

Towards Cationic Gallium Derivatives: Metallacycles from the Reactions of Organogallium Compounds with Tetraorganodichalcogenoimidodiphosphinates and a New *N*-(Diphenylthiophosphinyl)thioureato Ligand

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The organometallic complexes of general formulae $[\text{Me}_2\text{Ga}\{\eta^2\text{-E,E'}\text{-}[\text{R}_2\text{P(E)NP(E')R'}_2]\}]$ [$\text{R} = \text{R}' = \text{Ph}$, $\text{E} = \text{E}' = \text{O}$ (**1**); $\text{R} = \text{R}' = \text{Ph}$, $\text{E} = \text{E}' = \text{S}$ (**2**); $\text{R} = \text{R}' = \text{Ph}$, $\text{E} = \text{E}' = \text{Se}$ (**3**); $\text{R} = \text{R}' = \text{Ph}$, $\text{E} = \text{O}$, $\text{E}' = \text{S}$ (**4**); $\text{R} = \text{Me}$, $\text{R}' = \text{Ph}$, $\text{E} = \text{S}$, $\text{E}' = \text{O}$ (**5**)] and $[\text{Me}_2\text{Ga}\{\eta^2\text{-S,S'}\text{-}[\text{Ph}_2\text{P(S)NC(S)(C}_9\text{H}_{10}\text{N})]\}]$ (**6**) were obtained by facile methane elimination reactions from GaMe_3 and the acidic ligands L^1H [$(\text{XPPH}_2)_2\text{NH}$ ($\text{X} = \text{O}, \text{S}, \text{Se}$), $(\text{OPPh}_2)(\text{SPPH}_2)\text{NH}$, and $(\text{OPMe}_2)(\text{SPPH}_2)\text{NH}$] and L^2H [$\text{Ph}_2\text{P(S)NHC(S)(C}_9\text{H}_{10}\text{N})$] in toluene. Replacement of one phosphorus atom by a carbon atom in the ligand skeleton of L^1H gave the new ligand L^2H , which, upon reaction with

GaMe_3 , gave compound **6**, which shows no significant structural differences with respect to **1–5**. Therefore, L^2H does not induce partial planarity in the six-membered ring, indicating the necessity for replacing both phosphorus atoms of the ligand by carbon atoms, as in the β -diketonate-type derivatives, in order to impose ring planarity. Thus, despite originating from a variety of ligands with differing donor atoms and substituents at the phosphorus atoms, all complexes show little structural differences.

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Introduction

Comparisons between the bonding in organic and inorganic (carbon-free) analogs are widely sought throughout chemistry and have led to a higher understanding of electronically related systems. In particular, the consequences of π -electron delocalization in planar chelate rings have been traditionally assessed by comparison of their properties with those of their nonplanar counterparts arising from atom substitution.^[1,2]

In this light, tetraorganodichalcogenoimidodiphosphinato $\{[\text{R}_2\text{P(E)NP(E')R'}_2]\}^-$ ($\text{E} = \text{E}' = \text{chalcogen}$) (L^1) and *N*-(diorganothiophosphinyl)thioureato $\{[\text{R}_2\text{P(S)NC(S)R''}_2]\}^-$ (L^2) ligands can be regarded as inorganic analogs of the much used β -diketonate ligands. It is the flexi-

bility of the six-membered $\text{M}\{\eta^2\text{-E,E'}\text{-(EPNPE')}\}$ (M = main group or transition metal) ring derived from L^1 that has been credited for the variety of structural and coordination modes encountered, a number of which have even given rise to supramolecular structures or proved to be potential building blocks for the design of new materials; others have found prospective industrial use in catalytic systems or biological applications.^[3,4] Accordingly, the last decade has seen a considerable growth in the investigations of complexes bearing this kind of ligands, yet surprisingly only a discrete number of organometallic gallium derivatives have been isolated.

From the first organogallium derivative of L^1 , $[\text{Et}_2\text{Ga}\{\eta^2\text{-Se,Se'}\text{-}[\text{Ph}_2\text{P(Se)NP(Se)Ph}_2]\}]$ ^[5] (**3-Et**), to Uhl's organodigallium(II) compounds, $[\{(\text{Me}_3\text{Si})_2\text{HC}\}_2\text{Ga}\{\eta^2\text{-O,O'}\text{-}[\text{Ph}_2\text{P(O)NP(O)Ph}_2]\}]$, $[\{(\text{Me}_3\text{Si})_2\text{HC}\}\text{Ga}\{\mu\text{-}\eta^2\text{-O,O'}\text{-}[\text{Ph}_2\text{P(O)NP(O)Ph}_2]\}_2]$, and $[\{(\text{Me}_3\text{Si})_2\text{HC}\}\text{Ga}\{\eta^2\text{-S,S'}\text{-}[\text{Ph}_2\text{P(S)NP(S)Ph}_2]\}_2]$,^[6] this class of compounds has given insights into the feasibility of preparation and stability towards ligand-redistribution reactions.

Perhaps more importantly, however, cationic gallium species with chelating ligands are desirable for applications in homogeneous catalytic reactions such as alkene polymerization to prevent undesirable ligand exchange/redistribution reactions. Amongst some of the most representative examples are those gallium cations supported by sal-

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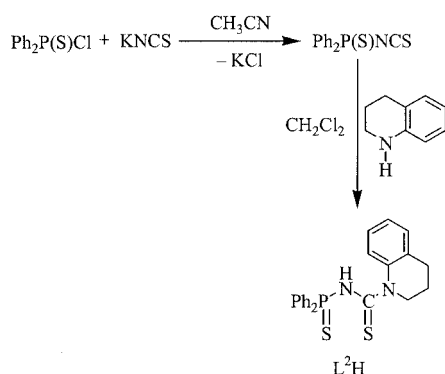
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omphen,^[7] amidinate,^[8,9] β -diketonate^[10] and more recently terphenyl^[11] ligands. In these systems, ligand bite angles and steric protection play a crucial role in the prevention of nucleophilic attack, besides allowing electronic and steric control. Indeed, Jordan has demonstrated that along the cationic amidinate series $[\{\text{MeC}(\text{N}i\text{Pr})_2\}_2\text{Ga}_2\text{Me}_3]^+$, $[\{t\text{BuC}(\text{N}i\text{Pr})_2\}\text{GaMe}_2\{t\text{BuC}(\text{N}i\text{Pr})_2\}\text{GaMe}]^+$ and $[\{t\text{BuC}(\text{N}i\text{Bu})_2\}\text{GaMe}]^+$, susceptibility to dimerization decreases, as does nucleophilic addition.^[8,9]

In our search for new organogallium cations we recently started a program to systematically explore the incorporation of bulky wide-bite-angle tetraorganodichalcogenoimidodiphosphinato (L^1) and *N*-(diorganothiophosphinyl)thiourea (L^2) ligands at organogallium centers. The ligands in these complexes are closely related to the bis(iminophosphorano)methanide ligand system, which has been used to prepare the monomeric aluminum complexes $[\kappa N, \kappa N' - \{\text{Ph}_2\text{P}(\text{Me}_3\text{SiN})_2\text{CH}\}\text{AlR}_2]$ ($R = \text{Me}, \text{Bu}$) and $[\kappa N, \kappa N' - \{\text{Ph}_2\text{P}(\text{Me}_3\text{SiN})_2\text{CH}\}\text{Al}(\text{Cl})\text{Et}]$, and the dimetallic complex $[\kappa C, \kappa C', \kappa N, \kappa N' - \{\text{Ph}_2\text{P}(\text{Me}_3\text{SiN})_2\text{C}\}(\text{Me}_2\text{Al})_2]$. These complexes show catalytic activity towards ethylene polymerization when activated by trityl tetrafluoroborate, presumably due to formation of a cationic species.^[12] Herein we report the facile synthesis and characterization of complexes of general formulae $[\text{Me}_2\text{Ga}\{\eta^2-E, E' - [\text{R}_2\text{P}(\text{E})\text{NP}(\text{E}')\text{R}'_2]\}]$ and $[\text{Me}_2\text{Ga}\{\eta^2-S, S' - [\text{Ph}_2\text{P}(\text{S})\text{NC}(\text{S})\text{R}'']\}]$ which were envisioned to be good precursors of organometallic cationic species.

Results and Discussion

The synthesis of the new proligand $L^2\text{H}$ was carried out in two steps. First, diphenyl isothiocyanide was synthesized according to reported general procedures for the synthesis of similar types of ligands from $\text{Ph}_2\text{P}(\text{S})\text{Cl}$ and KNCS .^[13–15] The purified product was then treated with tetrahydroquinoline in CH_2Cl_2 , yielding $L^2\text{H}$ after treatment with hexane (Scheme 1). Crystals suitable for X-ray diffraction analysis were deposited from hexane at -20°C . The molecular structure is shown in Figure 1 and the collection and crystal data are given in the Exp. Sect.



Scheme 1. The synthesis of the new ligand $L^2\text{H}$

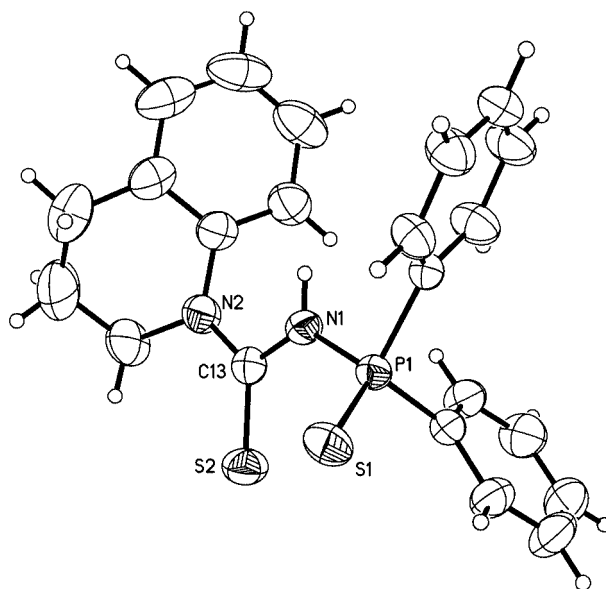
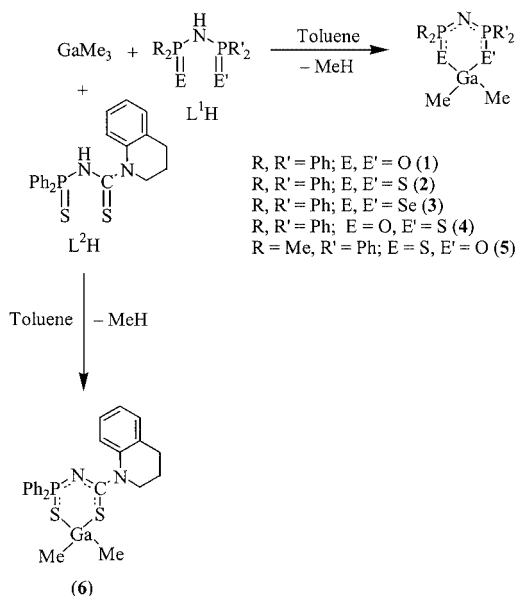


Figure 1. Molecular structure of $L^2\text{H}$ with thermal ellipsoids at 50% probability level

The organogallium compounds of general formulae $[\text{Me}_2\text{Ga}\{\eta^2-E, E' - [\text{R}_2\text{P}(\text{E})\text{NP}(\text{E}')\text{R}'_2]\}]$ [$R = R' = \text{Ph}, E = E' = \text{O}$ (**1**); $R = R' = \text{Ph}, E = E' = \text{S}$ (**2**); $R = R' = \text{Ph}, E = E' = \text{Se}$ (**3**); $R = R' = \text{Ph}, E = \text{O}, E' = \text{S}$ (**4**); $R = \text{Me}, R' = \text{Ph}, E = \text{S}, E' = \text{O}$ (**5**)] and $[\text{Me}_2\text{Ga}\{\eta^2-S, S' - [\text{Ph}_2\text{P}(\text{S})\text{NHC}(\text{S})(\text{C}_9\text{H}_{10}\text{N})]\}]$ (**6**) were obtained in good yields by room temperature methane elimination reactions between GaMe_3 and the ligands $L^1\text{H}$ or $L^2\text{H}$ in toluene, as depicted in Scheme 2.



Scheme 2. General synthesis of complexes **1–6**

Apart from the organogallium complexes mentioned in the introduction, only one other Ga derivative bearing this

type of ligand has been structurally characterized. The inorganic tris(chelate) $[\text{Ga}\{\eta^2\text{-O,O'}\text{-}[\text{Ph}_2\text{P}(\text{O})\text{NP}(\text{O})\text{PPh}_2]_3\}]$ exhibits a slightly distorted octahedral GaO_6 core as well as three six-membered $\text{Ga}(\text{OPNPO})$ rings.^[16] On the other hand, the coordination chemistry with thiophosphorylthiourea (L^2) type ligands is much less developed. Only a few complexes of this kind have been reported and, to the best of our knowledge, no group-13 derivatives have been isolated. Interestingly, the formation of a cavity that would host an alkaline metal ion led to the X-ray diffraction study of cadmium and palladium dinuclear *N*-thiophosphorylated thiourea complexes from α,ω -diamines that allow the connection of two units of tetracoordinate transition metal centers.^[15]

Complexes **1–6** were characterized by physical (m.p.), chemical (C, H and N analysis), and spectroscopic techniques (multinuclear NMR and IR spectroscopy). In addition, solid-state structures of **1**, **2**, **4**, **5** and **6** were obtained by single-crystal X-ray diffraction.

The first indications of the complexation of L^1 and L^2 were given by the absence of $\nu(\text{NH})$ bands in the IR spectra and of the NH resonances in the ^1H NMR solution spectra of the products, particularly in complexes **2–6**.^[3] Moreover, as expected for metal coordination, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra show a high-field shift of the resonance signals for the homoleptic complexes **2** and **3**, and for the P–O resonance of the mixed-chalcogen species. Furthermore, in the case of the selenium derivative **3** there is a considerable decrease in the $^1J_{\text{P,Se}}$ coupling constant with respect to the free ligand (Table 1). On the contrary, there is a small down-field change in the chemical shift of the $^{31}\text{P}\{^1\text{H}\}$ NMR resonance of **1**, although it should be noted that in the tetraphenylimidodiphosphinic acid (L^1H) used as precursor, the acidic hydrogen atom is probably located in an intermolecular $\text{O} \cdots \text{H} \cdots \text{O}$ bridge^[17] which does not permit straightforward deductions.

Table 1. Selected spectroscopic parameters of complexes **1–6** compared to acidic ligands L^1H and L^2H

	$^{31}\text{P}\{^1\text{H}\}$ NMR of complex	$^{31}\text{P}\{^1\text{H}\}$ NMR of acidic ligand
1	26.4 (s) ^[a]	19.4 (s) ^{[3][b]}
2	36.7 (s) ^[b]	55.7 (s) ^{[18][c]}
3	29.3 (s, $^1J_{\text{P,Se}} = 534$ Hz) ^[c]	53.0 (s, $^1J_{\text{P,Se}} = 793$ Hz) ^{[19][b]}
4	27.1 (d, $^2J_{\text{P,P}} = 3.6$ Hz, PS) ^[a]	56.1 (d, $^2J_{\text{P,P}} = 17.5$ Hz, PS)
	34.8 (d, $^2J_{\text{P,P}} = 3.6$ Hz, PO) ^[a]	23.1 (d, $^2J_{\text{P,P}} = 17.5$ Hz, PO) ^{[20][b]}
5	39.2 (d, $^2J_{\text{P,P}} = 7.3$ Hz, PS) ^[a]	63.0 (d, $^2J_{\text{P,P}} = 19.5$ Hz, PS)
	24.7 (d, $^2J_{\text{P,P}} = 7.3$ Hz, PO) ^[a]	23.9 (d, $^2J_{\text{P,P}} = 19.5$ Hz, PO) ^{[21][b]}
6	41.1 (s) ^[a]	56.9 (s) ^[b]

[a] C_6D_6 . [b] CDCl_3 . [c] $[\text{D}_6]\text{THF}$.

Crystals of complexes **1–6** (Figures 2–6, respectively) suitable for X-ray analysis were grown from saturated hexane solutions at -20°C . The molecular structures of the five complexes show a six-membered metallacycle with the geometry around the gallium center being that of a distorted tetrahedron (see below). The dimethylgallium frag-

ment is found to coordinate in a bidentate fashion to the L^1 or L^2 ligands (Tables 2 and 3). Although the crystals of **3** diffracted, we were unable to obtain an acceptable refinement of the data, which, however, show good similarities with those of the already reported diethyl analogue $[\text{Et}_2\text{Ga}\{\eta^2\text{-Se,Se'}\text{-}[\text{Ph}_2\text{P}(\text{Se})\text{NP}(\text{Se})\text{Ph}_2]\}]$ (**3-Et**).^[5]

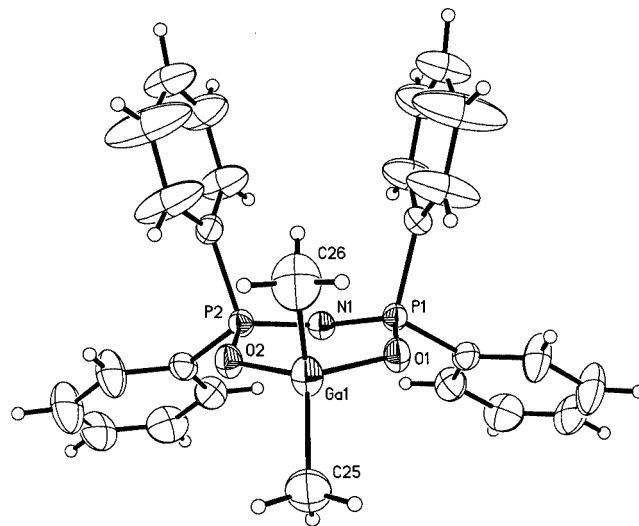


Figure 2. Molecular structure of **1** with thermal ellipsoids at 30% probability level

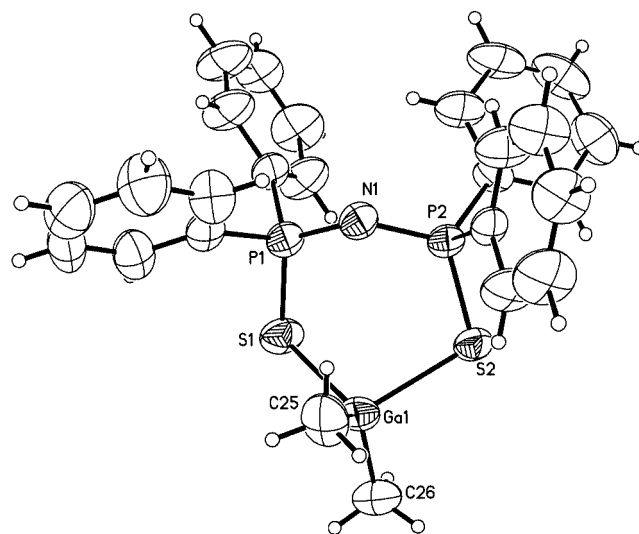


Figure 3. Molecular structure of **2** with thermal ellipsoids at 30% probability level

Compared to the free acidic ligands, the structural features of the complexes are as expected, with the P–E and P–E' distances enlarged and the P–N distances shortened evidencing changes in bond orders. The P–O distances in the complexes — 1.526(3) and 1.527(3) Å (**1**), 1.530(3) Å (**4**) and 1.527(1) Å (**5**) — are longer than typical P=O distances [cf. $\text{Ph}_2\text{P}(\text{O})\text{OH}$:^[22] P=O 1.526(6), P=O 1.486(6) Å]. Accordingly, the P–S distances — 2.037(2) and 2.040(1) Å (**2**), 2.030(2) Å (**4**), and 2.011(1) Å (**6**) — are also longer than the distances of typical P=S bonds (1.89–1.96 Å). The

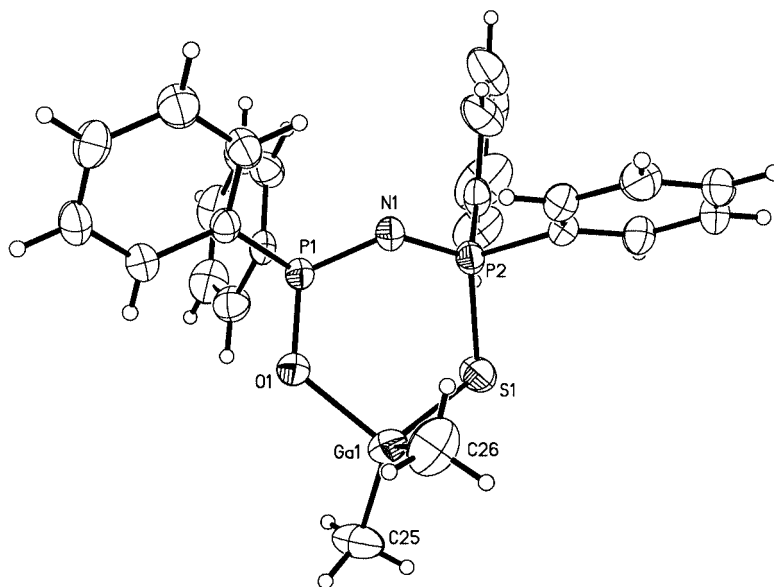


Figure 4. Molecular structure of **4** with thermal ellipsoids at 30% probability level

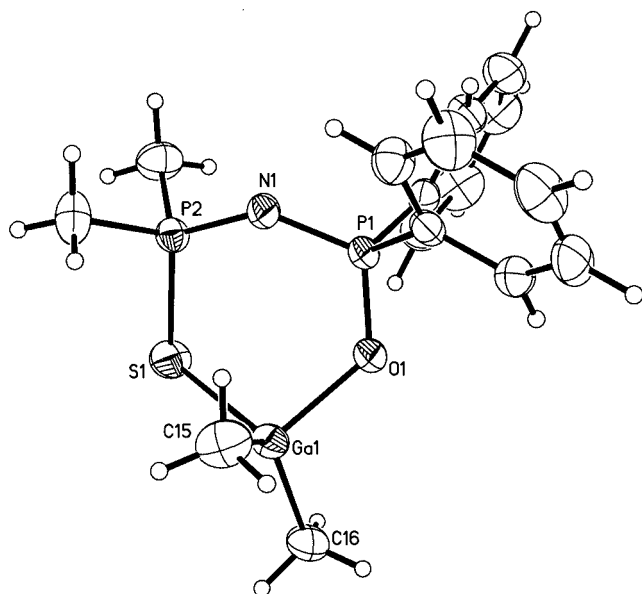


Figure 5. Molecular structure of **5** with thermal ellipsoids at 30% probability level

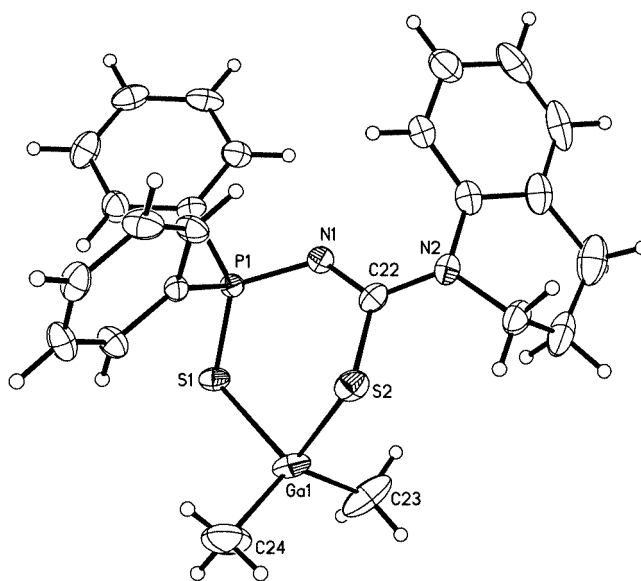


Figure 6. Molecular structure of **6** with thermal ellipsoids at 50% probability level

P–N bond lengths range from 1.59 to 1.61 Å and are somewhat shorter than typical P–N bond lengths {cf. [2-(Me₂NCH₂)C₆H₄]TeSPPH₂=NPPH₂=S:^[23] P–S 2.057(1), P=S 1.945(1), P–N 1.612(3), P=N 1.557(3) Å} as expected due to a higher bond order.

In contrast, along the series, the C–Ga–C angles of the dimethylgallium fragments are practically the same, ranging from 125.3(2)° in **6** to 127.6(3)° in **4**. Additionally, apart from the dioxo derivative, comparisons of the P–N–P (or P–N–C) angles of the complexes with respect to those of the free ligands show little tendency to variation, with the largest difference being 6.4° in complex **2**. Amongst all the complexes, these angles differ very little as they range only from 123.4(1) Å in **1** to 138.1(2) Å in **2** (Table 3).

As demonstrated by the X-ray analysis, the conformations of the six-membered metallacycles are diverse: **1** is a chair with the Ga and N(1) atoms at the apices, **2** adopts an envelope conformation with Ga out of the plane, **4** has a twist-boat conformation also with Ga and N(1) at the apices, and **5** and **6** are both boats with Ga and N(1), and P(1) and S(2), respectively, at the apices. The closely related selenium derivative [Et₂Ga{η²-Se,Se-[Ph₂P(Se)NP(Se)-Ph₂]}] (**3-Et**)^[5] shows a distorted boat conformation with Se and P atoms at the apices. A nonplanar ring is a common feature of complexes derived from tetraorganodichalcogenoimidodiphosphinato ligands, as demonstrated by the variety of examples encountered in main-group and transition-metal chemistry. On the contrary, replacing phos-

Table 2. Selected bond lengths [Å] and angles [°] for complexes **1**, **2**, **4**, **5** and **6**

1	Ga(1)–C(25)	1.938(5)	O(2)–Ga(1)–O(1)	97.9(1)
	Ga(1)–C(26)	1.994(7)	C(25)–Ga(1)–C(26)	126.0(4)
	Ga(1)–O(1)	1.951(3)	O(1)–Ga(1)–C(26)	107.7(3)
	Ga(1)–O(2)	1.953(3)	O(1)–Ga(1)–C(25)	107.7(3)
	O(1)–P(1)	1.527(3)	O(2)–Ga(1)–C(25)	107.7(3)
	O(2)–P(2)	1.526(3)	O(2)–Ga(1)–C(26)	106.9(3)
	P(1)–N(1)	1.590(3)		
	P(2)–N(1)	1.591(3)		
2	Ga(1)–C(25)	1.958(5)	S(2)–Ga(1)–S(1)	99.2(1)
	Ga(1)–C(26)	1.978(5)	C(25)–Ga(1)–C(26)	126.1(2)
	Ga(1)–S(1)	2.380(1)	S(1)–Ga(1)–C(26)	104.5(2)
	Ga(1)–S(2)	2.416(2)	S(1)–Ga(1)–C(25)	110.8(2)
	S(1)–P(1)	2.040(1)	S(2)–Ga(1)–C(25)	110.9(2)
	S(2)–P(2)	2.037(2)	S(2)–Ga(1)–C(26)	101.9(2)
	P(1)–N(1)	1.593(3)		
	P(2)–N(1)	1.588(3)		
4	Ga(1)–C(25)	1.957(5)	O(1)–Ga(1)–S(1)	99.1(1)
	Ga(1)–C(26)	1.963(5)	C(25)–Ga(1)–C(26)	127.6(3)
	Ga(1)–O(1)	1.945(3)	O(1)–Ga(1)–C(26)	107.3(2)
	Ga(1)–S(1)	2.389(1)	O(1)–Ga(1)–C(25)	106.8(2)
	O(1)–P(1)	1.530(3)	S(1)–Ga(1)–C(25)	102.1(2)
	S(1)–P(2)	2.030(2)	S(1)–Ga(1)–C(26)	110.3(2)
	P(1)–N(1)	1.596(3)		
	P(2)–N(1)	1.601(3)		
5	Ga(1)–C(15)	1.942(3)	O(1)–Ga(1)–S(1)	96.3(1)
	Ga(1)–C(16)	1.937(3)	C(15)–Ga(1)–C(16)	127.1(2)
	Ga(1)–O(1)	1.932(2)	O(1)–Ga(1)–C(15)	108.3(1)
	Ga(1)–S(1)	2.377(1)	O(1)–Ga(1)–C(16)	104.8(1)
	O(1)–P(1)	1.527(2)	S(1)–Ga(1)–C(15)	109.8(1)
	S(1)–P(2)	2.041(1)	S(1)–Ga(1)–C(16)	106.2(1)
	P(1)–N(1)	1.577(2)		
	P(2)–N(1)	1.612(2)		
6	Ga(1)–C(24)	1.960(4)	S(2)–Ga(1)–S(1)	103.4(1)
	Ga(1)–C(23)	1.961(4)	C(24)–Ga(1)–C(23)	125.3(3)
	Ga(1)–S(1)	2.3886(9)	S(1)–Ga(1)–C(24)	110.7(1)
	Ga(1)–S(2)	2.3535(9)	S(1)–Ga(1)–C(23)	104.8(1)
	S(1)–P(1)	2.011(1)	S(2)–Ga(1)–C(23)	109.3(1)
	S(2)–C(22)	1.758(3)	S(2)–Ga(1)–C(24)	101.4(1)
	P(1)–N(1)	1.614(2)		
	C(22)–N(1)	1.325(4)		

phorus with carbon in the ligand skeleton, as in the tetrahedral imidoamidinato complex $[\text{Me}_2\text{Ga}\{\eta^2\text{-N,N'}\text{-[HNC}(\text{CF}_3)\text{NC}(\text{CF}_3)\text{NH}]\}]^{[27]}$ leads to all atoms of the ring being coplanar. In addition, a small number of planar gallacycle rings have been structurally characterized as derivatives of β -diketonate ligands. For example, four-coordinate $[\text{GaCl}_2(\text{bdk})]^{[10]}$ [bdk = (2,4-pentanedionato), acac and (2,2,6,6-tetramethylheptanedionato)], $[\text{GaMeCl}(\text{acac})]^{[28]}$ and $[\text{GaCl}\{\text{N}(\text{SiMe}_3)_2\}(\text{acac})]^{[28]}$ all show planar six-membered GaO_2C_3 rings with O–Ga–O bite angles ranging from 96.1 to 99.3°. It is thus significant that in complex **6** replacement of one phosphorus atom by a carbon atom does not induce partial planarity in the ring.

Perhaps the most striking feature is the fact that along a series of chemically differing ligands, the structural variation is not as large as expected, despite the well-documented versatility of the PNP ligand.

The fact that the bite angles of the ligands in the complexes studied are in the range 96.3–108.4° (see Table 3) is indicative of their prospective good potential as cationic precursors. Steric protection for catalytically active metal centers can be provided by bulky multidentate ligands, and various examples have been reported with late transition metals^[29] as well as aluminum.^[30] Indeed, large bite angles in cationic, three-coordinate aluminum complexes have proved to be an effective approach to stabilize these highly reactive species. Bulky aluminum amidinate complexes $[\{\text{RC}(\text{NR}')_2\}\text{AlMe}]^+$ with small bite angles (N–Al–N angle of about 70° in neutral derivatives) are thermally unstable but the *N,N'*-diaryldiketiminato complex $[\{\text{HC}(\text{CMeNAr})_2\}\text{AlMe}_2]$ (Ar = 2,6-*i*-Pr₂C₆H₃) with a larger bite angle (N–Al–N angle of about 96°) and bulky *N*-aryl substituents yield a stable, three-coordinate cation upon abstraction of the alkyl group.^[31] Moreover, in contrast to most precursors documented in the literature, the family of complexes reported herein is easily accessible and requires little purification. Current work in our laboratory is focused in this direction, treating complexes **1–6** and others with strong Lewis acids. The results of this work will be reported shortly.

Table 3. Selected structural features of organogallium metallacycles **1**, **2**, **4**, **5**, **6** and $[\text{Et}_2\text{Ga}\{\eta^2\text{-Se,Se'}\text{-[Ph}_2\text{P}(\text{Se})\text{NP}(\text{Se})\text{Ph}_2]\}]$ (**3-Et**)^[5]

	P–N–P or P–N–C angle in ligand [°]	P–N–P or P–N–C angle in complex [°]	E–Ga–E' angle [°]	Me–Ga–Me angle [°]	(PENPE')Ga or (PSNCS)Ga ring conformation	Nonbonding E–E' length [Å]
1	180 ^[17]	123.4(1)	97.9(1)	126.0(4)	chair	O(1)–O(2) 2.94
2	131.7(5) ^[24]	138.1(2)	99.2(1)	126.1(2)	envelope-	S(1)–S(2) 3.65
3-Et ^[5]	132.3(2) ^[25]	129.8(3) ^[5]	108.4(1) ^[5]	125.5(4) ^[5]	boat ^[5]	Se(1)–Se(2) 4.09
4	131.4(3) ^[26]	125.4(2)	99.1(1)	127.6(3)	twist boat	O(1)–S(1) 3.31
5	126.5 ^[20]	131.1(1)	96.3(1)	127.1(2)	boat	O(1)–S(1) 3.22
6	128.8(1)	124.1(2)	103.4(1)	125.3(2)	boat	S(1)–S(2) 3.72

Conclusion

Gallium metallacycles derived from dichalcogenoimido-diphosphinato ligands were obtained by facile methane elimination reactions. In the new complexes, the Ga center is in a distorted tetrahedral environment forming part of a six-membered metallacycle. The conformations of these rings do not correlate with the nature of the chalcogen nor with the substituents at the phosphorus or carbon atoms, but in all cases a nonplanar ring was observed. Exchanging a phosphorus atom by a carbon atom in the metallacycle ring does not result, even partially, in a planar structure of complex **6**.

Experimental Section

General Remarks: All glassware was rigorously dried in an oven at 130 °C for 24 h, assembled hot, and then allowed to cool under argon. All the manipulations of the air-sensitive compounds were conducted using standard inert-gas bench-top and glove-box techniques. Solvents were dried with sodium or potassium/benzophenone and freshly distilled prior to use. The L¹H ligands were synthesized according to literature methods: (XPPH₂)₂NH (X = O,^[32] S,^[33] Se^[33]), (OPPh₂)(SPPH₂)NH,^[34] and (OPMe₂)(SPPH₂)NH.^[35] NMR spectroscopic data (¹H, ¹³C and ³¹P) were obtained with Varian-Inova 400 MHz and Varian-Gemini-200 MHz instruments at 19 °C. Chemical shifts are reported relative to SiMe₄ for ¹H and ¹³C, 85% H₃PO₄ for ³¹P and are in ppm. Microanalyses were obtained with an Elemental Vario EL III instrument in the CHNS operation mode. Infrared spectra were recorded as KBr pellets with a Bruker Equinox 55 Spectrometer and are reported in cm⁻¹.

Synthesis of Ph₂P(S)NHC(S)(C₉H₁₀N) (L²H): Tetrahydroquinoline (0.65 mL, 5.1 mmol) was added to a stirred solution of Ph₂P(S)NCS (1.42 g, 5.1 mmol) in CH₂Cl₂ (20 mL). After 4 h, the solvent was removed under vacuum, hexane (30 mL) was added and the mixture stirred for a further 2 h. The white solid deposited was filtered and dried under vacuum. Yield: 1.89 g (90%), m.p. 71–73 °C. Selected ¹H NMR data (CDCl₃, 300 MHz): δ = 3.97 (s, 1 H, NH) ppm. ¹³C NMR (CDCl₃, 75.4 MHz): δ = 150.50 (C=S) ppm. ³¹P NMR (CDCl₃, 121.4 MHz): δ = 56.89 (s) ppm. IR: ν̄ = 3309 (νNH), 1445 (νCN), 1103 (νCS), 957, 882 (νPN), 647 (νPS) cm⁻¹. Crystals suitable for X-ray diffraction analysis were grown from hexane solution.

Synthesis of [Me₂Ga{η²-O,O'-[Ph₂P(O)NP(O)Ph₂}] (1): A solution of trimethylgallium (0.08 g, 0.70 mmol) in toluene (10 mL) was added to a stirred suspension of (OPPh₂)₂NH (0.3 g, 0.72 mmol) in toluene (20 mL), causing vigorous gas evolution and the formation of a clear colorless solution which was stirred for 4 h. Removal of the volatiles under reduced pressure produced a viscous substance, which was treated with hexane (5 mL) and stirred until the deposition of a white solid. The solid was separated from the solution by cannula filtration and dried under high vacuum. The remaining hexane solution at -20 °C deposited suitable crystals for X-ray analysis. Yield 0.27 g (87%), m.p. 77–78 °C. ¹H NMR (CDCl₃, 400 MHz): δ = -0.31 (s, 6 H, GaCH₃), 7.34–7.40 (m, 12 H, C₆H₅), 7.75 (m, 8 H, C₆H₅) ppm. ¹³C NMR (CDCl₃, 100.6 MHz): δ = -4.52 (s, CH₃Ga), 128.30–131.26 (C₆H₅), 136.04 (d, ¹J_{C,P} = 140 Hz, *ipso*-C₆H₅) ppm. ³¹P{¹H} NMR (C₆D₆, 161.8 MHz): δ = 26.43 (s) ppm. IR: ν̄ = 3072 (m), 2960 (m), 2718 (w), 2365 (w),

2336 (w), 200.22 (w), 1959 (w), 1893 (w), 1814 (w), 1674 (w), 1590 (w), 1482 (m), 1436 (s), 1126 (s), 691 (s) 590 (s) cm⁻¹. C₂₆H₂₆GaNO₂P₂ (516.14): calcd. C 60.50, H 5.08, N 2.71; found C 60.43, H 5.03, N 2.72.

Compounds **2–6** were prepared in a similar manner to **1**.

[Me₂Ga{η²-S,S-[Ph₂P(S)NP(S)Ph₂}] (2): (SPPH₂)₂NH (0.30 g, 0.67 mmol) and trimethylgallium (0.08 g, 0.70 mmol) afforded **2** as a white solid. Yield 0.30 g (82%), m.p. 103–105 °C. ¹H NMR (CDCl₃, 400 MHz): δ = -0.25 (s, 6 H, CH₃Ga), 7.35 (m, 12 H, C₆H₅), 7.83 (m, 8 H, C₆H₅P) ppm. ¹³C NMR (CDCl₃, 100.6 MHz): δ = -0.79 (s, GaCH₃), 128.41–131.36 (C₆H₅), 137.31 (d, ¹J_{C,P} = 140 Hz, *ipso*-C₆H₅) ppm. ³¹P{¹H} NMR (CDCl₃, 161.8 MHz): δ = 36.71 (s) ppm. IR: ν̄ = 3069.3 (w), 2962.3 (m), 2901.4 (w), 1999.5 (w), 1892.5 (w), 1809.7 (w), 1674 (w), 1582.8 (w), 1476.7 (m), 1433 (m), 1258.9 (m), 1196.4 (s), 1104.7 (s), 1022.8 (s), 807.5 (s), 743.7 (s), 694.8 (s), 577.5 (s), 530.3 (s) cm⁻¹. C₂₆H₂₆GaNP₂S₂ (548.26): calcd. C 56.96, H 4.78, N 2.55, S 11.70; found C 57.01, H 4.79, N 2.60, S 11.87.

[Me₂Ga{η²-Se,Se-[Ph₂P(Se)NP(Se)Ph₂}] (3): (SePPH₂)₂NH (0.3 g, 0.55 mmol) and trimethylgallium (0.063 g, 0.55 mmol) generated **3** as a white solid. Yield 0.31 g (88%), m.p. 143 °C. ¹H NMR (CDCl₃, 400 MHz): δ = -0.11 (s, ¹J_{C,H} = 162, ³J_{Se,H} = 4 Hz, 6 H, GaCH₃), 7.34–7.44 (m, 12 H, C₆H₅), 7.81 (m, 8 H, C₆H₅) ppm. ¹³C{¹H} (CDCl₃, 100.6 MHz): δ = 0.20 (GaCH₃), 128.2–131.4 (C₆H₅), 136.8 (dd, ¹J_{P,C} = 98.49, ²J_{C,Se} 4.19 Hz, *ipso*-C₆H₅) ppm. ³¹P{¹H} NMR (CDCl₃, 81 MHz): δ = 29.3 (s, ¹J_{P,Se} = 525 Hz) ppm. IR: ν̄ = 3060 (w), 1583 (w), 1477 (w), 1433 (m), 1210 (s), 1108 (s), 1025 (w), 925 (w), 803 (m), 691 (s), 562 (s), 516 (m), 486 (m) cm⁻¹. C₂₆H₂₆GaNP₂Se₂ (642.08): calcd. C 48.64, H 4.08, N 2.18; found C 48.85, H 4.11, N 2.14.

[Me₂Ga{η²-S,O-[Ph₂P(S)NP(O)Ph₂}] (4): Compound **4** was obtained as a white solid from (SPPH₂)NH(OPPh₂) (0.3 g, 0.69 mmol) and trimethylgallium (0.08 g, 0.70 mmol). Yield 0.27 g, 73%, m.p. 83–85 °C. ¹H NMR (200 MHz, C₆D₆): δ = 0.22 (s, 6 H, GaCH₃), 6.98 (m, 12 H, C₆H₅), 7.96 (m, 8 H, C₆H₅) ppm. ¹³C NMR (50.3 MHz, C₆D₆): δ = -1.50 (s, GaCH₃), 128.59 (m, and C₆H₅), 131.58 (m, C₆H₅), 136.23 (d, ¹J_{C,P} = 105 Hz, *ipso*-C₆H₅), 139.32 (d, ¹J_{C,P} = 83 Hz, *ipso*-C₆H₅) ppm. ³¹P{¹H} NMR (161.8 Hz, C₆D₆): δ = 27.07 (d, ²J_{P,P} = 3.56 Hz, GaOPPh₂), 34.78 (d, ²J_{P,P} = 3.56 Hz, GaSPPH₂) ppm. IR: ν̄ = 3053.2 (m), 2966 (s), 2909 (m), 2712 (w), 1968 (w), 1890 (w), 1825 (w), 1775 (m), 1674 (w), 1591 (m), 1482 (m), 1433 (s), 1410 (s), 1050 (s), 867 (s), 700 (s), 549 (s) cm⁻¹. C₂₆H₂₆GaNOP₂S (532.20): calcd. C 58.67, H 4.92, N 2.63, S 6.03; found C 58.68, H 5.01, N 2.62, S 5.98.

[Me₂Ga{η²-S,O-[Me₂P(S)NP(O)Ph₂}] (5): White compound **5** was synthesized from (SPMe₂)(OPPh₂)NH (0.22 g, 0.71 mmol) and trimethylgallium (0.08 g, 0.70 mmol). Yield 0.25 g (87%), m.p. 116–118 °C. ¹H NMR (400 MHz, C₆D₆): δ = 0.35 (s, 6 H, GaCH₃), 1.39 (d, ²J_{P,H} = 26.4 Hz, 6 H, GaPCH₃), 7.03 (m, 6 H, C₆H₅), 7.90 (m, 4 H, C₆H₅) ppm. ¹³C NMR (50.3 Hz, C₆D₆): δ = -1.17 (s, GaCH₃), 26.37 (dd, ¹J_{C,P} = 122.56, ³J_{C,P} = 5.01 Hz, PCH₃), 128.64 (m, C₆H₅), 131.63 (m, C₆H₅) ppm. ³¹P{¹H} NMR (161.82 MHz, C₆D₆): δ = 25.61 (d, ²J_{P,P} = 7.29 Hz, GaOPPh₂), 39.18 (d, ²J_{P,P} = 7.29 Hz, GaSPMe₂) ppm. IR: ν̄ = 3053 (m), 2966.0 (s), 2909 (m), 2712 (w), 1968 (w), 1890 (w), 1825 (w), 1755 (w), 1674 (w), 1591 (w), 1482 (m), 1433 (s), 1410 (s), 1050 (s), 867 (s), 700 (s), 549 (s) cm⁻¹. C₁₆H₂₂GaNOP₂S (408.07): calcd. C 47.09, H 5.43, N 3.43, S 7.86; found C 47.13, H 5.51, N 3.39.

[Me₂Ga{η²-S,S-[Ph₂P(S)N(C)NC₉H₁₀}] (6): White compound **6** was synthesized from C₉H₁₀NC(S)NHP(S)(C₆H₅)₂ (0.27 g,

Table 4. Summary of crystallographic data for complexes L²H, **1**, **2**, **4**, **5** and **6**

	L ² H	1	2	4	5	6
Empirical formula	C ₂₂ H ₂₁ N ₂ PS ₂	C ₂₆ H ₂₆ GaNO ₂ P ₂	C ₂₆ H ₂₆ GaNP ₂ S ₂	C ₂₆ H ₂₆ GaNOP ₂ S	C ₁₆ H ₂₂ GaNOP ₂ S	C ₂₄ H ₂₆ GaN ₂ PS ₂
Formula mass	408.50	516.14	548.26	532.20	408.07	507.28
Crystal system	monoclinic	orthorhombic	monoclinic	orthorhombic	triclinic	orthorhombic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>Cc</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>Pbca</i>	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ 2 ₁ 2 ₁
<i>a</i> [Å]	10.4437(8)	9.645(1)	14.257(6)	16.687(4)	9.162(1)	8.481(2)
<i>b</i> [Å]	22.2312(16)	14.842(1)	8.852(4)	15.943(4)	9.308(1)	16.596(4)
<i>c</i> [Å]	9.1690(7)	17.743(2)	21.635(9)	19.526(5)	12.921(1)	17.078(4)
α [°]	90	90	90	90	106.216(1)	90
β [°]	106.6740(10)	90	101.881(7)	90	93.480(1)	90
γ [°]	90	90	90	90	111.178(1)	90
<i>V</i> [Å ³]	2039.3(3)	2539.8(6)	2671.9(19)	5195(2)	970.30(14)	2403.8(10)
<i>Z</i>	4	4	4	8	2	4
<i>D</i> _{calcd.} ([g/cm ³])	1.331	1.350	1.363	1.361	1.397	1.402
<i>F</i> (000)	856	1064	1128	2192	420	1048
Crystal size [mm]	0.12 × 0.23 × 0.26	0.14 × 0.26 × 0.29	0.13 × 0.18 × 0.26	0.13 × 0.18 × 0.27	0.18 × 0.17 × 0.11	0.15 × 0.18 × 0.24
Temperature [K]	293	293	293	293	100	100
2 θ range [°]	3.6–55	5.6–50	2.9–50	4.1–50	3.3–52	3.4–50
No. of reflections collected	22836	8938	12838	45930	10895	8640
No. of independent reflections	4662 (<i>R</i> _{int} = 0.0342)	4380 (<i>R</i> _{int} = 0.0209)	4645 (<i>R</i> _{int} = 0.0591)	4569 (<i>R</i> _{int} = 0.0569)	4199 (<i>R</i> _{int} = 0.0171)	4150 (<i>R</i> _{int} = 0.0330)
No. of observed reflections	3706 [<i>F</i> > 4.0 σ (<i>F</i>)]	4225 [<i>F</i> > 4.0 σ (<i>F</i>)]	3439 [<i>F</i> > 4.0 σ (<i>F</i>)]	3978 [<i>F</i> > 4.0 σ (<i>F</i>)]	3763 [<i>F</i> > 4.0 σ (<i>F</i>)]	3687 [<i>F</i> > 4.0 σ (<i>F</i>)]
No. of parameters	244	291	291	291	203	273
<i>R</i>	0.0442	0.0377	0.0631	0.0604	0.0368	0.0295
<i>R</i> _w	0.1138	0.0984	0.1559	0.1369	0.1032	0.0598
GOF	1.038	1.084	0.969	1.230	1.080	0.958
Largest difference electron density [e/Å ³]	0.449/−0.311	0.711/−0.496	1.056/−0.927	0.545/−0.244	0.667/−0.165	0.416 and −0.220

0.66 mmol) and trimethylgallium (0.076 g, 0.66 mmol). Yield 0.25 g (75%). Selected ¹H NMR data (80.96 MHz, C₆D₆): δ = 0.35 (s, 6 H, GaCH₃), 2.23 (m, 2 H, CH₂), 3.94 (m, 2 H, CH₂), 4.27 (m, 2 H, CH₂), 6.89–7.91 (m, 13 H, aromatic H) ppm. ³¹P{¹H} NMR (80.96 MHz, C₆D₆): δ = 41.07 (s). C₂₄H₂₆GaN₂PS₂ (507.28): calcd. C 56.54, H 5.10, N 2.75, S 12.57; found C 56.81, H 5.21, N 2.64, S 12.43.

X-ray Crystallographic Study: Crystals suitable for X-ray diffraction for compounds L²H, **1**, **2**, **4**, **5** and **6** were obtained from saturated hexane solutions as described above. X-ray data were collected with a Bruker APEX CCD diffractometer with Mo-*K*_α radiation. The structures were refined using the software package SHELXTL vers. 6.1.^[36] All of the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were put into calculated positions. Absorption correction in all cases was applied using SADABS.^[37] Further details of the structure analyses are given in Table 4.^[38]

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