or glove-box techniques. Solvents were dried over sodium or potassium/benzophenone and freshly distilled prior to use. The ligands $Ph_2P(E)NHP(E')PPh_2$ (E, E′ = O,[34] S,[34] Se[35]), $Ph_2P(S)NHP(O)(OEt)_2$[24] and $Ph_2P(S)NHP(S)Me_2$[24] were synthesized according to literature methods.

NMR spectra were obtained on Varian-Inova-400 MHz and Varian-Gemini-200 MHz instruments. Chemical shifts are reported relative to $SiMe_4$ for ^1H and ^{13}C, 85% H_3PO_4 for ^{31}P and are in ppm. IR Spectra were recorded as KBr pellets on a Brucker Equinox 55 Spectrometer and are reported in cm^{-1}. Microanalyses were obtained on an Elementar Vario EL III instrument operating in the CHN mode.

Preparation of dihalogenated species

Synthesis of dichloro(*O*,*O*′-tetraphenylimidodiphosphinato) gallium(III), [Cl_2Ga-η²-{$Ph_2P(O)NP(O)Ph_2$-*O*,*O*′}] (1). A mixture of $K[(Ph_2P(O)NP(O)Ph_2]$ (0.5 g, 1.1 mmol) and $GaCl_3$ (0.19 g, 1.1 mmol) in CH_2Cl_2 (20 ml) was vigorously stirred for 12 h to afford a KCl precipitate which was separated by cannula filtration and disregarded. The solution was concentrated under vacuum and kept at −20 °C until crystallisation of **1**. Colorless **1** was separated by filtration and dried under reduced pressure. Yield 84%, mp 171–173 °C. IR (KBr, cm^{-1}): 3058 (w), 2964 (w), 1904 (w), 1821 (w), 1692 (w), 1588 (m), 1484 (w), 1437 (m), 1263 (m), 1216 (s), 1126 (s), 1063 (s), 920 (m), 804 (m), 732 (m), 690 (s), 550 (s), 507 (s). ^1H NMR ($CDCl_3$, 200 MHz, 293 K) δ: 7.3–7.5 (m, 12H, *m*-C_6H_5 + *p*-C_6H_5), 7.7–7.8 (m, 8H, *o*-C_6H_5). $^{13}C\{^1H\}$ ($CDCl_3$, 50.29 MHz, 293 K) δ: 128.6 (m, *m*-C_6H_5), 131.0 (m, *o*-C_6H_5), 132.3 (s, *p*-C_6H_5), 133.5 (d, $^1J_{PC}$ 109 Hz, *ipso*-C_6H_5). $^{31}P\{^1H\}$ ($CDCl_3$, 80.96 MHz, 293 K) δ: 33.8 (s). Anal. Calc. for $C_{24}H_{20}Cl_2GaNP_2O_2$: C, 51.75; H, 3.62; N, 2.51. Found: C, 51.61; H, 3.47; N, 2.55%.

Compounds **2** to **5** were prepared in a similar manner to **1**.

Synthesis of dichloro(*S*,*S*′-tetraphenyldithioimidodiphosphinato)gallium(III), [Cl_2Ga-η²-{$Ph_2P(S)NP(S)Ph_2$-*S*,*S*′}] (2). $K[(Ph_2P(S)NP(S)Ph_2]$ (0.5 g, 1.0 mmol) and $GaCl_3$ (0.18 g, 1.0 mmol) yielded **2** in 94% after stirring for 14 h. Crystals suitable for X-ray diffraction were grown from CH_2Cl_2–hexane solutions. Mp 166 °C. IR (KBr, cm^{-1}): 3063 (w), 2962 (w), 1809 (w), 1580 (w), 1476 (w), 1432 (m), 1210 (s), 1107 (m), 1024 (m), 802 (m), 690 (s), 560 (s), 514 (m), 483 (m). ^1H NMR ($CDCl_3$, 200 MHz, 293 K) δ: 7.4–7.6 (m, 12H, *m*-C_6H_5 + *p*-C_6H_5), 7.7–7.8 (m, 8H, *o*-C_6H_5). $^{13}C\{^1H\}$ ($CDCl_3$, 50.29 MHz, 293 K) δ: 128.8 (m, *m*-C_6H_5), 131.1 (m, *o*-C_6H_5); 132.5 (s, *p*-C_6H_5), 134.6 (d, $^1J_{PC}$ 106 Hz, *ipso*-C_6H_5). $^{31}P\{^1H\}$ ($CDCl_3$, 80.96 MHz, 293 K) δ: 38.2 (s). Anal. Calc. for $C_{24}H_{20}Cl_2GaNP_2S_2$: C, 48.93; H, 3.42; N, 2.38. Found: C, 48.89; H, 3.38; N, 2.45%.

Synthesis of dichloro(*Se*,*Se*′-tetraphenyldiselenoimidodiphosphinato)gallium(III), [Cl_2Ga-η²-{$Ph_2P(Se)NP(Se)Ph_2$-*Se*,*Se*′}] (3). $K[(Ph_2P(Se)NP(Se)Ph_2]$ (0.5 g, 0.86 mmol) and $GaCl_3$ (0.15 g, 0.86 mmol) yielded **3** in 85%. Mp 198–200 °C. IR (KBr, cm^{-1}): 3058 (w), 2964 (w), 1579 (w), 1477 (m), 1436 (m), 1260 (s), 1210 (s), 1103 (s), 1025 (s), 803 (s), 747 (m), 688 (s), 531 (s). ^1H NMR ($CDCl_3$, 200 MHz, 293 K) δ: 7.4–7.6 (m, 12H, *m*-C_6H_5 + *p*-C_6H_5), 7.6–7.8 (m, 8H, *o*-C_6H_5). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 50.29 MHz, 293 K) δ: 129.2 (m, *m*-C_6H_5), 131.0 (m, *o*-C_6H_5), 133.2 (s, *p*-C_6H_5), 132.6 (dd, $^1J_{PC}$ 104 Hz, $^3J_{PC}$ 4.17 Hz, *ipso*-C_6H_5). $^{31}P\{^1H\}$ ($CDCl_3$, 80.96 MHz, 293 K) δ: 33.7 (s, $^1J_{PSe}$ 447 Hz, $^2J_{PP}$ 9.3 Hz). Anal. Calc. for $C_{24}H_{20}Cl_2GaNP_2Se_2$: C, 42.21; H, 2.95; N, 2.05. Found: C, 41.80; H, 2.83; N, 2.13%.

Synthesis of dichloro(*S*,*O*′-diphenyldiethoxythioimidodiphosphinato)gallium(III), [Cl_2Ga-η²-{$Ph_2P(S)NP(O)(OEt)_2$-*S*,*O*}] (4). $K[(Ph_2P(S)NP(O)(OEt)_2]$ (0.51 g, 1.25 mmol) and $GaCl_3$ (0.22 g, 1.26 mmol) yielded **4** in 95% after 18 h stirring. Mp 63–64 °C. IR (KBr, cm^{-1}): 3059 (w), 2967 (m), 2590 (w), 1968 (w), 1896 (w), 1818 (m), 1773 (w), 1583 (m), 1479 (s), 1439 (s), 1256 (s, br), 1000 (s, br), 793 (s), 747 (s), 695 (s), 592 (s), 542 (s), 460 (m). ^1H NMR ($CDCl_3$, 200 MHz, 293 K) δ: 1.3 (dt, 6H, $^3J_{HH}$ 7.4 Hz, $^4J_{PH}$ 1 Hz, OCH_2CH_3), 4.1 (dq, $^3J_{HH}$ 7 Hz, $^3J_{HP}$ 7.9 Hz, OCH_2CH_3), 7.4–7.6 (m, 12H, *m*-C_6H_5 + *p*-C_6H_5), 7.8–7.9 (m, 8H, *o*-C_6H_5). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.58 MHz, 293 K) δ: 16.1 (d, $^3J_{PC}$ 7.7 Hz, OCH_2CH_3), 64.6 (d, $^2J_{PC}$ 6.1 Hz, OCH_2CH_3), 129.0 (d, $^3J_{PC}$ 14.5 Hz, *m*-C_6H_5), 131.1 (d, $^2J_{PC}$ 11.8 Hz, *o*-C_6H_5), 132.9 (d, $^4J_{PC}$ 3.0 Hz, *p*-C_6H_5), *ipso*-C_6H_5 not observed. $^{31}P\{^1H\}$ ($CDCl_3$, 161.92 MHz, 293 K) δ: 2.9 (d, $^2J_{PP}$ 24.4 Hz, PO), 35.0 (d, $^2J_{PP}$ 24.4 Hz, PS) Anal. Calc. for $C_{16}H_{20}Cl_2GaNP_2O_3S$: C, 36.76; H, 3.96; N, 2.75. Found: C, 37.58; H, 3.81; N, 2.91%.

Synthesis of dichloro(*S*,*S*′-dimethyldiphenyldithioimidodiphosphinato)gallium(III), [Cl_2Ga-η²-{$Ph_2P(S)NP(S)Me_2$-*S*,*S*′}] (5). $K[(Ph_2P(S)NP(S)Me_2]$ (0.31 g, 0.85 mmol) and $GaCl_3$ (0.15 g, 0.86 mmol) yielded **5** in 92% after 18 h stirring. Mp 138–140 °C. ^1H NMR ($CDCl_3$, 400 MHz, 293 K) δ: 1.9 (d, 6H, $^2J_{PH}$ 13.6 Hz, PMe_2), 7.5–7.6 (m, 12H, *m*-C_6H_5 + *p*-C_6H_5), 7.7–7.8 (m, 8H,

Table 4 Summary of crystallographic data for complexes **2**, **4**, **5**, **7** and **9** (refinement method: full-matrix least-squares on F^2).

	2	**4**	**5**	**7**	**9**
Formula	$C_{24}H_{20}Cl_2GaNP_2S_2$	$C_{16}H_{20}Cl_2GaNO_3P_2S$	$C_{14}H_{16}Cl_2GaNP_2S_2$	$C_{25}H_{23}ClGaNP_2S_2$	$C_{48}H_{40}Cl_4Ga_2N_2P_4Se_4$
M_r	589.13	508.97	464.99	568.71	1365.84
T/K	100(2)	293(2)	100(2)	100(2)	150(2)
λ/Å	0.71073	0.71073	0.71073	0.71073	0.71073 Å
Crystal system	Monoclinic	Triclinic	Triclinic	Orthorhombic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$Pbca$	$P\bar{1}$
a/Å	10.7275(12)	9.3056(10)	9.4244(7)	15.2636(18)	14.544(2)
b/Å	16.0085(17)	9.6427(10)	9.9156(7)	17.995(2)	15.672(2)
c/Å	15.2662(17)	14.6899(15)	11.1223(8)	18.335(2)	24.498(3)
α/°	90.0	76.044(2)	86.4200(10)	90.0	89.897(3)
β/°	98.097(2)	73.046(2)	85.5120(10)	90.0	89.963(3)
γ/°	90.0	62.095(2)	73.4930(10)	90.0	70.891(3)
V/Å^3	2595.5(5)	1105.7(2)	992.59(12)	5036.0(10)	5276.5(13)
Z	4	2	2	8	8
D_c/g cm^{-3}	1.508	1.529	1.556	1.500	1.719
μ/mm^{-1}	1.564	1.740	2.021	1.507	4.140
F(000)	1192	516	468	2320	2672
Crystal size/mm	0.18 × 0.23 × 0.27	0.22 × 0.33 × 0.37	0.15 × 0.22 × 0.37	0.14 × 0.18 × 0.27	0.17 × 0.24 × 0.26
θ range for data collection/°	1.85–25.02	1.46–27.04	1.84–27.02	2.07–27.05	1.38–27.07
Index ranges, hkl	−12 to 12, −19 to 10, −16 to 18	−11 to 11, −12 to 12, −18 to 18	−11 to 12, −12 to 12, −14 to 14	−19 to 19, −19 to 21, −6 to 23	−10 to 18, −19 to 19, −31 to 27
No. refl. collected	12984	12474	9674	21966	22640
No. indep. refl. (R_{int})	4566 (0.0297)	4785 (0.0292)	4263 (0.0209)	5319 (0.0271)	19831 (0.0211)
Data/restraints/params.	4566/0/247	4785/4/228	4263/0/201	5319/0/290	19831/0/1153
Goodness-of-fit on F^2	1.028	0.878	1.074	1.107	1.067
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0657$, $wR_2 = 0.1539$	$R_1 = 0.0522$, $wR_2 = 0.1710$	$R_1 = 0.0282$, $wR_2 = 0.0769$	$R_1 = 0.0514$, $wR_2 = 0.1427$	$R_1 = 0.0484$, $wR_2 = 0.1250$
Largest diff. peak, hole/e Å^{-3}	2.918, −2.647	1.456, −1.177	0.372, −0.300	0.823, −1.850	2.005, −1.203

o-C_6H_5). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.58 MHz, 293 K) δ: 25.3 (d, $^1J_{PC}$ 72.5 Hz, PMe_2), 129.1 (d, $^3J_{PC}$ 14.5 Hz, *m*-C_6H_5), 131.2 (d, $^2J_{PC}$ 12.17 Hz, *o*-C_6H_5), 132.9 (d, $^4J_{PC}$ 3.12 Hz, *p*-C_6H_5), 134.2 (d, $^1J_{PC}$ 107 Hz, *ipso*-C_6H_5). $^{31}P\{^1H\}$ ($CDCl_3$, 161.92 MHz, 293 K) δ: 44.0((br, $w_{1/2}$ 28.2 Hz, PMe_2), 36.5 (d, $^2J_{PP}$ 14.1 Hz, PPh_2). Anal. Calc. for $C_{14}H_{16}Cl_2GaNP_2S_2$: C, 36.16; H, 3.47; N, 3.01. Found: C, 36.02; H, 3.21; N, 3.15%.

Preparation of chloromethylated species

Synthesis of chloromethyl(*O*,*O*′-tetraphenylimidodiphosphinato)gallium(III), [ClMeGa-η²-{$Ph_2P(O)NP(O)Ph_2$-*O*,*O*′}] (6). $GaMe_2Cl$ was generated *in situ* by stirring $GaCl_3$ (0.05 g, 0.29 mmol) and $GaMe_3$ (0.07 g (0.61 mmol) in 10 ml toluene for 1 h. To this solution $(OPPh_2)_2NH$ (0.38 g, 0.91 mmol) in 10 ml toluene was added dropwise. The stirring was continued for a further 6 h after which the solution was concentrated under vacuum and kept at −20 °C until a white precipitate was obtained. Yield 93%, mp 177–178 °C. IR (KBr, cm^{-1}): 3058 (m), 2978 (w), 2917 (w), 2615 (w), 2323 (w), 2251 (w), 2060 (w), 1965 (w), 1899 (w), 1820 (w), 1775 (w), 1677 (w), 1591 (w), 1484 (m), 1437 (m), 1262 (br s), 1185 (s), 1126 (s), 1135 (s), 1094 (s), 1044 (s), 978 (s), 804 (s), 732 (s), 680 (s), 549 (s), 508 (s). ^1H NMR ($CDCl_3$, 200 MHz, 293 K) δ: 0.1 (s, 3H, GaMe), 7.3–7.5 (m, 12H, *m*-C_6H_5 + *p*-C_6H_5), 7.8 (m, 8H, *o*-C_6H_5). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.58 MHz, 293 K) δ: −5.3 (s, GaMe), 128.4 (m, *m*-C_6H_5), 131.0 (m, *o*-C_6H_5), 131.8 (m, *p*-C_6H_5), 135.3 (d, $^1J_{PC}$ 107 Hz, *ipso*-C_6H_5). $^{31}P\{^1H\}$ ($CDCl_3$, 161.92 MHz, 293 K) δ: 29.9 (s). Anal. Calc. for $C_{25}H_{23}ClGaNP_2O_2$: C, 55.96; H, 4.32; N, 2.61. Found: C, 56.31; H, 4.44; N, 2.74%.

Compounds **7** and **8** were obtained in a similar fashion to **6**.

Synthesis of chloromethyl(*S*,*S*′-tetraphenyldithioimidodiphosphinato)gallium(III), [ClMeGa-η²-{$Ph_2P(S)NP(S)Ph_2$-*S*,*S*′}] (7). Compound **7** was obtained from $GaCl_3$ (0.05 g, 0.29 mmol), $GaMe_3$ (0.07 g, 0.61 mmol) and $(SPPh_2)_2NH$ (0.4 g, 0.89 mmol). Crystals suitable for X-ray diffraction were grown from toluene solutions. Yield 92%, mp 177–178 °C. IR (KBr, cm^{-1}): 3054 (m). 2968 (w), 2365 (w), 1966 (w), 1900 (w), 1814 (w), 1581 (m), 1477 (m), 1433 (s), 1391 (w), 1339 (w), 1308 (w), 1260 (m), 1201 (s), 1105 (s), 1024 (m), 997 (m), 923 (w), 851 (w), 808 (m), 745 (s), 695 (s), 608 (m), 568 (s), 520 (m), 490 (m), 467 (m). ^1H NMR ($CDCl_3$, 200 MHz, 293 K) δ: 0.0 (s, 3H, GaMe), 7.3–7.5 (m, 12H, *m*-C_6H_5 + *p*-C_6H_5), 7.8 (m, 8H, *o*-C_6H_5). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 50.29 MHz, 293 K) δ: 1.5 (s, GaMe), 128.2 (m, *m*-C_6H_5), 131.1–132.0 (m, *o*- C_6H_5 + *p*-C_6H_5), 134.7 (d, $^1J_{PC}$ 103 Hz, *ipso*-C_6H_5). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 80.96 MHz) δ: 37.8 (s). Anal. Calc. for $C_{24}H_{20}Cl_2GaNP_2O_2$: C, 51.75; H, 3.62; N, 2.51. Found: C, 51.61; H, 3.47; N, 2.55%.

Synthesis of chloromethyl(*Se*,*Se*′-tetraphenyldiselenoimidodiphosphinato)gallium(III), [ClMeGa-η²-{$Ph_2P(Se)NP(Se)Ph_2$-*Se*,*Se*′}] (8). Compound **8** was obtained from $GaCl_3$ (0.04 g (0.23 mmol), $GaMe_3$ (0.05 g, 0.44 mmol) and $(SePPh_2)_2NH$ (0.36 g, 0.66 mmol). Yield 91%, mp 206–207 °C. IR (KBr, cm^{-1}): 3053 (w), 2969 (w), 2365 (w), 1991 (w), 1894 (w), 1813 (w), 1581 (w), 1474 (m), 1433 (s), 1331 (w), 1305 (w), 1200 (s), 1103 (s), 1023 (m), 994 (m), 846 (w), 797 (m), 744 (s), 722 (m), 690 (s), 577 (m), 537 (s), 507 (s), 467 (m). ^1H NMR ($CDCl_3$, 200 MHz, 293 K) δ: 0.1 (s, 3H, GaMe), 7.3–7.5 (m, 12H, *m*-C_6H_5 + *p*-C_6H_5), 7.8 (m, 8H, *o*-C_6H_5). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 50.29 MHz, 293 K) δ: 3.9 (s, GaMe), 128.5 (m, *m*-C_6H_5), 131.1 (m, *o*-C_6H_5), 132.0 (br s, *p*-C_6H_5), 134.7 (dd, $^1J_{PC}$ 101 Hz, $^3J_{PC}$ 6.5 Hz, *ipso*-C_6H_5). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 80.96 MHz) δ: 31.7 (s, $^1J_{PSe}$ 485 Hz, $^2J_{PP}$ 5.9 Hz). Anal. Calc. for $C_{25}H_{23}ClGaNP_2Se_2$: C, 45.32; H, 3.50; N, 2.11. Found: C, 45.18; H, 3.39; N, 2.18%.

Synthesis of tetrachlorogallatobis(*Se*,*Se*′-tetraphenyldiselenoimidodiphosphinato)gallium(III), [Ga-{η²-($Ph_2P(Se)NP(Se)Ph_2$-*Se*,*Se*′)}₂][$GaCl_4$] (9)

$K[Ph_2P(Se)NP(Se)Ph_2]$ (0.50 g, 0.86 mmol) and $GaCl_3$ (0.15 g, 0.86 mmol) were stirred in THF (20 ml). The solution was removed by cannula and formed KCl disregarded. The solution was then concentrated under vacuum and left for to crystallise slowly at −20 °C over a period of weeks. Yield 83%. Crystals of **9** were also obtained from slow crystallisation of **3** in CH_2Cl_2 after several weeks. ^1H NMR ($CDCl_3$, 200 MHz, 293 K) δ: 7.4–7.6

(m, 12H, *m*-C_6H_5 + *p*-C_6H_5), 7.7–7.8 (m, 8H, *o*-C_6H_5). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 80.96 MHz, 293 K) δ: 32.6 (s, $^1J_{PSe}$ 453 Hz). Anal. Calc. for $C_{48}H_{40}Cl_4Ga_2N_2P_4Se_4$: C, 42.21; H, 2.95; N, 2.05. Found: C, 42.12; H, 3.11; N, 2.17%.

X-Ray crystallographic studies

Single-crystal X-ray diffraction data for **2**, **4**, **5**, **7** and **9** were collected using the program SMART[36] on a Brucker APEX CCD diffractometer with monochromatized Mo-Kα radiation (λ = 0.71073 Å). Cell refinement and data reduction were carried out with the use of the program SAINT, the program SADABS was employed to make incident beam, decay and absorption corrections in the SAINT-Plus v. 6.0 suite.[37] Then, the structures were solved by direct methods with the program SHELXS and refined by full-matrix least-squares techniques with SHELXL in the SHELXTL v. 6.1 suite.[38] Hydrogen atoms were generated in calculated positions and constrained with the use of a riding model. The final models involved anisotropic displacement parameters for all non-hydrogen atoms. Except in the following cases, such refinements were straightforward. Further details of the structure analyses are given in Table 4. In compound **2** two carbon atoms of a phenyl ring (C19–C24) are disordered. They were constrained to fit a regular hexagon with the rest of the carbon atoms of the ring with C–C bond distances at 1.39 Å and constrained to the same isotropic thermal parameters. In compound **4** the two OEt moieties each attached to one phosphorus atom were refined restraining the O1–C13 and O2–C15 bond distances to 1.54 Å, and the C13–C14 and C15–C16 bond distances to 1.43 Å. The anisotropic thermal parameters of O1, C13 and C14 were fixed to the same value. Despite the high number of refinement cycles (up to 20) the maximum/shift error was not reduced to a satisfactory value and remained at 10.13, this may be a consequence of the poor quality of the crystal. Compound **9** was attempted to be solved in the monoclinic space group $P2_1/n$ but did not give a satisfactory solution. However, in the triclinic space group $P\bar{1}$ a straightforward solution was obtained.

CCDC reference numbers 248107–248111.

See http://www.rsc.org/suppdata/dt/b4/b412874e/ for crystallographic data in CIF or other electronic format.

Acknowledgements

UC-MEXUS and CONACYT (Project J30234-E) are thanked for generous financial support and postgraduate (S. C. L. and N. T. F.) and undergraduate (E. H. R.) studentships.

References

1 D. A. Atwood, *Coord. Chem. Rev.*, 1998, **176**, 407.
2 M. Bochmann and D. M. Dawson, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 2226.
3 M. P. Coles and R. F. Jordan, *J. Am. Chem. Soc.*, 1997, **119**, 8125.
4 F. Delpech, I. A. Guzei and R. F. Jordan, *Organometallics*, 2002, **21**, 1167.
5 M. A. Muñoz-Hernández, B. Sannigrahi and D. A. Atwood, *J. Am. Chem. Soc.*, 1999, **121**, 6747.
6 S. Dagorne, I. A. Guzei, M. P. Coles and R. F. Jordan, *J. Am. Chem. Soc.*, 2000, **122**, 274.
7 J. Klosin, G. R. Roof, E. Y. X. Chen and K. A. Abboud, *Organometallics*, 2000, **19**, 4684.
8 A. V. Korolev, F. Delpech, S. Dagorne, I. A. Guzei and R. F. Jordan, *Organometallics*, 2001, **20**, 3367.
9 D. A. Atwood, J. A. Jegier and D. Rutherford, *J. Am. Chem. Soc.*, 1995, **117**, 6997.
10 M. Bruce, V. C. Gibson, C. Redshaw, G. A. Solan, A. J. P. White and D. J. Williams, *Chem. Commun.*, 1998, 2523.
11 D. A. Atwood, *Main Group Chem. News*, 1998, **5**, 30.
12 R. J. Wehmschulte, J. M. Steele and M. A. Khan, *Organometallics*, 2003, **22**, 4678.
13 K. C. Kim, C. A. Reed, G. S. Long and A. Sen, *J. Am. Chem. Soc.*, 2002, **124**, 7662.
14 M. A. Muñoz-Hernández, A. Singer, D. A. Atwood and R. Cea-Olivares, *J. Organomet. Chem.*, 1998, **571**, 15.
15 V. Montiel-Palma, E. Huitrón-Rattinger, S. Cortés-Llamas, M. A. Muñoz-Hernández, E. López-Honorato, V. García-Montalvo and C. Silvestru, *Eur. J. Inorg. Chem.*, 2004, 3743.
16 A. V. Korolev, E. Ihara, I. A. Guzei, V. G. Young, Jr. and R. F. Jordan, *J. Am. Chem. Soc.*, 2001, **123**, 8291.
17 O. T. Beachley, J. R. Gardinier and M. R. Churchill, *Organometallics*, 2003, **22**, 1145.
18 O. T. Beachley, J. R. Gardinier, M. R. Churchill, D. G. Churchill and K. M. Keil, *Organometallics*, 2002, **21**, 946.
19 J.-H. Park, M. Afzaal, M. Helliwell, M. A. Malik, P. O'Brien and J. Raftery, *Chem. Mater.*, 2003, **15**, 4205.
20 C. Silvestru and J. E. Drake, *Coord. Chem. Rev.*, 2001, **223**, 117.
21 D. J. Williams, *Inorg. Nucl. Chem. Lett.*, 1980, **16**, 189.
22 A. M. Z. Slawin, J. Ward, D. J. Williams and J. D. Woollins, *Chem. Commun.*, 1994, 421.
23 P. Bahttacharyya, A. M. Z. Slawin, D. J. Williams and J. D. Woollins, *J. Chem. Soc., Dalton Trans.*, 1995, 2489.
24 G. Balazs, J. E. Drake, C. Silvestru and I. Haiduc, *Inorg. Chim. Acta*, 1999, **287**, 61.
25 R. Rösler, J. E. Drake, C. Silvestru, J. Yang, I. Haiduc and G. Espinoza-Pérez, *J. Chem. Soc., Dalton Trans.*, 1998, 73.
26 R. Rösler, C. Silvestru, G. Espinoza-Pérez, I. Haiduc and R. Cea-Olivares, *Inorg. Chim. Acta*, 1996, **241**, 47.
27 J. E. Drake, M. B. Hursthouse, M. Kulcsar, M. E. Light and C. Silvestru, *J. Organomet. Chem.*, 2001, **623**, 153.
28 M. M. Akobiya, V. I. Bregadze, L. M. Golubinskaya, S. Gundersen, A. Haaland, H. V. Volden, V. S. Mastryukov and I. F. Shishkov, *J. Organomet. Chem.*, 1994, **467**, 161.
29 R. J. Wehmschulte, J. M. Steele and M. A. Khan, *Organometallics*, 2003, **22**, 4678.
30 M. P. Coles, D. C. Swenson and R. F. Jordan, *Organometallics*, 1997, **16**, 5183.
31 O. T. Beachley, T. L. Royster and J. R. Arhar, *J. Organomet. Chem.*, 1992, **434**, 11.
32 O. T. Beachley and M. T. Mosscrop, *Organometallics*, 2000, **19**, 4550.
33 O. T. Beachley, D. B. Rosenblum, M. R. Churchill, C. H. Lake and L. M. Krajkowski, *Organometallics*, 1995, **14**, 4402.
34 F. T. Wang, J. Najdzionek, K. L. Leneker, H. Wasserman and D. M. Braitsch, *Synth. React. Inorg. Met.-Org. Chem.*, 1978, **8**, 119–125.
35 P. Bahttacharyya, J. Novasad, J. Phillips, A. M. Z. Slawin, D. J. Williams and J. D. Woollins, *J. Chem. Soc., Dalton Trans.*, 1995, 1607.
36 G. M. Sheldrick, SMART Bruker AXS, Inc., Madison, WI, USA, 2000.
37 G. M. Sheldrick, SAINT-Plus 6.0 Bruker AXS, Inc., Madison, WI, USA, 2000.
38 G. M. Sheldrick, SHELXTL 6.10 Bruker AXS, Inc., Madison, WI, USA, 2000.