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INORGANIC RINGS WITH GALLIUM ORGANYLS AND IMINODIPHOSPHINECHALCHOGENIDES

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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; iminodiphosphinechalchogenides; organogallium complexes

The number of neutral organogallium complexes that incorporate iminodiphosphinechalchogenide 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 $[(Me_3Si)_2HCGa-\mu-\{(OPPh_2)_2N\}]_2.^2$ 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 exchage/redistribution reactions. Atwood has reported the Salen supported binuclear cation $\{[Salomphen(^tBu)Ga-MeOH]_2Cl\}^{+}.^3$ Jordan reported the cationic gallium amidinate complexes $\{MeC(N^iPr)_2\}_2Ga_2Me_3^+, \{^tBuC(N^iPr)_2\}_GaMe_2-\{^tBuC(N^iPr)_2\}_GaMe^+, \}$

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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).

$$Me_{3}Ga + R_{2}P \xrightarrow{\begin{array}{c} H \\ N \\ X \end{array}} PR'_{2} \xrightarrow{\begin{array}{c} Toluene \\ - MeH \end{array}} R_{2}P \xrightarrow{\begin{array}{c} N \\ Y \\ Me \end{array}} PR'_{2}$$

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),

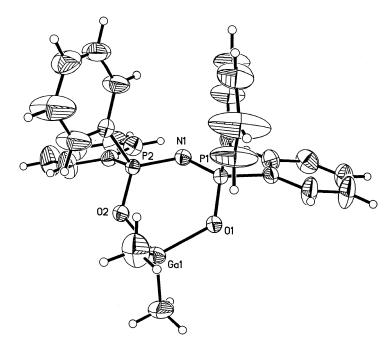


FIGURE 1 Molecular structure of 1.

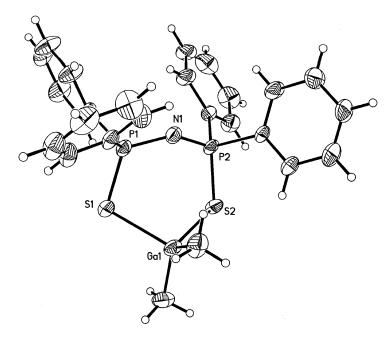


FIGURE 2 Molecular structure of 2.

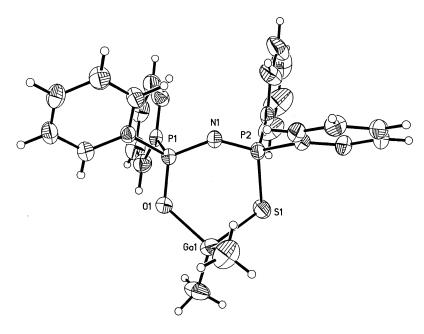


FIGURE 3 Molecular structure of 3.

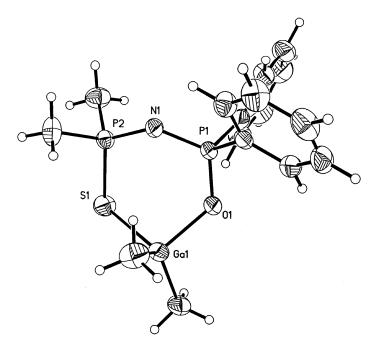


FIGURE 4 Molecular structure of 4.

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

TABLE I Relevant Structural Features of Organogallium Metallacycles 1–4

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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