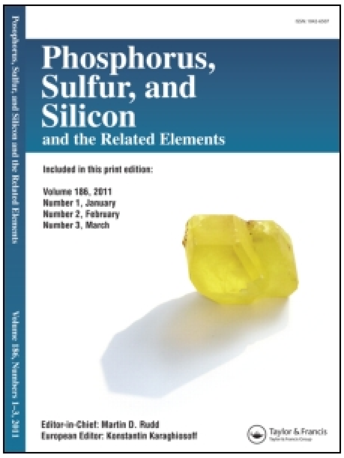

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INORGANIC RINGS WITH GALLIUM ORGANYLS AND IMINODIPHOSPHINECHALCOGENIDES

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The organometallic complexes of general formula $[Me_2Ga\{(XPR_2)(YPR'_2)N\}]$ *(R, R′ = Ph, X, Y = O, (**1**); R, R′ = Ph, X, Y = S (**2**); R, R′ = Ph, X = O, Y = S (**3**); R = Me, R′ = Ph, X = O, Y = S (**4**)) were obtained by alkane eliminations from* Me_3Ga *and the free acidic ligands, LH, in toluene solutions. Complexes **1–4** seem to be potential precursors to cationic gallium species.*

Keywords: Cations; iminodiphosphinechalcogenides; organogallium complexes

The number of neutral organogallium complexes that incorporate iminodiphosphinechalcogenide ligands, $[R_2P(X)NP(Y)R'_2]^-$, is scarce. The first example to be reported was $[Et_2Ga\{(SePPh_2)_2N\}]$.[1] Thereafter Uhl investigated the reaction of the tetraakyldigallium derivative $[\{(Me_3Si)_2HC\}_2Ga]_2$ with the acid $Ph_2P(O)NP(OH)Ph_2$ isolating $[\{(Me_3Si)_2HC\}_2Ga\{(OPPh_2)_2N\}]$ and $[(Me_3Si)_2HCGa\text{-}\mu\text{-}\{(OPPh_2)_2N\}]_2$.[2] The digallium complex $[(Me_3Si)_2HCGa\{(SPPh_2)_2N\}]_2$ also was prepared by the substituent exchange of $[(Me_3Si)_2HCGa]_2$ with the corresponding lithium salt of the dithio ligand.

Cationic gallium complexes with chelating ligands are desirable for applications in homogeneous catalysis to prevent undesirable ligand exchange/redistribution reactions. Atwood has reported the Salen supported binuclear cation $\{[Salomphen(^tBu)Ga\text{-}MeOH]_2Cl\}^+$.[3] Jordan reported the cationic gallium amidinate complexes $\{MeC(N^iPr)_2\}_2Ga_2Me_3^+$, $\{^tBuC(N^iPr)_2\}GaMe_2\text{-}\{^tBuC(N^iPr)_2\}GaMe^+$,

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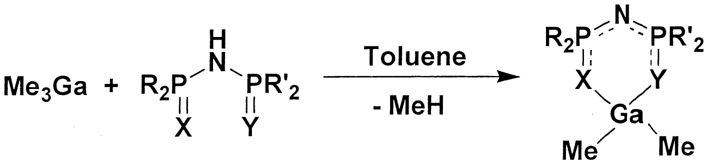
Address correspondence to Miguel-Ángel Muñoz-Hernández, Universidad Autónoma del Estado de Morelos, Centro de Investigaciones Químicas, Av. Universidad 1001, Col. Chamilpa, Cuernavaca, Morelos 62210, México. E-mail: mamund2@buzon.uaem.mx and $\{^tBuC(N^tBu)_2\}GaMe^+$ that are more stable than their aluminum counterparts.[4] Beachley recently reported the gallium β-diketonate cations $[Ga(acac)_2(thf)_2]^+$ (acac = 2,4-pentanedionato) and $[Ga(tmhd)_2(thf)_2]^+$ (tmhd = 2,2,6,6-tetramethylheptanedionato). In the solid state the cation with the acac ligand has a *trans* configuration. In solution it seems that the cations exist both in the *cis* and *trans* configurations.[5] On the search for new cationic organogallium complexes with potential applications to homogeneous catalysis we recently started a program to systematically explore the incorporation of iminodiphosphinechalchogenide ligands, $[R_2P(X)NP(Y)R'_2]^-$, on organogallium centers. Herein we report the synthesis and characterization of complexes with general formula $[Me_2Ga\{(XPR_2)(YPR'_2)N\}]$ that can be envisioned to be precursors to cationic species.

RESULTS AND DISCUSSION

The organometallic complexes of general formula $[Me_2Ga\{(XPR_2)(YPR'_2)N\}]$ (R, R′ = Ph, X, Y = O, (**1**); R, R′ = Ph, X, Y = S (**2**); R, R′ = Ph, X = O, Y = S (**3**); R = Me, R′ = Ph, X = O, Y = S (**4**)) were obtained by alkane elimination reactions from Me_3Ga and the ligands, LH, in toluene solutions (Scheme 1).



R, R' = Ph; X, Y = O (1)
R, R' = Ph; X, Y = S (2)
R, R' = Ph; X = O, Y = S (3)
R = Me, R' = Ph; X = O, Y = S (4)

SCHEME 1

Complexes **1–4** were characterized by physical (m.p.); chemical (C, H, analysis), and spectroscopic techniques (multinuclear NMR and IR). In addition, crystal structures of **1–4** were obtained by single crystal x-ray diffraction. The molecular structures of **1–4** reveal a metallacycle with a dimethylgallium fragment coordinated to the L^- ligand symetrically in a distorted tetrahedral environment (Figures 1–4).

The different conformations adopted by the six membered methallacycles, {P(X)NP(Y)}Ga, and the adequate ligand bite angles (Table I),

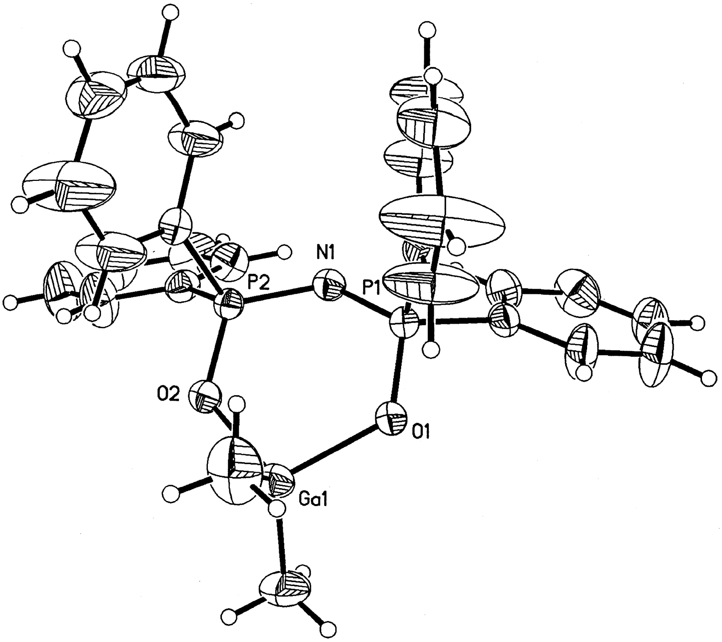


FIGURE 1 Molecular structure of **1**.

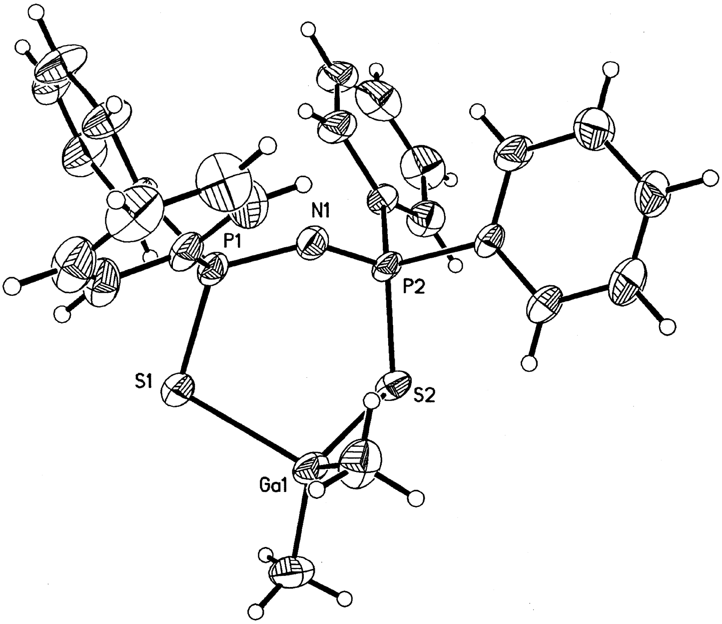


FIGURE 2 Molecular structure of **2**.

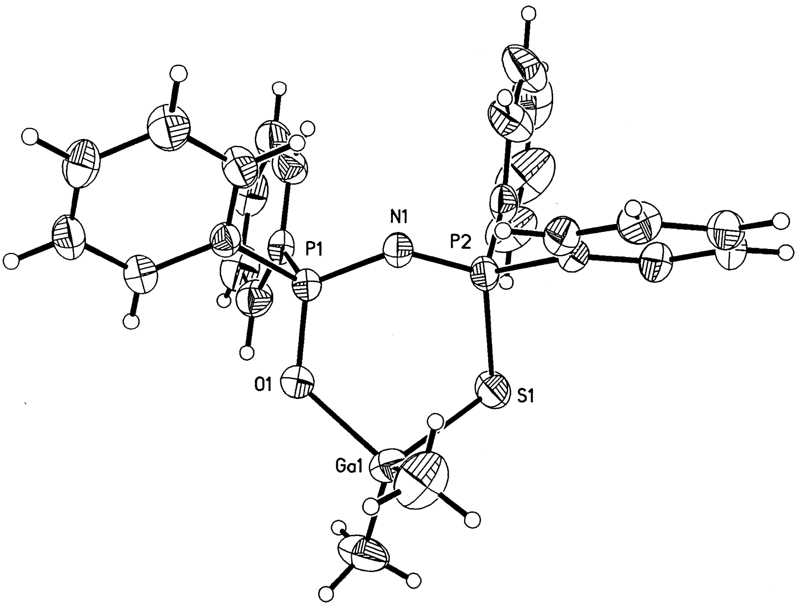


FIGURE 3 Molecular structure of **3**.

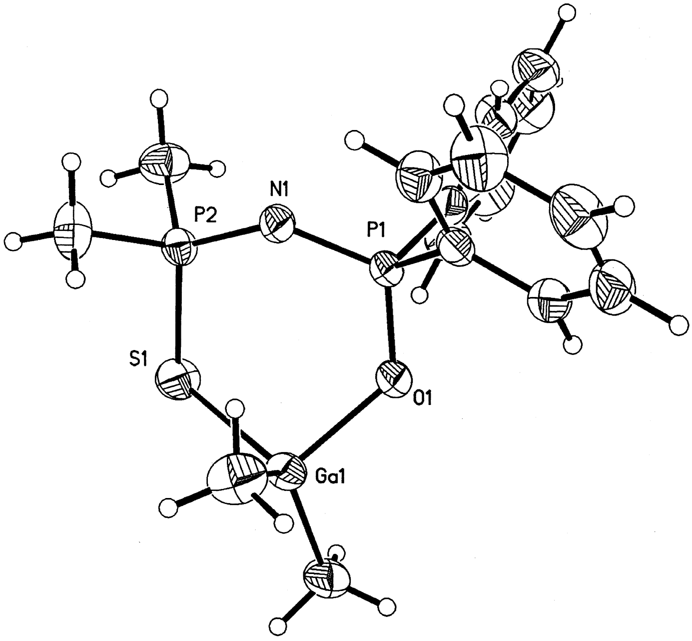
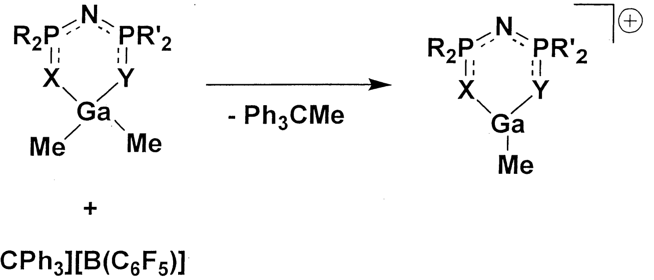


FIGURE 4 Molecular structure of **4**.

TABLE I Relevant Structural Features of Organogallium Metallacycles **1–4**

Complex	{P(X)NP(Y)}Ga conformation	Bite angle (°)	X–Y (Å)
1	Chair	97.87 (11)	O1-O2 2.944
2	Envelope	99.19 (5)	S1-S2 3.652
3	Twist boat	99.05 (9)	O1-S1 3.309
4	Boat	96.29 (7)	O1-S1 3.223

suggest that these complexes might stabilize cationic gallium compounds. Future work will be focused on this direction reacting complexes **1–4** and others with strong Lewis acids as $[CPh_3][B(C_6F_5)_4]$, which is one of the best reagents for the generation of cationic species (Scheme 2).



SCHEME 2

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