

Polyhedron 21 (2002) 1117-1123



# Synthesis and structural characterization of complexes derived from treatment of gallium trichloride with 3,5-diphenylpyrazole

Zhengkun Yu, Andrey V. Korolev, Mary Jane Heeg, Charles H. Winter\*

Department of Chemistry, Wayne State University, Detroit, MI 48202, USA

Received 1 November 2001; accepted 25 February 2002

# Abstract

The adduct GaCl<sub>3</sub>(Ph<sub>2</sub>pzH) (Ph<sub>2</sub>pzH, 3,5-diphenylpyrazole) was synthesized in 96% yield upon treatment of equimolar amounts of gallium trichloride with Ph<sub>2</sub>pzH in toluene at room temperature. The tetrachlorogallate salt [Ph<sub>2</sub>pzH<sub>2</sub>]<sup>+</sup>GaCl<sub>4</sub><sup>-</sup> was obtained in 93% yield by treatment of a 2:1 stoichiometry of gallium trichloride and Ph<sub>2</sub>pzH at room temperature, followed by recrystallization from toluene/dichloromethane. The X-ray crystal structures of GaCl<sub>3</sub>(Ph<sub>2</sub>pzH) and [Ph<sub>2</sub>pzH<sub>2</sub>]<sup>+</sup>GaCl<sub>4</sub><sup>-</sup> were determined, and reveal weak hydrogen bond interactions between the nitrogen-bound hydrogen atoms and gallium-bound chlorine atoms. Examination of the formation of [Ph<sub>2</sub>pzH<sub>2</sub>]<sup>+</sup>GaCl<sub>4</sub><sup>-</sup> arises from GaCl<sub>3</sub>(Ph<sub>2</sub>pzH) and gallium trichloride (1.0 equiv.) revealed that the hydrogen chloride used to form [Ph<sub>2</sub>pzH<sub>2</sub>]<sup>+</sup>GaCl<sub>4</sub><sup>-</sup> was isolated in 82% yield upon treatment of GaCl<sub>3</sub>(Ph<sub>2</sub>pzH) and gallium trichloride (1.0 equiv.) in toluene/dichloromethane, a mixture of ditolylmethane isomers was isolated in 330% yield based upon gallium trichloride. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Gallium pyrazole complexes; Tetrachlorogallate salt; Gallium trichloride; 3,5-diphenylpyrazole

# 1. Introduction

The coordination chemistry of complexes containing pyrazolato ligands has been extensively studied [1-3]. However, most of this work has focused on transition metal and organolanthanide complexes. Recently, there has been considerable interest in pyrazolato complexes of the Group 13 elements [4-39]. Most of the recent efforts have related to aluminum complexes [4-19]. Pyrazolato complexes of gallium are well known [20-39], although complexes containing bulky alkyl or aryl substituents in the 3- and 5-positions of the pyrazolato ligand have not been reported. Gallium trichloride is a relatively weak Lewis acid [40], but is known to form adducts with many nitrogen donor ligands [41-44]. The development of new source compounds for use in the chemical vapor deposition of metal nitride films is a long-term interest in our group [45], and complexes of

gallium with nitrogen heterocyclic ligands may serve as precursors to GaN films [46]. Of relevance to the present work, GaCl-containing precursors have been recently demonstrated to be extremely selective growth species in epitaxial film growth of gallium-based semiconductor materials [47]. In view of our recent reports of aluminum pyrazolato complexes [17-19], we sought to explore the synthesis of new gallium pyrazolato complexes. Herein, we describe the synthesis and structural characterization of products that are obtained upon treatment of gallium trichloride with diphenylpyrazole. Depending on the reaction conditions, the complexes GaCl<sub>3</sub>(Ph<sub>2</sub>pzH) and  $[Ph_2pzH_2]^+GaCl_4^-$  are obtained. The nitrogen-bound hydrogen atoms in these complexes participate in hydrogen chlorine bonding to atoms.  $[Ph_2pzH_2]^+GaCl_4^-$  is obtained upon capture of hydrogen chloride by GaCl<sub>3</sub>(Ph<sub>2</sub>pzH), and it is demonstrated that the hydrogen chloride originates from gallium trichloride-catalyzed chloromethylation of toluene by dichloromethane. To our knowledge, this is the first example of a Friedel-Crafts reaction with dichloromethane that is promoted by any gallium complex. Dichloromethane is a poor electrophile in Friedel-

<sup>\*</sup> Corresponding author. Tel.: +1-313-577-5224; fax: +1-313-577-1377.

E-mail address: chw@chem.wayne.edu (C.H. Winter).

Crafts reactions, and gallium compounds are at best moderate strength Lewis acids that should not be capable of activating dichloromethane [40]. Accordingly, observation of the chloromethylation reaction described herein is surprising.

# 2. Results and discussion

#### 2.1. Synthesis and characterization

Treatment of gallium trichloride with 3,5-diphenylpyrazole (Ph<sub>2</sub>pzH) in a 1:1 molar ratio in toluene at 23 °C led to the formation of the adduct GaCl<sub>3</sub>(Ph<sub>2</sub>pzH) (1), which was isolated as colorless crystals in 96% yield after crystallization from toluene at -20 °C (Eq. (1)). A similar reaction was conducted in an NMR tube in chloroform-d. The <sup>1</sup>H NMR spectrum after 24 h indicated that 1 was the only product that formed. The structure of 1 was established by a combination of spectral and analytical data, and by an X-ray crystal structure determination as described below. The <sup>1</sup>H NMR spectrum of **1** in chloroform-dshowed the nitrogen-bound hydrogen resonance at  $\delta$ 11.19, consistent with the coordinated Ph<sub>2</sub>pzH ligand. The infrared spectrum of 1 revealed a sharp, strong nitrogen-hydrogen absorption at  $3350 \text{ cm}^{-1}$  and weak nitrogen-hydrogen absorptions between 3274 and 3151  $\mathrm{cm}^{-1}$ .

$$\begin{array}{c} \operatorname{GaCl}_{3} + \underbrace{\overset{Ph}{\underset{N=N}{\longrightarrow}} Ph}_{H} & \underbrace{\overset{toluene}{_{23}^{\circ}C, 20 h}}_{H} & \overset{Ph}{\underset{H}{\longrightarrow}} \overset{Ph}{\underset{N=N}{\longrightarrow}} Ph}_{H} & \underset{GaCl_{3}}{\overset{N=N}{\underset{96\%}{\longrightarrow}}} \end{array}$$
(1)

When 1 was prepared using a 1.00:1.00 molar ratio of gallium trichloride and diphenylpyrazole and was recrystallized from toluene, the <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra revealed chemically distinct resonances for the two types of phenyl groups present in 1. Such an observation indicates that cleavage of the galliumnitrogen bond in 1, followed by hydrogen atom transfer between the pyrazole nitrogen atoms and recoordination to gallium, is slow on the NMR timescale. In some preparations of 1, only one type of phenyl group was observed in <sup>1</sup>H and <sup>13</sup>C $\{^{1}H\}$  NMR spectra of the product. An NMR tube experiment with recrystallized 1 demonstrated that excess gallium trichloride (up to one full equivalent) had no effect on the <sup>1</sup>H and  ${}^{13}C{}^{1}H$ NMR spectra of 1 in benzene- $d_6$  at ambient temperature, and two chemically distinct phenyl groups were observed. However, addition of as little as 5% excess diphenylpyrazole to recrystallized 1 led to the observation of a single type of phenyl resonance in the <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra at ambient temperature, indicating rapid exchange of the phenyl sites on the NMR timescale. We suggest that the excess diphenylpyrazole

promotes the exchange through a low energy associative transition state containing a 5-coordinate gallium center.

As noted above, 1 could be prepared as a single pure product through careful control of the gallium trichloride:diphenylpyrazole stoichiometry, followed by crystallization from toluene. However, treatment of gallium trichloride with Ph<sub>2</sub>pzH in a 2:1 ratio in toluene for 0.5 h, followed by recrystallization from toluene/dichloromethane for 16 h at -20 °C, afforded 3,5-diphenylpyrazolium tetrachlorogallate (2, 93%) as a colorless crystalline solid (Eq. (2)). The structure of 2 was established by a combination of spectral and analytical data, and by an X-ray crystal structure determination as described below. The <sup>1</sup>H NMR spectrum of 2 in chloroform-d revealed the nitrogen-bound hydrogen resonance at  $\delta$  12.76. The infrared spectrum showed medium intensity nitrogen-hydrogen absorptions between 3255 and 3174  $\text{cm}^{-1}$ , and the electron impact mass spectrum revealed the cation  $[Ph_2pzH_2]^+$  with 100% intensity. The microanalysis was consistent with the formulation of 2. The formation of 2 from 1 and 1.0 equiv. of gallium trichloride was monitored by <sup>1</sup>H NMR in toluene- $d_8$  and a toluene- $d_8$ /dichloromethane mixture (1.0 ml/0.2 ml) at ambient temperature. After 20 h in toluene- $d_8$ , the only product present was 1. However, 1 converted to 2 completely over 16 h at ambient temperature when dissolved in 5:1 toluene- $d_8$ /dichloromethane. During this time, the reaction mixture turned deep red and colorless crystals were observed to deposit on the walls of the NMR tube. These observations are consistent with the preparation of 2 outlined above. In addition, new resonances were observed in the <sup>1</sup>H NMR spectrum, suggesting the formation of new organic products.

$$2 \operatorname{GaCl}_{3} + \underbrace{\begin{array}{c} \operatorname{Ph-} \\ \operatorname{N-N} \\ \operatorname{H} \end{array}}_{H} \operatorname{Ph-} \underbrace{\begin{array}{c} \operatorname{toluene}/\operatorname{CH}_{2}\operatorname{Cl}_{2} \\ -20 \ ^{\circ}\operatorname{C}, \ 16 \ h_{+} \end{array}}_{2 \ ^{\circ}\operatorname{C}, \ 16 \ h_{+}} \operatorname{Ph-} \\ \operatorname{Ph-} \\ \operatorname{N-N} \\ \operatorname{GaCl}_{4}^{-} + \operatorname{"HGaCl}_{4}^{-} \\ \operatorname{H} \\$$

An experiment was performed in which gallium trichloride (1.0 equiv.) was treated with 1 (1.0 equiv.) in 90:10 toluene/dichloromethane at 20 °C for 16 h. Workup as described in the experimental section afforded 2 in 82% yield. In addition, a brown-red oil was isolated that was identified as three ditolylmethane isomers 3-5 (88% of mixture) and eight or more isomers of (methylbenzyl)ditolylmethane 6 (12% of mixture) by GLC/MS and by analysis of the <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra of the mixture (Scheme 1). The <sup>1</sup>H NMR spectrum indicated an 84:12:4 mixture of p,p'-ditolylmethane (3), o,p'-ditolylmethane (4), and o,o'-ditolylmethane (5). This identification was based upon comparison with methyl and methylene <sup>1</sup>H NMR chemical shifts that have been previously reported for



Scheme 1. Chloromethylation of toluene.

these compounds [48,49]. The GLC/MS of 3–5 all showed a parent ion of mass/charge 196, with a base peak of 181 corresponding to loss of a methyl group from the parent ion. In addition to the ditolylmethane isomers, eight or more methylene resonances were observed between  $\delta$  3.82 and 3.87 in the <sup>1</sup>H NMR spectrum of the red-brown oil. GLC/MS revealed at least eight minor components exhibiting parent ions of mass/charge 300, with base peaks of 195 corresponding to loss of a methylbenzyl group from isomeric (methylbenzyl)ditolylmethanes. The (methylbenzyl)ditolylmethane mixture was not characterized further, due to the small amount and large number of isomers.

Observation of the mixture containing 3-6 suggests that the pathway outlined in Scheme 1 is operant in the formation of 2 under the conditions of excess gallium trichloride. Gallium trichloride-promoted chloromethylation of toluene can proceed to afford ortho- and paraisomers of chloromethyltoluene as well as 'HGaCl<sub>4</sub>'. As noted in the introduction, this is the first example of a Friedel-Crafts alkylation reaction of dichloromethane that is promoted by any gallium compound. Gallium trichloride is considered to be a moderate strength Lewis acid at best [40], and gallium compounds have been frequently used as Friedel-Crafts reaction catalysts with reactive alkyl halides to avoid side products that are observed with more reactive aluminum-based Lewis acids [50-53]. The direct chloromethylation of aromatic compounds with dichloromethane using aluminum halide catalysts has been well documented [40,54-56]. In addition, an aluminum trichloride-promoted chloromethylation of an aluminum-bound phenoxy group by dichloromethane to give non-aromatic product was described [57]. Several reports have described the chloromethylation of toluene using Lewis acid catalysis and various reactive chloromethyl cation equivalents such as methoxyacetyl chloride, bis(chloromethyl) ether, or chloromethyl methyl ether [58]. Once formed, the intermediate chloromethyl-substituted aromatic compounds rapidly react to form diarylmethane derivatives. In the present work, the intermediate chloromethyltoluene isomers react rapidly with toluene to afford the mixtures of 3-5. The yield of 3-5 based upon gallium trichloride is about 330%, thus indicating that the formation of 3-5 is catalyzed by a gallium species present in the reaction mixture. The first equivalent of hydrogen chloride generated during the chloromethylation reaction is trapped by 1 to form 2. Thereafter, the fate of the hydrogen chloride is less clear. 'HGaCl<sub>4</sub>' has been previously described as a diethyl ether adduct [59]. However, the strongest bases remaining after complete formation of 2 are toluene and 3-6. It is possible that the deep red coloration of the reaction solution corresponds to the formation of arenium cations, which are known to be deeply colored in solution [60–63].

The central discovery described herein is the Friedel-Crafts chloromethylation of toluene promoted by 1, 2, or some other gallium species present in solution. The fact that gallium compounds can promote rapid Friedel-Crafts alkylation reactions using a poor electrophile such as dichloromethane is surprising in view of the extensive literature in this area [40]. The high solubility of 1 in toluene may be the reason why the chloromethylation reaction proceeds at such a rapid rate. In the present work, the Friedel-Crafts alkylation reaction manifested itself initially through the unexpected formation of 2 when 1 was recrystallized from toluene/dichloromethane mixtures. We expect that similar Friedel-Crafts reactions will occur in systems that contain what are presumed to be weak Lewis acids and poorly electrophilic alkyl halides.

# 2.2. Molecular structures of 1 and 2

The solid-state structures of 1 and 2 were determined by X-ray crystallography. Perspective views are shown in Figs. 1 and 2, crystallographic data are provided in Table 1, and selected bond lengths and angles are listed in Tables 2 and 3.

Complex 1 crystallizes as a monomer with distorted tetrahedral geometry about the gallium center. The Ga-N(1) bond distance is 1.971(2) Å. The nitrogen-hydrogen bond length is 0.759(4) Å. The nitrogen-bound hydrogen participates in intramolecular hydrogen bond-



Fig. 1. Perspective view of  $GaCl_3(Ph_2pzH)$  (1) with thermal ellipsoids at the 50% probability level.



Fig. 2. Perspective view of  $[Ph_2pzH_2]^+GaCl_4^-$  (2) with thermal ellipsoids at the 50% probability level.

Table 1					
Crystallographic	data	for	1	and	2

Formula	$C_{15}H_{12}Cl_{3}GaN_{2}$ (1)	$C_{15}H_{13}Cl_4GaN_2$ (2)
Formula weight	396.34	432.79
Space group	$P2_1/n$	$P2_1/n$
a(Å)	10.461(7)	11.8508(7)
b(Å)	12.882(9)	7.3609(4)
<i>C</i> (Å)	11.913(8)	21.0097(12)
$\beta(^{\circ})$	92.646(18)	96.2560(10)
V (Å <sup>3</sup> )	1603.8(19)	1821.8(2)
Ζ	2	4
T (K)	295 (2)	295(2)
λ (Å)	0.71073	0.71073
$\rho_{\text{calc.}}(\text{g cm}^{-3})$	1.641	1.578
$\mu  ({\rm mm}^{-1})$	2.208	2.093
R(F) (%)	3.23	2.96
$R_{\rm w}(F)$ (%)	7.16	7.42

$$R(F) = \Sigma ||F_{o}| - |F_{c}|| / \Sigma |F_{o}|. R_{w}(F)^{2} = [\Sigma w (F_{o}^{2} - F_{c}^{2})^{2} / \Sigma w (F_{o}^{2})^{2}]^{1/2}.$$

Table 2 Selected bond lengths (Å) and angles (°) for 1

Bond lengths			
Ga-N(1)	1.971(2)	Ga-Cl(1)	2.1448(13)
Ga-Cl(2)	2.1589(15)	Ga-Cl(3)	2.1568(17)
N(1) - N(2)	1.365(5)	N(1)-C(1)	1.348(3)
N(2) - C(3)	1.347(3)	N(2)-H	0.759(3)
$(N2)H \cdot \cdot \cdot Cl(3)$	2.625(4)		
Bond angles			
Cl(1)-Ga-Cl(2)	110.85(5)	Cl(1)-Ga-Cl(3)	112.28(6)
Cl(2)-Ga-Cl(3)	110.85(5)	N(1)-Ga-Cl(1)	109.19(8)
N(1)-Ga-Cl(2)	111.79(9)	N(1)-Ga-Cl(3)	101.56(7)
Ga - N(1) - N(2)	116.74(17)	Ga - N(1) - C(1)	135.98(18)
N(2)-H-Cl(3)	127.96(3)	., .,	

ing to Cl(3), with a hydrogen-chlorine distance of 2.625(4) Å. The N(2)–H(N2)–Cl(3) angle is 127.96(3)°. There are no significant intermolecular hydrogen bonds. The gallium–chlorine bond distances range from 2.1448(13)–2.1589(15) Å. All three gallium–chlorine bond lengths are identical within the precision of the structure determination, suggesting that the intramolecular hydrogen bond to Cl(3) is weak. The N(1)–Ga–Cl(3) angle (101.56(7)°) is smaller than the related values

Table 3 Selected bond lengths (Å) and angles (°) for **2** 

Bond lengths			
Ga-Cl(1)	2.1718(6)	Ga-Cl(2)	2.2032(6)
Ga-Cl(3)	2.1607(7)	Ga-Cl(4)	2.1521(7)
N(1) - N(2)	1.345(3)	N(1)-C(1)	1.339(3)
N(2) - C(3)	1.338(3)	H(N1) - N(1)	0.937(3)
H(N2) - N(2)	0.827(3)	H(N1)-Cl(1)	2.533(3)
H(N2)-Cl(2')	2.663(3)	H(N2)-Cl(2'')	2.573(3)
Bond angles			
Cl(1)-Ga-Cl(2)	103.90(3)	Cl(1)-Ga-Cl(3)	112.68(3)
Cl(1)-Ga-Cl(4)	111.53(3)	Cl(2)-Ga-Cl(3)	110.15(3)
Cl(2)-Ga-Cl(4)	110.41(3)	Cl(3)-Ga-Cl(4)	108.15(3)
N(1)-N(2)-C(3)	109.5(2)	N(2)-N(1)-C(1)	109.7(2)
N(1)-H(N1)-Cl(1)	132.88(3)	N(2)-H(N2)-Cl(2')	165.65(3)
N(1)-H(N1)-Cl(2')	127.68(3)		

for N(1)–Ga–Cl(1) (109.19(8)°) and N(1)–Ga–Cl(2) (111.79(9)°). This distortion may arise from the weak hydrogen bond associated with Cl(3).

Complex 2 crystallizes with a diphenylpyrazolium ion that contains several different hydrogen bonds to the tetrachlorogallate ion. The geometry about the gallium atom is distorted tetrahedral. The gallium-chlorine bond distances range from 2.1521(7) to 2.2032(6) Å, and are slightly longer than the range found in 1 due to the reduced Lewis acidity of the gallium center in the tetrachlorogallate ion. The chlorine-gallium-chlorine angles range between  $103.90(3)^{\circ}$  and  $112.68(3)^{\circ}$ . The nitrogen-hydrogen bond lengths are 0.937(5) and 0.827(5) Å. The nitrogen-bound hydrogen atoms are hydrogen-bonded to chlorine atoms of the tetrachlorogallate ion with bond lengths of 2.533(3) $((N1)H \cdot \cdot \cdot Cl(1)),$ 2.663(5)  $((N1)H \cdot \cdot \cdot Cl(2')),$ and 2.573(4) Å ((N2)H···Cl(2'')). The nitrogen-hydrogenchlorine angles associated with the hydrogen bonds are 132.88(3)°, 127.68(3)°, and 165.65(3)°, respectively. The nitrogen-hydrogen bond lengths are similar to the value found in 1. Interestingly, the two chlorine atoms involved in weak hydrogen bonding (Cl(1), Cl(2)) exhibit slightly longer gallium-chlorine bond lengths than the two chlorine atoms that are not involved in hydrogen bonding (Cl(3), Cl(4)). These bond length differences, while small, suggest slightly stronger hydrogen bonding in 2, compared with 1. Stronger hydrogen bonding in 2 can be rationalized on the basis of more electrophilic hydrogen atoms and more electron rich chlorine atoms due to the presence of ions in the solid.

The gallium–nitrogen bond length in **1** is very similar to values ranging from 1.97 to 2.00 Å that have been documented in gallium–pyrazolate complexes [20–39]. The X-ray crystal structures of several pyrazolium salts of the formula [t-Bu<sub>2</sub>pzH]<sup>+</sup>X<sup>-</sup> (X = Cl, Br) have been reported [64,65]. These compounds form distinct dimeric aggregates featuring ten-membered X<sub>2</sub>H<sub>4</sub>N<sub>4</sub> rings in the solid state that are held together by strong, linear N–H···X hydrogen bonding. Ten-membered rings are present in 2, but these rings are present as part of an extended hydrogen bonded network, as opposed to the dimeric units in the pyrazolium halide salts. In 3,5-di*tert*-butylpyrazolium chloride [64,65], the nitrogenchlorine distance containing the hydrogen bond was 3.057(2) Å, the H···Cl distance was 2.12(3) Å, and the nitrogen-hydrogen-chlorine angle was  $175(3)^{\circ}$ . By contrast, in 2 the related values were 3.244(2)-3.380(2)Å, 2.533(4) - 2.663(4) Å, and  $127.68(5)^{\circ} - 165.65(5)^{\circ}$ . These values for 2 suggest much weaker hydrogen bonding than is present in 3,5-di-tert-butylpyrazolium chloride. The order of hydrogen bonding strength is consistent with the lone pairs of electrons on GaCl<sub>4</sub><sup>-</sup> being much less basic than those of chloride ion. Similar weak  $E-H \cdot \cdot \cdot X$  hydrogen bonding (E = O, N; X = halogen) is well established in the solid state structures of other metal halide complexes containing EH fragments within the crystal [66].

# 3. Experimental

#### 3.1. General considerations

All manipulations were performed under argon using either drybox or Schlenk-line techniques. Gallium trichloride was purchased from Strem Chemical Company. Ph<sub>2</sub>pzH was prepared using a reported procedure [67]. <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra were obtained at 500 or 300 and 125 or 75 MHz, respectively, in the indicated solvents. Infrared spectra were recorded using KBr discs. Mass spectra were obtained on a Kratos MS-50 spectrometer in the electron impact mode or on a Hewlett–Packard Model 5980 GLC/MS instrument. Elemental analyses were performed by Midwest Microlab, Indianapolis, IN. Melting points are uncorrected.

#### 3.2. Synthesis of $GaCl_3(Ph_2pzH)$ (1)

A 100 ml Schlenk flask was charged with a stir bar, gallium trichloride (0.42 g, 2.4 mmol), and diphenylpyrazole (0.52 g, 2.4 mmol). Toluene (30 ml) was added by syringe to form a colorless solution. This mixture was stirred at ambient temperature for 24 h. The volatile components were removed under reduced pressure to afford spectroscopically pure 1 as a white powder (0.91 g, 96%). X-ray and analytical quality crystals were obtained by recrystallization from toluene at -20 °C: m.p. 157–158 °C; IR (KBr, cm<sup>-1</sup>) 3350 (s), 3274 (w), 3151 (w), 1610 (m), 1569 (s), 1273 (m), 1182 (m), 1108 (m), 1085 (m), 990 (m), 821 (w), 761 (s), 705 (w), 703 (m), 684 (s), 563 (s); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 23 °C,  $\delta$ ) 11.19 (br. s, 1 H, NH), 7.77 (m, 2H, Ph CH), 7.65, (m, 2 H, Ph CH), 7.57 (m, 3 H, Ph CH), 7.51 (m, 3 H, Ph CH), 6.91 (d, J = 3.0 Hz, 1 H, pyrazole CH);  ${}^{13}C{}^{1}H$  NMR (CDCl<sub>3</sub>, 23 °C, ppm) 156.33 (s, CPh), 147.39 (s, CPh), 131.64 (s, *p*-*C*H of Ph), 130.92 (s, *p*-*C*H of Ph), 129.82 (s, *m*-*C*H of Ph), 129.00 (s, *m*-*C*H of Ph), 128.85 (s, *o*-*C*H of Ph), 127.86 (s, *ipso*-*C* of Ph), 126.34 (s, *o*-*C*H of Ph), 125.39 (s, *ipso*-*C* of Ph), 105.79 (s, *C*H of pyrazolato); MS (EI, 70 eV) 220 ([Ph<sub>2</sub>pzH]<sup>+</sup>, 100%).

*Anal.* Calc. for C<sub>15</sub>H<sub>12</sub>Cl<sub>3</sub>GaN<sub>2</sub>: C, 45.46; H, 3.05; N, 7.07. Found: C, 45.68; H, 3.13; N, 6.99%.

# 3.3. Synthesis of $[Ph_2pzH_2]^+$ GaCl<sub>4</sub><sup>-</sup> (2)

A 100 ml Schlenk flask, equipped with a stir bar and a rubber septum, was charged with 1 (0.26 g, 0.66 mmol), gallium trichloride (0.12 g, 0.66 mmol), and toluene (10 ml). To this stirred solution was added dichloromethane (0.5 ml). The solution color changed immediately to yellow and deepened to dark red after 0.5 h. The reaction solution was placed in a -20 °C freezer for 16 h. Yellow crystals formed during this time, and a dark red oil separated. The crystals were collected on a medium glass frit and were washed with 1:1 toluene/ pentane (18 ml) followed by pentane (18 ml). Vacuum drying afforded white crystals. The washings were combined, producing more white crystals. These crystals were collected on a medium glass frit, washed with pentane (18 ml), and dried under vacuum. The crystals were combined to afford 2 as a colorless solid (0.26 g, 93%): m.p. 135-136 °C; IR (KBr, cm<sup>-1</sup>) 3255 (m), 3219 (m), 3191 (m), 3174 (m), 1613 (m), 1590 (m), 1262 (w), 1227 (w), 1208 (w), 1188 (w), 1162 (w), 1095 (w), 1070 (w), 1053 (w), 1019 (w), 950 (w), 918 (w), 835 (w),765 (s), 704 (w), 691 (w), 681 (m); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 23 °C, δ) 12.76 (s, 2H, NH), 7.75 (m, 4H, Ph CH), 7.62 (m, 6H, Ph CH), 7.15 (t,  ${}^{4}J_{HH} = 3.0$  Hz, 1H, pyrazolato CH); <sup>13</sup>C{1H} NMR (CDCl<sub>3</sub>, 23 °C, ppm) 149.60 (s, pyrazolato CPh), 132.94 (s, p-CH of Ph), 130.21 (s, m-CH of Ph), 126.85 (s, o-CH of Ph), 123.95 (s, ipso-C of Ph), 102.02 (s, CH of pyrazolato); MS (EI, 70 eV) 221  $([Ph_2pzH_2]^+, 100\%).$ 

*Anal.* Calc. for C<sub>15</sub>H<sub>13</sub>Cl<sub>4</sub>GaN<sub>2</sub>: C, 41.62; H, 3.03; N, 6.47. Found: C, 41.49; H, 3.07; N, 6.55%.

# 3.4. Isolation of ditolylmethane isomers upon treatment of **1** with excess gallium trichloride

A Schlenk flask was charged with a stir bar, 1 (0.26 g, 0.66 mmol) and gallium trichloride (0.12 g, 0.66 mmol). Toluene (10 ml) was added to the flask to produce a colorless solution. Immediately thereafter, dichloromethane (1 ml) was added. The solution color changed to yellow and deepened to medium red within 0.5 h. The solution was stirred at ambient temperature for 6 h, and the volatiles were removed under reduced pressure to leave a dark red oil. Hexane (20 ml) was added to this oil to afford a pale yellow solution and colorless crystals in the dark red oil. This mixture was kept at ambient temperature for 16 h without stirring. The solution was

decanted from the oily residue, and the oily residue was washed again with hexane (6 ml). The hexane extracts were combined and the volatile components were removed under reduced pressure, leaving a red oil (0.41 g) that was identified as a mixture of **3–6** by GLC MS and by correlation of the <sup>1</sup>H NMR spectrum with previously reported values for ditolylmethane isomers. For further data, see below and in the text. The hexane-insoluble crystals were collected on a medium glass frit and then washed with 1:1 toluene/ hexane (18 ml) and hexane (18 ml). Drying under vacuum for 1 h afforded spectroscopically pure 2 as a pale brown crystalline solid (0.23 g, 82%). The identity of 2 was confirmed by comparison of its <sup>1</sup>H and  $^{13}C{^{1}H}$  NMR spectra with those of authentic material described above.

Data for the ditolylmethane mixture:

*p*,*p*'-ditolylmethane (**3**, 84%): partial <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$ ) 3.88 (s, C*H*<sub>2</sub>), 2.29 (s, 2C*H*<sub>3</sub>) [lit.<sup>28</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$ ) 3.89 (s, C*H*<sub>2</sub>), 2.23 (s, 2C*H*<sub>3</sub>)]; GLC/MS 196 (*M*<sup>+</sup>, 57%), 181 (*M*<sup>+</sup> – CH<sub>3</sub>, 100%). *o*,*p*'-ditolylmethane (**4**, 12%): partial <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$ ) 3.93 (s, C*H*<sub>2</sub>), 2.28 (s, C*H*<sub>3</sub>), 2.22 (s, C*H*<sub>3</sub>) [lit.<sup>27</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$ ) 3.93 (s, C*H*<sub>2</sub>), 2.30 (s, C*H*<sub>3</sub>), 2.23 (s, C*H*<sub>3</sub>)]; GLC/MS 196 (*M*<sup>+</sup>, 63%), 181 (*M*<sup>+</sup> – CH<sub>3</sub>, 100%). *o*,*o*'-ditolylmethane (**5**, 4%): partial <sup>1</sup>H NMR

 $(CDCl_3, \delta)$  3.91 (s,  $CH_2$ ), 2.28 (s,  $2CH_3$ ) [lit.<sup>28</sup> <sup>1</sup>H NMR (CDCl\_3,  $\delta$ ) 3.91 (s,  $CH_2$ ), 2.26 (s,  $2CH_3$ )]; GLC/MS 196 ( $M^+$ , 61%), 181 ( $M^+$  – CH<sub>3</sub>, 100%).

#### 3.5. X-ray structure determinations of 1 and 2

Single crystals of 1 and 2 were mounted in thin-walled capillaries under a nitrogen atmosphere. Crystallographic data were collected at room temperature (295 K) on a Siemens–Bruker automated P4/CCD diffractometer with monochromated Mo K $\alpha$  radiation. Frames (1650) were collected at 10 s and integrated with the manufacturer's SMART and SAINT software. Absorption corrections were applied with Sheldrick SADABS program and the structure was solved and refined using programs of SHELXL-97 [68]. Hydrogen atoms were placed in observed and calculated positions.

# 4. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, quoting No. 173005 for **1** and No. 173006 for **2**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1233-336033; email: deposit@ccdc.cam.ac.uk or www: http:// www.ccdc.cam.ac.uk).

# Acknowledgements

We are grateful to the National Science Foundation (Grant No. CHE-9807269) and the Defense Advanced Research Projects Agency for support of this research.

#### References

- [1] A.P. Sadimenko, S.S. Basson, Coord. Chem. Rev. 147 (1996) 247.
- [2] G. La Monica, G.A. Ardizzoia, Prog. Inorg. Chem. 46 (1997) 151.
- [3] J.E. Cosgriff, G.B. Deacon, Angew. Chem., Int. Ed. Engl. 37 (1998) 286.
- [4] G.B. Deacon, E.E. Delbridge, C.M. Forsyth, P.C. Junk, B.W. Skelton, A.H. White, Aust. J. Chem. 52 (1999) 733.
- [5] C.C. Chang, T.Y. Her, F.Y. Hsieh, C.Y. Yang, M.Y. Chiang, G.H. Lee, Y. Wang, S.M. Peng, J. Chin. Chem. Soc. (Taipei) 41 (1994) 783.
- [6] A. Arduini, A. Storr, J. Chem. Soc., Dalton Trans., (1974) 203.
- [7] H.-D. Hausen, K. Locke, J. Weidlein, J. Organomet. Chem. 429 (1992) C27.
- [8] J. Lewinski, J. Zhchara, P. Gos, E. Grabska, T. Kopec, I. Madura, W. Marciniak, I. Prowotorow, Chem. Eur. J. 6 (2000) 3215.
- [9] A. Looney, G. Parkin, A.L. Rheingold, Inorg. Chem. 30 (1991) 3099.
- [10] A. Looney, G. Parkin, Polyhedron 9 (1990) 265.
- [11] M.H. Chisholm, N.W. Eilerts, J.C. Huffman, Inorg. Chem. 35 (1996) 445.
- [12] D.J. Darensbourg, E.L. Maynard, M.W. Holtcamp, K.K. Klausmeter, J.H. Reibenspies, Inorg. Chem. 35 (1996) 2682.
- [13] W. Zheng, N. Mösch-Zanetti, H.W. Roesky, M. Hewitt, F. Cimpoesu, T.R. Schneider, A. Stasch, J. Prust, Angew. Chem., Int. Ed. Engl. 39 (2000) 3099.
- [14] W. Zheng, N. Mösch-Zanetti, H.W. Roesky, M. Noltemeyer, M. Hewitt, H.-G. Schmidt, T.R. Schneider, Angew. Chem., Int. Ed. Engl. 39 (2000) 4276.
- [15] W. Zheng, H.W. Roesky, M. Noltemeyer, Organometallics 20 (2001) 1033.
- [16] W. Zheng, H. Hohmeister, N. Mösch-Zanetti, H.W. Roesky, M. Noltemeyer, H.-G. Schmidt, Inorg. Chem. 40 (2001) 2363.
- [17] Z.K. Yu, J.M. Wittbrodt, M.J. Heeg, H.B. Schlegel, C.H. Winter, J. Am. Chem. Soc. 122 (2000) 9338.
- [18] Z.K. Yu, M.J. Heeg, C.H. Winter, Chem. Commun., (2001) 353.
- [19] Z.K. Yu, J.M. Wittbrodt, A. Xia, M.J. Heeg, H.B. Schlegel, C.H. Winter, Organometallics 20 (2000) 4301.
- [20] D.F. Rendle, A. Storr, J. Trotter, J. Chem. Soc., Dalton Trans. (1973) 2252.
- [21] D.F. Rendle, A. Storr, J. Trotter, Can. J. Chem. 53 (1975) 2944.
- [22] D.F. Rendle, A. Storr, J. Trotter, J. Chem. Soc., Dalton Trans. (1975) 176.
- [23] D.J. Patmore, D.F. Rendle, A. Storr, J. Trotter, J. Chem. Soc., Dalton Trans. (1975) 718.
- [24] D.F. Rendle, A. Storr, J. Trotter, Can. J. Chem. 53 (1975) 2930.
- [25] K.S. Chong, S.J. Rettig, A. Storr, J. Trotter, Can. J. Chem. 56 (1978) 1212.
- [26] K.R. Breakell, S.J. Rettig, D.L. Singbeil, A. Storr, J. Trotter, Can. J. Chem. 56 (1978) 2099.
- [27] K.S. Chong, S.J. Rettig, A. Storr, J. Trotter, Can. J. Chem. 57 (1978) 1335.

- [28] K.R. Breakell, S.J. Rettig, A. Storr, J. Trotter, Can. J. Chem. 57 (1979) 139.
- [29] K.S. Chong, S.J. Rettig, A. Storr, J. Trotter, Can. J. Chem. 58 (1980) 1080.
- [30] K.S. Chong, S.J. Rettig, A. Storr, J. Trotter, Can. J. Chem. 58 (1978) 1091.
- [31] S.J. Rettig, A. Storr, J. Trotter, Can. J. Chem. 59 (1981) 2391.
- [32] B.M. Louie, A. Storr, J. Trotter, Can. J. Chem. 62 (1984) 633.
- [33] B.M. Louie, A. Storr, J. Trotter, Can. J. Chem. 63 (1985) 3019.
- [34] E.C. Onyiriuka, S.J. Rettig, A. Storr, Can. J. Chem. 64 (1986) 321.
- [35] G.A. Banta, B.M. Louie, E.C. Onyiriuka, S.J. Rettig, A. Storr, Can. J. Chem. 64 (1986) 373.
- [36] D.L. Reger, S.J. Knox, L. Lebioda, Inorg. Chem. 28 (1989) 3092.
- [37] D.L. Reger, S.J. Knox, L. Lebioda, Organometallics 9 (1990) 2218.
- [38] F. Kratz, B. Nuber, J. Weiss, B.K. Keppler, Polyhedron 11 (1992) 487.
- [39] P. Hodge, B. Piggott, Chem. Commun. (1998) 1933.
- [40] G.A. Olah (Ed.), Friedel-Crafts and Related Reactions, vol. I–IV, Wiley Interscience, New York, 1963, p. 1965.
- [41] D. Pahari, V.K. Jain, Main Group Metal Chem. 20 (1997) 691.
- [42] N. Burford, T.S. Cameron, D.J. LeBlanc, P. Losier, S. Sereda, G. Wu, Organometallics 16 (1997) 4712.
- [43] S. Schulz, L. Martinez, J.L. Ross, Adv. Mater. Opt. Electron. 6 (1996) 185.
- [44] W.R. Nutt, J.S. Blanton, A.M. Boccanfuso, L.A. Silks, A.R. Garber, J.D. Odom, Inorg. Chem. 30 (1991) 4136.
- [45] For leading references, see: C.H. Winter, Aldrichimica Acta 33 (2000) 3.
- [46] M.A. Munoz-Hernandez, M.S. Hill, D.A. Atwood, Polyhedron 17 (1998) 2237.
- [47] T.F. Kuech, Semicond. Sci. Technol. 8 (1993) 967.
- [48] D. Guijarro, B. Mancheno, M. Yus, Tetrahedron 49 (1993) 1327.
  [49] I.O. Shapiro, M. Nir, R.E. Hoffman, M. Rabinovitz, J. Chem.
- Soc., Perkin Trans. 2 (1994) 1519.
- [50] C.R. Smoot, H.C. Brown, J. Am. Chem. Soc. 78 (1956) 6245.

- [51] C.R. Smoot, H.C. Brown, J. Am. Chem. Soc. 78 (1956) 6249.
- [52] H. Ulich, A. Keutmann, A. Geierhaas, Z. Elektrochem. 49 (1943) 292.
- [53] H. Ulich, Angew. Chem. 55 (1942) 37.
- [54] J. Lavaux, M. Lombard, Bull. Soc. Chim. Fr. (1910) 913-915.
- [55] H. Wang, L.D. Kispert, H. Sang, J. Chem. Soc., Perkin Trans. II (1989) 1463.
- [56] J.H. Clark, K. Martin, A.J. Teasdale, S.J. Barlow, J. Chem. Soc., Chem. Commun. (1995) 2037.
- [57] M.D. Healy, J.W. Ziller, A.R. Barron, Organometallics 11 (1992) 3041.
- [58] For leading references, see: F.P. DeHaan, M. Djaputra, M.W. Grinstaff, C.R. Kaufman, J.C. Keithly, A. Kumar, M.K. Kuwayama, K.D. Macknet, J. Na, B.R. Patel, M.J. Pinkerton, J.H. Tidwell, R.M. Villahermosa, J. Org. Chem. 62 (1997) 2694.
- [59] R.J.H. Clark, B. Crociani, A. Wasserman, J. Chem. Soc. (A) (1970) 2458.
- [60] C.A. Reed, N.A.P. Fackler, K.-C. Kim, D. Stasko, D.R. Evans, P.D.W. Boyd, C.E.F. Rickard, J. Am. Chem. Soc. 121 (1999) 6314.
- [61] R. Rathore, S.H. Loyd, J.K. Kochi, J. Am. Chem. Soc. 116 (1994) 8414.
- [62] G.A. Olah, R.H. Schlosberg, D.P. Kelly, G.D. Mateescu, J. Am. Chem. Soc. 92 (1970) 2546.
- [63] H.H. Perkampus, E. Baumgarten, Angew. Chem., Int. Ed. Engl. 3 (1964) 776.
- [64] C. Fernandez-Castano, C. Foces-Foces, N. Jagerovic, J. Elguero, J. Mol. Struc. 355 (1995) 265.
- [65] C. Foces-Foces, L. Infantes, R.M. Claramunt, C. Lopez, N. Jagerovic, J. Elguero, J. Mol. Struc. 415 (1997) 81.
- [66] For leading references, see: G. Aullon, D. Bellamy, L. Brammer, E.A. Bruton, A.G. Orpen, Chem. Commun. (1998) 653.
- [67] J. Elguero, E. Gonzalez, R. Jacquier, Bull. Soc. Chim. Fr. (1968) 707.
- [68] G. Sheldrick, SHELX-97, Institut f
  ür Anorg. Chemie, Tammannstrasse 4, D-37077 G
  öttingen, Germany.