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## **Chiral Multichromic Single Crystals for Optical Devices**

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Prepared by  
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## **LDRD Final Report on Chiral Multichromic Single Crystals for Optical Devices (LDRD 99406)**

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### **Abstract**

This report summarizes our findings during the study of a novel system that yields multi-colored materials as products. This system is quite unusual as it leads to multi-chromic behavior in single crystals, where one would expect that only a single color would exist. We have speculated that these novel solids might play a role in materials applications such as non-linear optics, liquid crystal displays, piezoelectric devices, and other similar applications. The system examined consisted of a main-group alkyl compound (a *p* block element such as gallium or aluminum) complexed with various organic di-imines. The di-imines had substituents of two types – either alkyl or aromatic groups attached to the nitrogen atoms. We observed that single crystals, characterized by X-ray crystallography, were obtained in most cases. Our research during January–July, 2006, was geared towards understanding the factors leading to the multi-chromic nature of the complexes. The main possibilities put forth initially considered a) the chiral nature of the main group metal, b) possible reduction of the metal to a lower-valent, radical state, c) the nature of the ligand(s) attached to the main group metal, and d) possible degradation products of the ligand leading to highly-colored products. The work carried out indicates that the most likely explanation considered involves degradation of the aromatic ligands (a combination of c) and d), as the experiments performed can clearly rule out a) and b).



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# Chiral Multichromic Single Crystals for Optical Devices

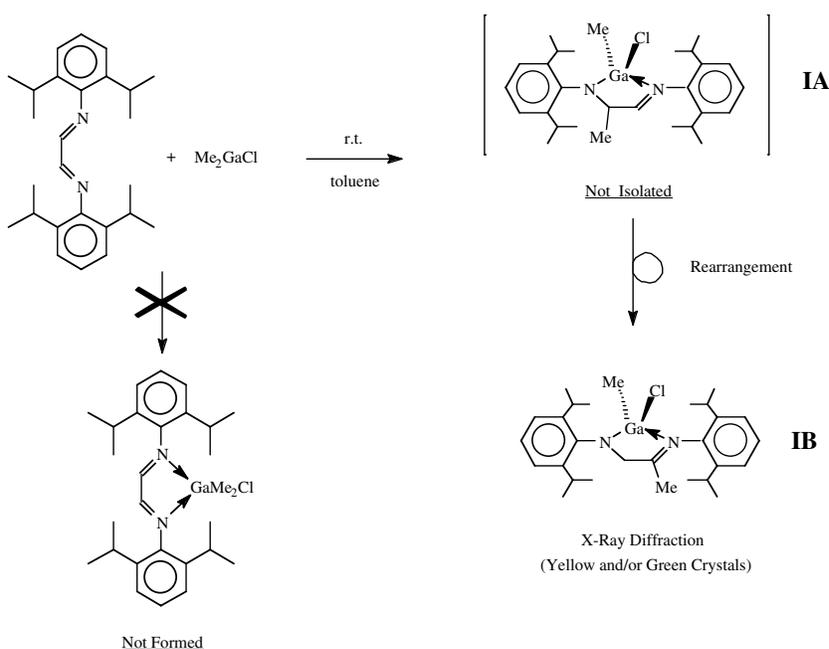
## General Introduction and Background

An unprecedented class of chiral multichromic (di-colored) crystals have been investigated. These novel materials were discovered approximately 10 years ago by Kemp (R.A. Kemp and L. Chen, unpublished results, Union Carbide Corporation). The individual crystals that are prepared are crystallographically identical, and can be grown colorless, yellow, or green. It is also shown that for the first time to our knowledge that the crystals can be prepared multichromic *within the same single crystal*. These materials have the previously unknown property of simultaneously being multicolored as well as existing as individual single crystals. The crystals formed are not small – rather they are near 2 mm in length. Multicolored crystals are known in the literature; however, there are significant differences between previously known compounds and these new complexes. For example, many minerals are used for gemstones due to their polychromatic nature (Nassua, *Amer. Min.*, **63**, 219, 1978). These minerals may have crystalline components within them, and slight variations in chemical composition (metal dopants) may lead to the multichromic nature of the gems, among other reasons. Some of the gems, such as opals, are amorphous. Other materials change colors upon a exposure to light (photochromic), when a small electrical charge is passed through the material (electrochromic), or upon change in temperature (thermochromic). As well, there are materials that scatter light differently depending on which face is exposed to the viewer. There is a recent increase in interest in crystals with selectively dyed faces, where organic dyes are deliberately added that selectively adsorb on certain crystal faces (Kahr, *Chem. Rev.*, **101**, 893, 2001). However, in none of these cases do the multicolored crystalline materials exist as individual single crystals.

Recently, chiral molecules have been widely studied for nonlinear optical applications because they are inherently noncentrosymmetric, and thus possess potential for frequency-doubling of laser radiation. Such second-harmonic generation (SHG), in which incident light of frequency  $\omega$  is doubled to  $2\omega$ , (e.g.  $\lambda = 1.06 \mu\text{m}$  to 523 nm) is critical for optical frequency through THz spectroscopy, among other applications. These chiral gallium di-imine complexes have not been evaluated for SHG efficiency, which may be a natural application. The ability to grow materials with tailored absorption and emission spectra is another potential application. In addition, the ability to produce colorless crystals as well as materials with single energy level or dual energy levels may enable unique combinations of SHG and absorption/emission properties, which are unknown at this point (yellow defects at  $\lambda = 430 \text{ nm}$ , and green defect states are  $\lambda = 430 \text{ nm}$  and  $\lambda = 690 \text{ nm}$ ). Further, the thermal and atmospheric stability of these defect states is not known, which may have applications as optical atmospheric tamper sensors, temperature history sensors, or radiation scintillator materials. Many chiral, SHG-active materials also show ferroelectric behavior due to their structural and electrical asymmetry, which enables a broad variety of applications, including liquid crystal display elements, piezoelectrics, nonvolatile memory elements and electro-optic circuit elements (polarizers, switches). To summarize, a wide range of attractive optical and physical device properties are observed in chiral materials, yet nothing is known about Ga-di-imine complexes and their potential applications.

With the onslaught of incremental advances made by the numerous academic, national laboratory, and industrial chemists and material scientists working on synthesizing new materials, it is extremely rare to come across a new class of compounds that are essentially completely new and novel. One could say that the overall goal of most scientists working in materials chemistry is to come up with either new materials, or new uses for old materials, but on most occasions these new materials are extensions to those already known. The reason for this is simple – in order to have the “best chance” for success, one logically researches “smaller”, more incremental steps beyond what is already known. This type of research can be quite valuable – in fact, the vast majority of industrially-sponsored research in chemistry consists of this incremental approach. However, in order to make fundamental breakthroughs in any area of science it is essential that one breaks with tradition and metaphorically “lose sight of the shore.” By the very nature of this act, the act of exploring scientific regions well outside the “normal” areas studied, one has reduced the certainty of success, but has increased dramatically the opportunity to make fundamental and innovative discoveries, and in our case, to invent new materials with interesting properties and uses. This is the approach we have chosen to take in this LDRD.

The synthesis of the known gallium di-imine compound **1** is shown below in **Scheme 1** (1). The synthesis begins with the addition of the bulky aryl-substituted di-imine ([2,6-(Me<sub>2</sub>CH)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>]N=CHCH=N[2,6-(CHMe<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>]) to Me<sub>2</sub>GaCl. Rather than forming the



expected Lewis acid-base adduct, after initial complexation the Me<sub>2</sub>GaCl adds across the C=N bond of the di-imine, and then a rearrangement occurs in which the methyl group migrates from an sp<sup>3</sup> carbon to an sp<sup>2</sup> carbon. While somewhat unusual, this rearrangement can be followed easily by and unequivocally by <sup>1</sup>H NMR, and related rearrangements have been seen before (van Koten, *J. Organomet. Chem.*, **181**, 271 (1979)). This rearrangement is shown in **Scheme 2**. Generated upon this addition and rearrangement

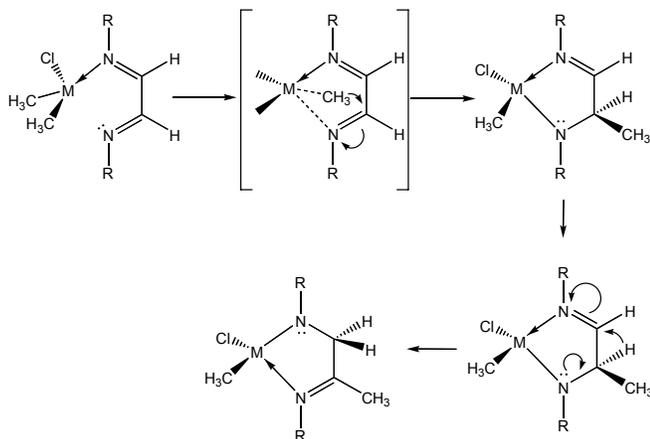
**Scheme 1.** Synthesis of di-chromic crystals.

is a chiral Ga atom. A very interesting feature of this preparation is that three types of crystals are simultaneously isolated from this reaction – there are crystals obtained that are dark green in color, bright yellow in color, and mixed yellow/green crystals (with a single sharp interface between the colors). Mixed green/yellow faceted crystals can also be isolated (with sharp color interfaces). An example of a yellow/green crystal is shown in **Figure 1**. These faceted crystals

resemble the face-selective dyed crystals mentioned earlier, and are all formed simultaneously in the reaction mixture. Each form of the crystals has been isolated and characterized. All of the samples of **1** – no matter what color – have identical  $^1\text{H}$  and  $^{13}\text{C}$  spectra, elemental analysis, and most amazingly, *all have identical structures in single crystal X-ray diffraction studies*. Focusing the X-ray beam on either part of the mixed green/yellow crystals give identical structures. It is also believed to the best of our knowledge that no other materials that produce compounds with identical single crystal X-ray structures with such radically different colors. We have expanded the number of these compounds by preparing analogs of **1** with other aromatic groups on the diimine to yield colored materials; however, replacement of the aryl groups with *t*-butyl groups affords colorless crystals in initial experiments (*vide infra*).

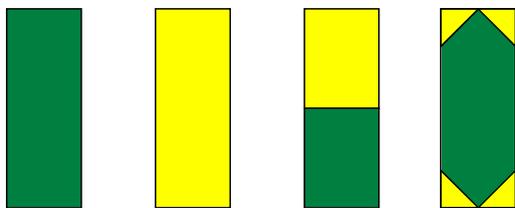


**Figure 1.** Single crystals of Ga-diimine complex.

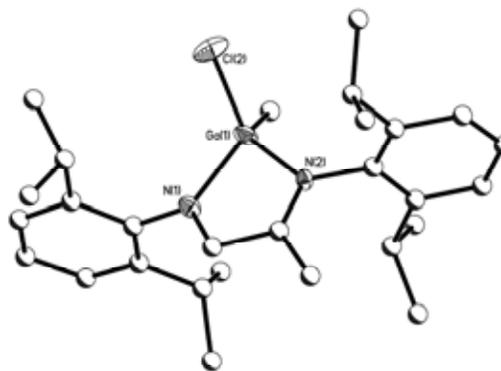


**Scheme 2.** Possible Rearrangement Route to Yield **1**

**Figure 2** shows pictorially some of the multi-colored type of single crystals that have been observed from the reaction to produce **1**. As well, the single crystal X-ray diffraction structure of **1** is shown in **Figure 3**, thus confirming its identity.



**Figure 2.** Single crystals of Ga-diimine complex formed and isolated simultaneously.



**Figure 3.** Crystal structure of **1B**.

Why are these crystals colored at all, much less multichromic? The major goals of this LDRD are to understand a) the range of ligands and metals that can be used to generate these dichromic crystals, b) the origin of the color(s) in the crystals, c) how to control the morphology of

the colored crystals, and d) to possibly exploit these novel materials in optical applications. Several initial hypotheses can be put forth to possibly explain the observations seen above. The experiment with the alkyl substituent on the di-imine giving colorless crystals may indicate that the colors result from an extended  $\pi$ -system network present in the aryl di-imine ligand system. One could postulate that the intense colors may be generated by a mixed-valence  $\text{Ga}^{\text{II}}/\text{Ga}^{\text{III}}$  complex caused by a reductive process. As well, a highly colored, paramagnetic  $\text{Ga}^{\text{II}}$  species may be present in amounts too small to negatively affect the NMR spectra, yet enough to change the color of the crystals. Small amounts of highly-colored ligand degradation products may also be present in the crystals, selectively growing along certain faces as in the dyed crystals. The fact that we generate chiral solids may also play a role.

Chiral molecules have been widely studied recently for nonlinear optical applications because they are inherently noncentrosymmetric, and thus possess potential for frequency-doubling of laser radiation. Such second-harmonic generation (SHG), in which incident light of frequency  $\omega$  is doubled to  $2\omega$ , (e.g.  $\lambda = 1.06 \mu\text{m}$  to 532 nm is critical for optical frequency through THz spectroscopy, among other applications.) These chiral gallium di-imine complexes have not been evaluated for SHG efficiency, which may be a natural application.

As discussed above, the ability to grow materials with tailored absorption and emission spectra is another potential application. In addition, the ability to produce colorless crystals as well as materials with single energy level yellow defects ( $\lambda = 430 \text{ nm}$ ), or dual energy level green defect states ( $\lambda = 430 \text{ nm}$  and  $\lambda = 690 \text{ nm}$ ) may enable unique combinations of SHG and absorption/emission properties, which are unknown at this point. Further, the thermal and atmospheric stability of these defect states is not known, which may have applications as optical atmospheric tamper sensors, temperature history sensors, or radiation scintillator materials. Existing programs in these areas may be leveraged to examine the potential of using these gallium di-imine complexes as replacement materials.

Many chiral, SHG-active materials also show ferroelectric behavior due to their structural and electrical asymmetry, which enables a broad variety of applications, including liquid crystal display elements, piezoelectrics, nonvolatile memory elements and electro-optic circuit elements (polarizers, switches). To summarize, a wide range of attractive optical and physical device properties are observed in chiral materials, yet nothing is known about gallium di-imine complexes and their potential applications in the synthesis of new materials.

## **Summary of Research Plan**

The major goals of this project are understand a) the range of ligands and metals that can be used to generate these dichromic crystals, b) the origin of the color(s) in the crystals, c) how to control the morphology of the colored crystals, and d) to possibly exploit these novel materials in optical applications. Several initial hypotheses can be put forth to possibly explain the observations seen above. The experiments with the alkyl substituent on the di-imine giving colorless crystals may indicate that the intense colors result from an extended  $\pi$ -system network present in the aryl di-imine ligand system. One could postulate that the intense colors may be generated by a mixed-valence  $\text{Ga}^{\text{II}}/\text{Ga}^{\text{III}}$  complex caused by a reductive process, or a highly colored, paramagnetic  $\text{Ga}^{\text{II}}$  species may be present in amounts too small to negatively affect the

NMR spectra, yet enough to change the color of the crystals. Small amounts of highly-colored ligand degradation products may also be present in the crystals, selectively growing along certain faces as in the dyed crystals. The fact that chiral solids are generated may also play a role. A range of metals in Group 13 along with a variety of ligand variations to pinpoint the nature of the colored crystals have been investigated. As an example, if the  $\pi$ -network of the ring is important, one can imagine “tuning” the system by appropriate substitution on the aromatic rings (e.g., adding more  $\pi$ -electrons via side chains to affect the absorption). If the chiral nature of the central atom is important, one can imagine utilizing substituents on the main group atom to change the optical characteristics.

## Listing of Complexes

**Table 1** shows a listing of the metal complexes prepared in this study, and the experimental details for the preparation of each compound is given in the Experimental Section.

**Table 1.** Table of Complexes Prepared in this Study

Compound		Metal Complex	Di-imine Used (R-N=CH-CH=N-R) <i>R Group is Listed</i>
1		Me <sub>2</sub> GaCl	[2,6-(Me <sub>2</sub> CH) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> ]-
2		Me <sub>2</sub> GaCl	[2,4,6-(CH <sub>3</sub> ) <sub>3</sub> C <sub>6</sub> H <sub>2</sub> ]-
3		Me <sub>3</sub> Ga	[2,6-(Me <sub>2</sub> CH) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> ]-
4		MeGaCl <sub>2</sub>	[2,6-(Me <sub>2</sub> CH) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> ]-
5		GaCl <sub>3</sub>	[2,6-(Me <sub>2</sub> CH) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> ]-
6		GaMe <sub>3</sub>	[2,6-(Me <sub>2</sub> CH) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> ]- *
7		Me <sub>2</sub> AlCl	[2,6-(Me <sub>2</sub> CH) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> ]-
8		Me <sub>2</sub> AlCl	[2,4,6-(CH <sub>3</sub> ) <sub>3</sub> C <sub>6</sub> H <sub>2</sub> ]-
9		Me <sub>2</sub> AlCl	[2,6-(Me) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> ]-
10		Me <sub>2</sub> AlCl	[2,6-(Me <sub>2</sub> CH) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> ]- *
11		Me <sub>2</sub> GaCl	C <sub>6</sub> H <sub>11</sub> - (cyclohexyl)
12		Me <sub>2</sub> GaCl	Me <sub>3</sub> C- (t-butyl)
13		Me <sub>2</sub> AlCl	Me <sub>3</sub> C- (t-butyl)
14		Me <sub>2</sub> AlCl	C <sub>6</sub> H <sub>11</sub> - (cyclohexyl)
15		Me <sub>2</sub> GaCl	[2,6-(Me) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> ]-

\* Di-imine used the [-C(CH<sub>3</sub>)-C(CH<sub>3</sub>)-] backbone instead of the parent (-CH-CH-) backbone

## Experimental

Standard air-sensitive techniques were generally used, as all products other than the starting di-imines are air and/or moisture sensitive. Products were prepared either using a drybox or a Schlenk vacuum line. Details of X-ray structures will be published separately.

### Synthesis of Gallium and Aluminum Complexes

#### **Compound 1**

*Synthesis of (Imine)GaMeCl* (imine = [2,6-(Me<sub>2</sub>CH)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>]N=CHCH=N[2,6-(CHMe<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>])

The di-imine (1.00 g, 2.66 mmol) was added slowly to a colorless solution of Me<sub>2</sub>GaCl (0.415 g, 2.66 mmol, 1.0 equiv.) in toluene. The solution turned deep orange instantaneously. After 12 hours, the color of the solution became dark green and stick-shaped yellow crystals of **1** began to form. Cooled to -30°C and washed with cold pentane. <sup>1</sup>H NMR (δ, in C<sub>6</sub>D<sub>6</sub>): 6.98-7.27 (m, 6H, (i-Pr)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>), 4.57 (d, 1H, J = 23 Hz, N=C(Me)-CHH-N), 4.32 (sept, 1H, J = 7 Hz, CHMe<sub>2</sub>), 3.88 (d, 1H, J = 23 Hz, N=C(Me)-CHH-N), 3.38 (sept, 1H, J = 6 Hz, CHMe<sub>2</sub>) 3.20 (sept, 1H, J = 6 Hz, CHMe<sub>2</sub>), 2.90 (sept, 1H, J = 7 Hz, CHMe<sub>2</sub>), 1.52 (d, 3H, J = 6 Hz, CHMe<sub>2</sub>), 1.48 (d, 3H, J = 6 Hz, CHMe<sub>2</sub>), 1.45 (d, 3H, J = 7 Hz, CHMe<sub>2</sub>), 1.25 (s, 3H, N=C(Me)-CHH-N), 1.25 (d, 3H, J = 7 Hz, CHMe<sub>2</sub>), 1.24 (d, 3H, J = 6 Hz, CHMe<sub>2</sub>), 1.16 (d, 3H, J = 7 Hz, CHMe<sub>2</sub>), 0.98 (d, 3H, J = 7 Hz, CHMe<sub>2</sub>), 0.86 (d, 3H, J = 6 Hz, CHMe<sub>2</sub>), 0.01 (s, 3H, GaCH<sub>3</sub>). X-ray data were collected (rkaf02) R<sub>1</sub>=6.06% (7.88% all) wR=17.51% (19.27% ref). Yield 60%, m.p. 170°C with decomposition to orange solid; continued heating to 210°C leaves red liquid which will solidify to a green solid at R.T. Using polarized light it can be seen that the “green” tips of the crystals have both “green” (λ<sub>max</sub> 690 nm) and “yellow/red” (λ<sub>max</sub> 430 nm) absorptions in them, but the “yellow/orange” sections of the crystals are devoid of “green” band. EPR was done at room temperature and at -20°C.

#### **Compound 2**

*Synthesis of (Imine)GaMeCl* (imine = [2,4,6-(CH<sub>3</sub>)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>]N=CHCH=N[2,4,6-(CH<sub>3</sub>)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>])

The di-imine (0.500 g, 1.71 mmol) was added slowly to a colorless solution of Me<sub>2</sub>GaCl (0.231 g, 1.71 mmol, 1.0 equiv) in toluene (6 mL) and the solution turned dark orange. The reaction was immediately placed in the freezer. Orange block crystals were isolated at -20°C. 58.4% crystalline yield, MP 87°C (decomposition). <sup>1</sup>H NMR needs to be done at 0°C degrees or in the solid state. <sup>1</sup>H NMR (δ, in C<sub>6</sub>D<sub>6</sub>): 8.84 (d, 1H, N=C(Me)-CHH-N), 7.61 (d, 1H, N=C(Me)-CHH-N), 7.09-6.82 (m, 4H, (Me)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>), 2.38-1.97 (m, 18H, (Me)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>), -0.19 (s, 6H, Ga(CH<sub>3</sub>)<sub>2</sub>). X-ray structure (rkaf16) R<sub>1</sub>=5.68% (6.78% all) wR=18.22% (19.23% all).

#### **Compound 3**

*Synthesis of (Imine)GaMe<sub>2</sub>* (imine = [2,6-(Me<sub>2</sub>CH)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>]N=CHCH=N[2,6-(CHMe<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>])

The di-imine (1.00 g, 2.66 mmol) was added slowly to a colorless solution of Me<sub>3</sub>Ga (0.305 g, 2.66 mmol, 1.0 equiv.) in toluene. The solution turned orange instantaneously. The reaction was stirred for 18 hours. Yellow crystals were isolated via slow evaporation. Crystals were orange, colorless, and green. X-ray data were collected (rkaf04) R<sub>1</sub>=4.89% (8.92% all) wR=14.04% (17.76% ref). 99.2% crystalline yield. MP 136-138°C. <sup>1</sup>H NMR (δ, in CD<sub>2</sub>Cl<sub>2</sub>): 6.95-7.40 (m,

6H, (i-Pr)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>), 4.49 (s, H, N=C(Me)-CHH-N), 3.62 (sept, 2H, CHMe<sub>2</sub>), 2.98 (sept, 2H, CHMe<sub>2</sub>), 1.93 (s, 3H, N=C(Me)-CHH-N), 1.31 (d, 12H, CHMe<sub>2</sub>), 1.18 (d, 12H, CHMe<sub>2</sub>), -0.43 (s, 3H, Ga(CH<sub>3</sub>)<sub>2</sub>).

#### Compound 4

*Synthesis of (Imine)GaMeCl<sub>2</sub> (imine = [2,6-(Me<sub>2</sub>CH)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>]N=CHCH=N[2,6-(CHMe<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>])*  
The di-imine (1.00 g, 2.66 mmol) was added slowly to a colorless solution of MeGaCl<sub>2</sub> (0.414 g, 2.66 mmol, 1.0 equiv.) in toluene. The solution turned dark red instantaneously. The reaction was stirred for 18 hours. Orange crystals were isolated via slow evaporation. X-ray data were obtained (rkaf03) R1=5.37% (12.17% all) wR=13.53% (17.08% ref). Roughly quantitative crude yield.

#### Compound 5

*Synthesis of (Imine)GaCl<sub>3</sub> (imine = [2,6-(Me<sub>2</sub>CH)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>]N=CHCH=N[2,6-(CHMe<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>])*  
GaCl<sub>3</sub> (0.468 g, 2.66 mmol) was dissolved in toluene (5 mL). The di-imine (1.00 g, 2.66 mmol) was slowly added. The reaction mixture turned dark red. The reaction was stirred for 18 hours. Crystals formed immediately from the dark red solution via slow evaporation in the dry box. 68% crystalline yield. X-ray data were collected (rkaf09) R1=9.64% (19.87% all) wR=34.64% (37.28% ref).

#### Compound 6

*Synthesis of (Imine)GaMe<sub>2</sub> (imine = [2,6-(Me<sub>2</sub>CH)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>]N=C(CH<sub>3</sub>)C(CH<sub>3</sub>)=N[2,6-(CHMe<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>])*

The di-imine (0.500 g, 1.24 mmol) was dissolved in toluene (3 mL). GaMe<sub>3</sub> (0.142 g, 1.24 mmol, 1.0 equiv) was added slowly. The reaction mixture was yellow. The reaction was stirred for 3 hours. Yellow crystals were isolated by slow evaporation. X-ray data were collected (rkaf13) R1=5.64% (8.11% all) wR=16.84% (17.65% ref). <sup>1</sup>H NMR (δ, in C<sub>6</sub>D<sub>6</sub>): 7.30-7.00 (m, 6H, (i-Pr)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>), 3.92 (sept, 2H, CHMe<sub>2</sub>), 3.04 (sept, 2H, CHMe<sub>2</sub>), 1.40 (d, 6H, CHMe<sub>2</sub>), 1.37 (s, 3H, N=C(Me<sub>2</sub>)-C(Me)-N), 1.28 (d, 6H, CHMe<sub>2</sub>), 1.25 (d, 6H, CHMe<sub>2</sub>), 1.20 (s, 6H, N=C(Me<sub>2</sub>)-C(Me)-N), 0.97 (d, 6H, CHMe<sub>2</sub>), -0.07 (s, 6H, GaCH<sub>3</sub>).

### Aluminum Complexes

#### Compound 7

*Synthesis of (Imine)AlMeCl (imine = [2,6-(Me<sub>2</sub>CH)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>]N=CHCH=N[2,6-(CHMe<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>])*  
The di-imine (1.00 g, 2.66 mmol) was added slowly to a colorless solution of Me<sub>2</sub>AlCl (2.66 mL, 2.66 mmol, 1.0 equiv) in toluene (5 mL) the solution turned dark orange. The reaction was stirred for 14 hours and the reaction turned pale yellow. Yellow crystals were isolated by slow evaporation. The compound acquired a green color over time in the drybox. X-ray data were collected (rkaf05) R1=12.42 (15.62 all) wR=40.81 (43.55 ref). <sup>1</sup>H NMR (δ, in C<sub>6</sub>D<sub>6</sub>): 6.98-7.28 (m, 6H, (i-Pr)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>), 4.35 (d, 1H, J = 23 Hz, N=C(Me)-CHH-N), 4.20 (sept, 1H, J = 7 Hz, CHMe<sub>2</sub>), 3.86 (d, 1H, J = 23 Hz, N=C(Me)-CHH-N), 3.53 (sept, 1H, J = 7 Hz, CHMe<sub>2</sub>) 3.16 (sept, 1H, J = 6 Hz, CHMe<sub>2</sub>), 3.00 (sept, 1H, J = 7 Hz, CHMe<sub>2</sub>), 1.53 (d, 3H, J = 7 Hz, CHMe<sub>2</sub>), 1.44 (d, 3H, J = 6 Hz, CHMe<sub>2</sub>), 1.41 (d, 3H, J = 7 Hz, CHMe<sub>2</sub>), 1.24 (s, 3H, N=C(Me)-CHH-N), 1.28 (d, 3H, J = 6 Hz, CHMe<sub>2</sub>), 1.21 (d, 3H, J = 6 Hz, CHMe<sub>2</sub>), 1.17 (d, 3H, J = 7 Hz, CHMe<sub>2</sub>), 0.95 (d, 3H, J = 7 Hz, CHMe<sub>2</sub>), 0.86 (d, 3H, J = 7 Hz, CHMe<sub>2</sub>), -0.33 (s, 3H, AlCH<sub>3</sub>). Yield 99.6%. m.p. 210°C, slight orange color at 230°C (orange liquid.)

### Compound 8

*Synthesis of (Imine)AlMeCl (imine = [2,4,6-(CH<sub>3</sub>)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>]N=CHCH=N[2,4,6-(CH<sub>3</sub>)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>])*

The di-imine (0.500 g, 1.71 mmol) was added slowly to a colorless solution of Me<sub>2</sub>AlCl (1.71 mL, 1.71 mmol, 1.0 equiv) in toluene (4 mL) the solution turned dark orange. The reaction was stirred for 14 hours and the reaction turned pale yellow. Yellow crystals were isolated by slow evaporation. X-ray data were collected (rkaf06). R1=6.80% (9.87% all) wR=18.25% (20.84% ref). 73.7% crystalline yield. <sup>1</sup>H NMR (δ, in C<sub>6</sub>D<sub>6</sub>): 6.88-7.11 (m, 4H, (Me)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>), 4.49 (d, 1H, N=C(Me)-CHH-N), 2.36 (s, 9H, N=C(Me)-CHH-N), (*p*-Me)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>, 2.32 (s, 3H, (*o*-Me)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>), 2.28 (s, 3H, (*o*-Me)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>), 2.17 (s, 3H, (*o*-Me)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>), 1.98 (s, 3H, (*o*-Me)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>), -0.60 (s, 3H, AlCH<sub>3</sub>).

### Compound 9

*Synthesis of (Imine)AlMeCl (imine = [2,6-(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>]N=CHCH=N[2,6-(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>])*

The di-imine (0.500 g, 1.89 mmol) was added slowly to a colorless solution of Me<sub>2</sub>AlCl (1.89 mL, 1.89 mmol, 1.0 equiv) in toluene (9 mL) the solution turned dark orange. The reaction was immediately placed in the freezer. X-ray data were collected (rkaf08). R1=7.73% (12.39% all) wR=18.87% (21.45% ref) Crystals were isolated via slow evaporation at -20°C. Crystals were thermally unstable and so <sup>1</sup>H NMR will need to be done at low temperature or solid state.

### Compound 10

*Synthesis of (Imine)AlMeCl (imine=[2,6-(Me<sub>2</sub>CH)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>]N=C(CH<sub>3</sub>)C(CH<sub>3</sub>)=N[2,6-(CHMe<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>])*

The di-imine (0.500 g, 1.24 mmol) was dissolved in toluene (3 mL). Me<sub>2</sub>AlCl (1.24 mL, 1.24 mmol, 1.0 equiv) was added slowly drop-wise. The reaction was stirred for 30 minutes. Yellow/green needle crystals were isolated by slow evaporation. X-ray data were collected (rkaf14) R1=9.63% (18.09% all) wR=25.80% (32.74% ref).

### Cationic/Anionic Species

### Compound 11

*Synthesis of (Imine)GaMeCl (imine=[C<sub>6</sub>H<sub>11</sub>]N=CHCH=N[C<sub>6</sub>H<sub>11</sub>])*

The di-imine (0.500 g, 2.26 mmol) was added slowly to a colorless solution of Me<sub>2</sub>GaCl (0.307 g, 2.26 mmol, 1.0 equiv) in toluene (5 mL) the solution turned light green. The reaction was immediately placed in the freezer. White crystals were isolated at -20°C. X-ray data were collected (rkaf07), with the crystals slowly obtaining an orange color in the freezer, and unstable at room temperature. Quantitative yield if calculated by gallium weight. R1=3.05% (5.06% all) wR=8.46% (9.99% ref). m.p. 65°C. Apparent loss of toluene upon continued heating at 95°C with decomposition from orange to black. Thermally unstable in solution - <sup>1</sup>H NMR has to be done at 0°C degrees or solid state.

### Compound 12

*Synthesis of (Imine)Me<sub>2</sub>GaCl (imine = [Me<sub>3</sub>C]N=CHCH=N[CMe<sub>3</sub>])*

The di-imine (0.500 g, 2.97 mmol) was dissolved in toluene (3 mL). Me<sub>2</sub>GaCl (0.402 g, 2.97 mmol) was slowly added. The reaction was exothermic. White crystals formed immediately from the dark orange solution. The reaction was allowed to stir overnight. Larger orange crystals fell out of the solution as it became darker in color. The solution was allowed to slowly evaporate.

The crystals were washed with cold pentane (rkaf10), R1=5.48% (8.97% all) wR=16.81% (18.66% ref). <sup>1</sup>H NMR (δ, C<sub>6</sub>D<sub>6</sub>): 9.13 (s, 2H, N=CH-CH=N), 1.08 (s, 18H, C-(CH<sub>3</sub>)<sub>3</sub>), 0.47 (s, 6H, (CH<sub>3</sub>)<sub>2</sub>Ga), -0.20 (s, 6H, (CH<sub>3</sub>)<sub>2</sub>GaCl<sub>2</sub>).

### Compound 13

*Synthesis of (Imine)Me<sub>2</sub>AlCl (imine = [Me<sub>3</sub>C]N=CHCH=N[CM<sub>3</sub>])*

The di-imine (0.500 g, 2.97 mmol) was dissolved in toluene (3 mL). Me<sub>2</sub>AlCl (2.97 mmol) was slowly added. The reaction was exothermic. Crystals formed immediately from the dark orange solution. The reaction was placed in the freezer (-20°C). Larger orange crystals fell out of the solution and were isolated. X-ray data were collected (rkaf11) R1=7.16% (21.50% all) wR=21.38% (26.26% ref).

### Non-crystalline Complexes

#### Compound 14

*Synthesis of (Imine)AlMeCl (imine = [C<sub>6</sub>H<sub>11</sub>]N=CHCH=N[C<sub>6</sub>H<sub>11</sub>])*

The di-imine (0.500 g, 2.26 mmol) was added slowly to a colorless solution of Me<sub>2</sub>AlCl (2.26 mL, 2.26 mmol, 1.0 equiv) in toluene (5 mL) the solution turned dark green. The reaction was immediately placed in the freezer. Crystals were not isolated.

#### Compound 15

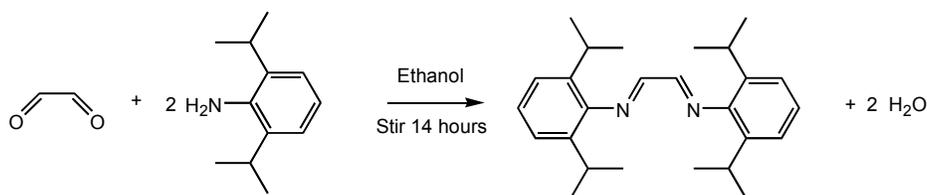
*Synthesis of (Imine)GaMeCl (imine = [2,6-(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>]N=CHCH=N[2,6-(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>])*

The di-imine (0.500 g, 1.89 mmol) was added slowly to a colorless solution of Me<sub>2</sub>GaCl (0.256 g, 1.89 mmol, 1.0 equiv) in toluene (9 mL) and the solution turned dark orange. Tetrahydrofuran (1 mL) was added to fully dissolve all the reactants and the reaction then turned light orange. The reaction was immediately placed in the freezer. Orange and yellow crystals were isolated in 54% crystalline yield. The thermally unstable complex, as identified by low temperature <sup>1</sup>H NMR, indicates the formation of the intramolecular rearrangement product. No crystal structure was obtained.

### Syntheses of Starting Materials

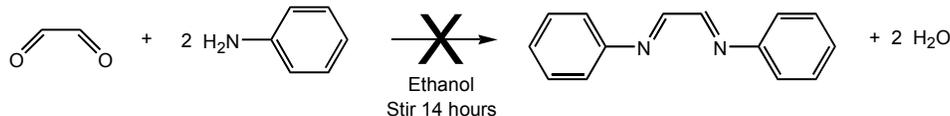
*Synthesis of [2,6-(Me<sub>2</sub>CH)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>]N=CHCH=N[2,6-(CHMe<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>]*

Into a 250 mL round bottom flask equipped with a magnetic stirbar was charged 10.04 g (56.65 mmol, 1.99 equiv) of 2,6-diisopropylaniline and 130 mL of ethanol. Glyoxal (4.17 g, 40 wt % in H<sub>2</sub>O, 28.45 mmol, 1 equiv) was added dropwise to the stirred solution, which acquired a bright yellow color within minutes of the glyoxal addition, and the solution was refluxed for 12 hours and then cooled to room temperature. The volume of solvent was reduced to ~100 mL on a rotavap (45°C), and the yellow insoluble material was isolated by filtration, and was then washed with cold ethanol. A second crop was obtained by further concentration of the mother liquor, filtration, and washing of the resultant solid with two 5 mL portions of 0°C ethanol. The combined yellow solids were crushed with a mortar and pestle, washed twice with 20 mL aliquots of ethanol at 0°C, and dried in vacuo. Isolated yield: 8.31 g of yellow powder, 22.1 mmol, 78% yield. m.p. 102-103°C. <sup>1</sup>H NMR (δ, in CDCl<sub>3</sub>, 25°): 1.24 (d, J = 6.8 Hz, 24H, CH(CH<sub>3</sub>)<sub>2</sub>), 2.97 (septet, J = 6.8 Hz, 4H, CH(CH<sub>3</sub>)<sub>2</sub>), 7.21 (m, 6H, overlapping C<sub>6</sub>H<sub>3</sub>), 8.13 (s, 2H, NCH).



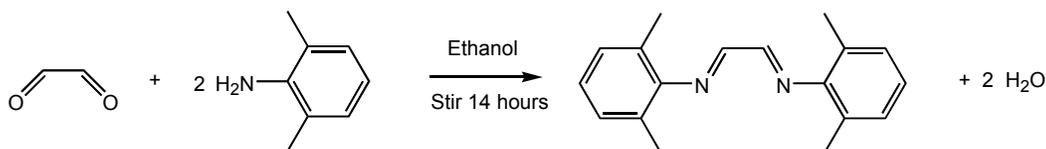
*Attempted synthesis of  $[C_6H_5]N=CHCH=N[C_6H_5]$*

Into a 250 mL round bottom flask equipped with a magnetic stirbar was charged 20.50 g (1.99 equiv) of aniline and 130 mL of ethanol. Glyoxal (15.97 g, 40 wt % in  $H_2O$ , 1 equiv) was added dropwise to the stirred solution, which acquired a bright yellow color within minutes of the glyoxal addition, and then the solution was stirred for 14 hours. The volume of solvent was reduced to ~100 mL on a rotavap ( $45^\circ C$ ), and the yellow insoluble material was a tar, which could not be isolated. Literature also reports that the target product cannot be isolated. (Kilegman and Barnes; *J. Org. Chem.*, **35**, 3140, 1970).



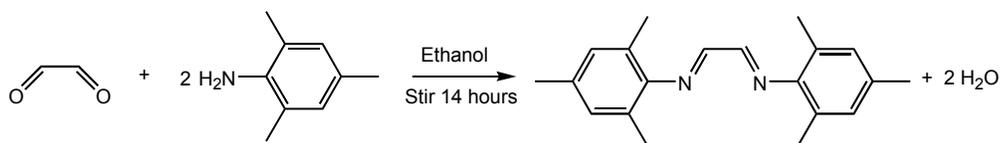
*Synthesis of  $[2,6-(CH_3)_2C_6H_3]N=CHCH=N[2,6-(CH_3)_2C_6H_3]$*

Into a 250 mL round bottom flask equipped with a magnetic stirbar was charged 9.8g (1.99 equiv) of aniline and 130 mL of ethanol. Glyoxal (5.86 g, 40 wt % in  $H_2O$ , 1 equiv) was added dropwise to the stirred solution, which acquired a bright yellow color within minutes of the glyoxal addition. The solution was stirred for 14 hours. The volume of solvent was reduced to ~100 mL on a rotavap ( $45^\circ C$ ), and the yellow insoluble material was isolated by filtration and was then washed with cold ethanol. The solid was dried in vacuo. Isolated yield: 9.07 g of yellow powder, 34.34 mmol, 85% yield. m.p.  $151-152^\circ C$ .  $^1H$  NMR ( $\delta$ , in  $C_6D_6$ ) 7.86 (s, 1H), 6.93 (m, 3H), 2.06 (s, 6H).



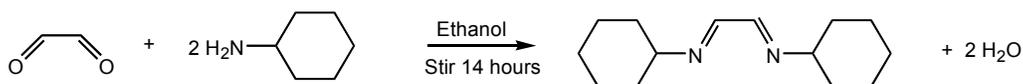
*Synthesis of  $[2,4,6-(CH_3)_3C_6H_2]N=CHCH=N[2,4,6-(CH_3)_3C_6H_2]$*

Into a 250 mL round bottom flask equipped with a magnetic stir bar was charged 28.4 g (1.99 equiv) of 2,4,6-trimethylaniline and 130 mL of ethanol. Glyoxal (15.24 g, 40 wt % in  $H_2O$ , 1 equiv) was added dropwise to the stirred solution, which acquired a bright yellow color within minutes of the glyoxal addition; and then the solution was stirred for 14 hours. The volume of solvent was reduced to ~100 mL on a rotavap ( $45^\circ C$ ), and the yellow insoluble material was isolated by filtration and was then washed with cold ethanol. The solid was dried in vacuo. Isolated yield: 25.80 g of yellow powder, 88.2 mmol, 84% yield. m.p.  $155-156^\circ C$ .  $^1H$  NMR ( $\delta$ , in  $CDCl_3$ ): 2.20 (s, 12H, 2,6- $(CH_3)_2-C_6H_2$ ), 2.33 (s, 6H, 4- $CH_3-C_6H_2$ ), 6.95 (s, 4H,  $C_6H_2$ ), 8.15 (s, 2H, NCH)



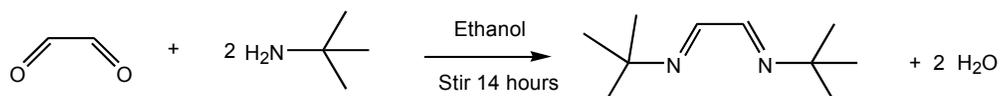
*Synthesis of  $[C_6H_{11}]N=CHCH=N[C_6H_{11}]$*

Into a 250 mL round bottom flask equipped with a magnetic stir bar was charged 20.55 g (1.99 equiv) of cyclohexylamine and 130 mL of ethanol. Glyoxal (15.02 g, 40 wt % in  $H_2O$ , 1 equiv) was added dropwise to the stirred solution, which acquired an orange color with a white precipitate; and then the solution was stirred for 14 hours. The product was filtered off and washed with ethanol. Isolated yield: 21.69 g of white powder, 98.4 mmol, 95% yield, m.p. 145-147°,  $^1H$  NMR ( $\delta$ , in  $C_6D_6$ ): 1.67 (m, 20H) 3.20 (m, 1.9H) 7.93 (s 1.9H).



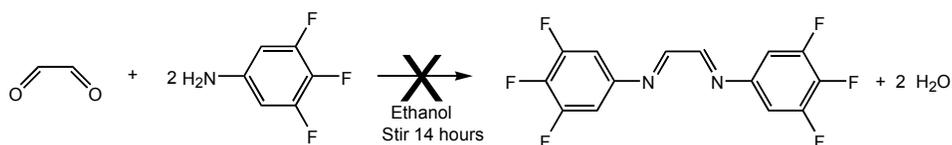
*Synthesis of  $[C_4H_9]N=CHCH=N[C_4H_9]$*

Into a 250 mL round bottom flask equipped with a magnetic stir bar was charged 7.00 g (1.99 equiv) of tert-butylamine and 130 mL of ethanol. Glyoxal (6.94 g, 40 wt % in  $H_2O$ , 1 equiv) was added dropwise to the stirred solution, which acquired a bright yellow color within minutes of the glyoxal addition; whereby the solution was stirred for 14 hours. The solvent was removed and the white solid was isolated by filtration. The solid was dried in vacuo. The product was dried with  $MgSO_4$  and recrystallized from ether. m.p. 39-43°, sublimation at 40° / 1mm Hg, gave an analytically pure sample; Found C, 71.60; H, 11.60; N, 16.47; Calc'd for  $C_{10}H_{20}N_2$ : C, 71.43; H, 11.90; N, 16.67%; Mol. wt. 168 (mass spec). Isolated yield: 5.07 g of white powder, 30.14 mmol, 63% yield.  $^1H$  NMR ( $\delta$ , in  $C_6D_6$ ): 1.26 (s 18.2H); 7.96 (s 1.8H).



*Attempted synthesis of  $[R-N=CH-CH=N-R]$   $R=3,4,5$ -trifluoroaniline*

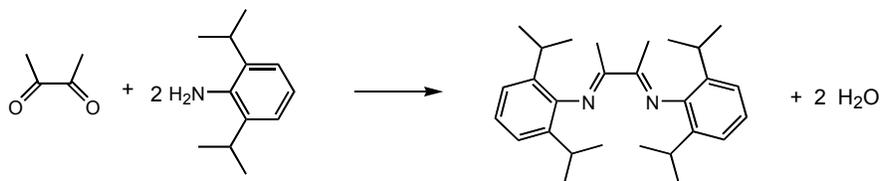
1.05 g (2.00 equiv.) of 3,4,5-trifluoroaniline was placed in a flask and dissolved in toluene. Glyoxal (0.52 g, 40% weight in water) was added dropwise. The reaction mixture was stirred for 18 hours. Solvent was removed in vacuo. The product was taken into the box was a tar. A useable product was not isolated.



*Synthesis of  $[2,6-(Me_2CH)_2C_6H_3]N=C(CH_3)C(CH_3)=N[2,6-(CHMe)_2C_6H_3]$*

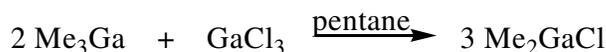
In a 250 mL round bottom flask equipped with a magnetic stir bar was charged 21.54 g (121.50 mmol, 1.99 equiv) of 2,6-diisopropylaniline and 130 mL of methanol. 2,3-butanedione (5.23 g,

60.75 mmol, 1 equiv) was added dropwise at 0°C to the stirred solution. Formic acid was added as a catalyst. A precipitate formed and the solution acquired a bright yellow color within minutes of the addition. The reaction was stirred for 20 hours. The yellow insoluble material was isolated by filtration and was then washed with cold methanol and dried in vacuo. The product was redissolved in pentane and MgSO<sub>4</sub> was used as a drying agent. After stirring 6 hours the solution was filtered and all solvent was removed in vacuo. Isolated yield: 18.67 g of yellow powder, 46.17 mmol, 76% yield. m.p. 95-97°C. <sup>1</sup>H NMR (δ, in C<sub>6</sub>D<sub>6</sub>): 1.17 (d, 24H, CH(CH<sub>3</sub>)<sub>2</sub>), 2.87 (s, 4H, CH(CH<sub>3</sub>)<sub>2</sub>), 2.15 (s, 6H, N=C(CH<sub>3</sub>)-C(CH<sub>3</sub>)=N), 7.13 (s, 6H, overlapping C<sub>6</sub>H<sub>3</sub>).



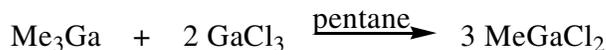
#### *Synthesis of dimethylgallium chloride*

Trimethylgallium (6.8 g, 59.2 mmol) was dissolved in 20 mL of pentane in a round bottom flask under inert gas. To this solution is added dropwise with continuous stirring a concentrated solution of 5.15 g (29.3 mmol) of GaCl<sub>3</sub> in pentane at room temperature, which gave an exothermic reaction. The less than stoichiometric amount of GaCl<sub>3</sub> is necessary to avoid the formation of MeGaCl<sub>2</sub>. After all the GaCl<sub>3</sub> has been added the mixture was stirred for 1 hour at room temperature, the solvent was removed, the residue was distilled under vacuum. Yield 90%. Dimethylgallium chloride (m.p. 45-46°C, b.p. 164-165°C /730 torr, 75-77°C /30 torr) is dimeric in gas phase and solution (benzene). It has a low sensitivity to oxygen, but is very sensitive to moisture. It is poorly soluble in diethyl ether, petroleum ether, cyclohexane, benzene, and CCl<sub>4</sub>. <sup>1</sup>H NMR (δ, in C<sub>6</sub>D<sub>6</sub> 1% TMS): 0.19 (s, 6H, Me<sub>2</sub>GaCl)



#### *Synthesis of methylgallium dichloride*

Trimethylgallium (0.326 g, 2.84 mmol) was dissolved in 20 mL of pentane in a round bottom flask under inert gas. To this solution is added dropwise with continuous stirring a concentrated solution of 1.00 g (5.68 mmol) of GaCl<sub>3</sub> in pentane at room temperature, leading to an exothermic reaction. After all the GaCl<sub>3</sub> had been added the mixture was stirred for 1 hour at room temperature, the solvent is removed. Yield 90%. methylgallium dichloride m.p. 81-82°C. <sup>1</sup>H NMR (δ, in C<sub>6</sub>D<sub>6</sub>): 0.08 (s, 3H, MeGaCl<sub>2</sub>)



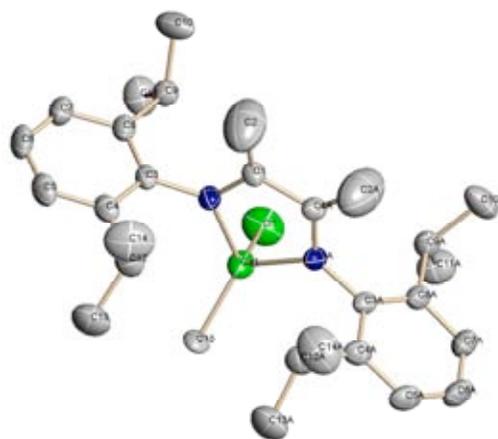
## Discussion and Conclusions

We have discovered an unprecedented class of chiral single crystals that are multichromic. We can prepare individual single crystals that are crystallographically identical, yet may be grown colorless, yellow, or green from crystal to crystal, or to our knowledge, for the first time, multicolored *within the same crystal*. These novel materials are based on *s,p* block elements (main group elements such as Ga and Al) that contain chiral chelating ligands. In preliminary work we have shown that chemical variations in the backbone ligands enable single crystals that maintain multichromism at all viewing angles and reasonable temperatures; the materials are not doped but appear subtly structurally altered during growth.

We started by synthetically preparing several known substituted di-imines via known literature reaction pathways. Starting gallium complexes were also prepared via literature routes, and the aluminum starting materials were purchased. We then synthesized and crystallographically characterized a number of new compounds, varying the key components in order to determine what experimental factors play a role in setting the color(s) of the materials. Major experimental synthetic variables studied included choice of metal (Ga, Al) and structural variations (primarily electronic) on the ligand backbone. We originally had several hypotheses concerning possible causes of the multichromic behavior, speculating that the colors may arise from a) a highly-colored and lower valent Ga complex, b) an artifact of the chiral nature of the species, or c) a very small amount of a very highly-colored ligand degradation product.

Compound **1** was prepared and characterized. The intramolecular rearrangement product is proposed to form via **Schemes 1** and **2**. Neither the coordination product (presumed initially formed) nor **IA** was isolated. The  $^1\text{H}$  NMR indicates the presence of a single enantiomeric species. The X-ray structure (**Figures 3** (ORTEP) and **4** (ball and stick)) indicates the two enantiomeric species co-crystallized.

In order to check several of our hypotheses we performed the following experiments. We thought that the colors may come from a reduction of  $\text{Ga}^{\text{III}}$  to  $\text{Ga}^{\text{II}}$ , a species that would be a free radical. To test this we examined both solid and solutions of **1** by electron paramagnetic resonance (EPR). Typical spectra obtained are shown in **Figure 5**. While a radical species is indeed present, it shows no hint of being a  $\text{Ga}^{\text{II}}$  species – the EPR spectrum clearly shows this to be an organic radical species. Through our experimental work we have found no evidence of a  $\text{Ga}(\text{II})$  species at any point in any of the syntheses – and so we conclude that the source of the color cannot be a reduced  $\text{Ga}(\text{II})$  species. As well, we have prepared achiral as well as chiral Ga and Al species that exhibit multiple colors. Replacement of the  $\text{GaMe}_2\text{Cl}$  starting material with  $\text{GaMe}_3$  leads to an achiral product after the migration of the methyl group (compound **6**). We have also replaced Ga with



**Figure 4.** Ball and stick structure of **1**.

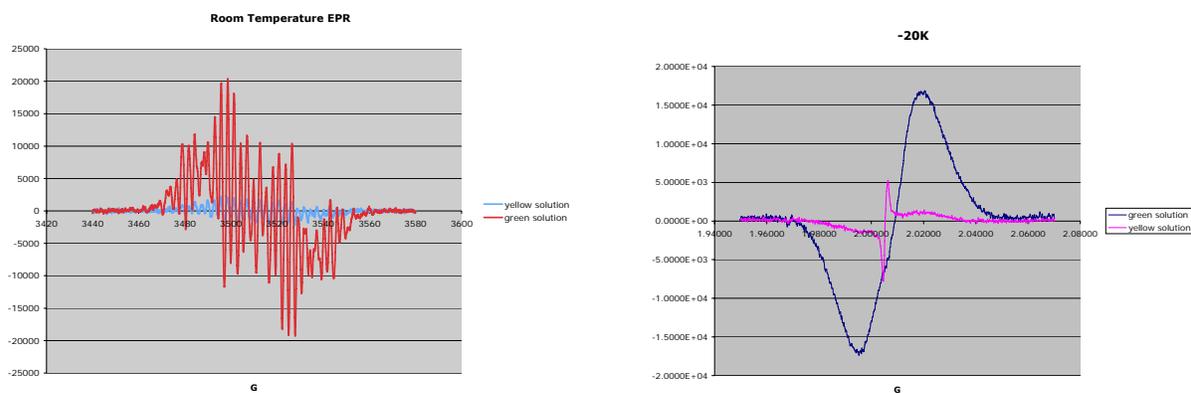
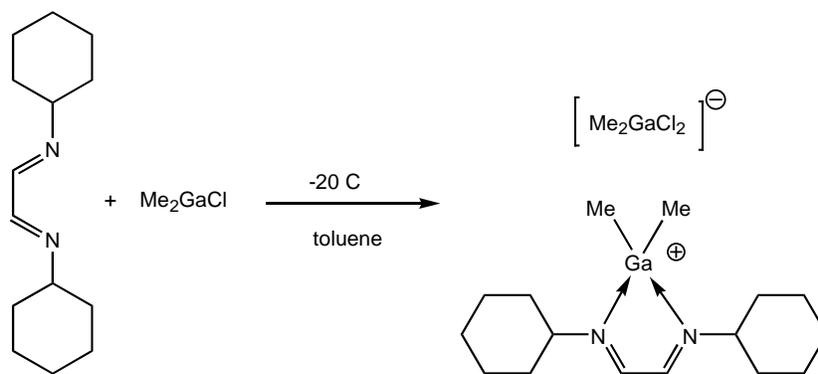
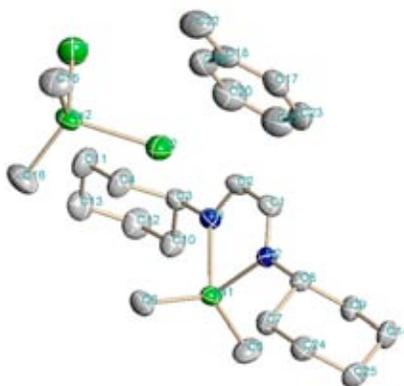


Figure 5. EPR Spectra of 1.

Al complexes and have seen similar behavior with Al that we saw with Ga. Hence, the unusual colors that we observe cannot be due solely to the presence of Ga. We have also prepared these Ga and Al complexes with a wide range of backbone-substituted ligands. Our best hypothesis at this point as to the cause of the colors involves the degradation (possible oxidative products?) of the backbone of the di-imine ligand. We observe the most intense colors when the backbone of the di-imine ligand contains an *aromatic* group. Our working hypothesis currently is that there is a small amount of ligand degradation that occurs while the complexes are being formed; the aromatic ligands are degraded to give small amounts of a *very highly colored species*. Interestingly, we believe that this impurity grows selectively along certain faces of the crystal as it is being formed (hence, the sharp demarcation lines or the faceted nature of the materials). Model experiments designed to deliberately degrade the ligand structure in the absence of the metalloid species have not given highly-colored species as yet. Alkyl substituted ligands give colorless crystals in general – never do we see the intensity of colors that are present with the aromatic ligands. The alkyl substituted ligands also do not give intramolecular rearrangement products but rather give cation/anion species, such as exemplified in the structure of **11** (Figure 6). However, we can say with certainty that this new class of multi-colored compounds is not due to differences in the chiral nature of the central metalloid, which was a motivating factor in our study as chiral compounds can be used in non-linear optical applications. Further study to further determine the exact nature of the ligand decomposition products will be required to prove this theory.



**Figure 6.** Example of a Cation/Anion Pair



**Summary:** This LDRD has led to several conclusions that are applicable to those working in the general area of materials science, and the specific area of chiral main group compounds. We have shown that these multi-colored species can be prepared with a range of ligands and metals other than gallium. However, the colors do not appear to be a result of any chiral nature of the crystal or a reduced gallium or aluminum species, but rather the colors appear to be due to trace amounts of ligand degradation products that are highly-colored. The complexes that gave the most intense colors all used aromatic groups as part of the di-imine backbone. It is likely that small amounts of these aromatic compounds are decomposing, forming highly-colored species, and then incorporating into the growing crystal lattice of the main group complex. There is enough of the highly-colored impurity to alter the colors, yet not enough present to grossly affect the crystal structure of the complexes. This study could be the beginning of a more formal program to understand the effects of minute levels of ligand impurities on the colors and properties of single crystals of main group compounds.

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