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Synthesis, Characterization, and Structure of [$GaCl_3$(NHC)] Complexes

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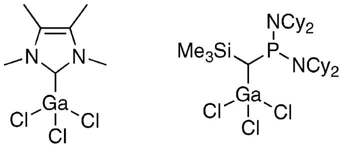
Summary: The reaction of $GaCl_3$ with 1 equiv of NHC ligand (NHC = N-heterocyclic carbene) at room temperature in pentane yielding the corresponding 1:1 adduct [$GaCl_3$(NHC)] is reported. Using IPr (N,N′-bis(2,6-diisopropylphenyl)imidazol-2-ylidene), IMes (N,N′-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene), and IPrMe (1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene), three NHC-containing Ga^{III} adducts have been synthesized in good yields and fully characterized by ^1H and ^{13}C NMR, HRMS, elemental analysis, and X-ray diffraction studies for the first time. The solid-state structure of [$GaCl_3$(IMes)] presented, as a special feature, two different positions of the main molecule with an occupation ratio of 50%. These positions of the molecule are shifted with respect to each other along the c-axis by 0.96 Å.

Introduction

N-Heterocyclic carbenes (NHCs) are now well established as excellent σ-donor ligands.[1] They are widely used for stabilizing transition metal complexes and enhancing the activity of catalytic species.[2] They have notably permitted the synthesis of a number of monomeric group 13 compounds since the isolation and characterization of [AlH_3(IMes)] (IMes = *N*,*N*′-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene) by Arduengo.[3] Surprisingly, while similar adducts of NHC group 13 trihydride ([MH_3(NHC)]) and trimethyl ([MMe_3(NHC)]) have been isolated,[4,5] little attention has been paid to the corresponding trihalide adducts.[6−8] Thus, only two carbene-containing $GaCl_3$ adducts (**1** and **2**, Figure 1) have been reported to date to the best of our knowledge.[9] Furthermore, the only NHC-containing $GaCl_3$ adduct, [$GaCl_3$(ITM)] (**1**) (ITM = 1,3,4,5-tetramethylimidazol-2-ylidene), could not be crystallized and studied by X-ray analysis;[9b] the structural nature of [$GaCl_3$(NHC)] adducts therefore remains elusive. The identity of the NHC in **1** is quite peculiar, as it is a NHC with very small steric hindrance, a feature that precludes any generalization about the synthetic route for bulkier N-heterocyclic carbenes.



1 **2**

Figure 1. Previously reported carbene−$GaCl_3$ adducts.

This is somewhat surprising since gallium trichloride is arguably the most utilized species in Ga^{III}-catalyzed organic transformations,[10] and NHCs attached to the gallium center could enhance and/or modulate the catalytic activity. Further-

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(1) For reviews, see: (a) Díez-González, S.; Nolan, S. P. *Coord. Chem. Rev.* **2007**, *251*, 874−883. (b) Hahn, F. E. *Angew. Chem., Int. Ed.* **2006**, *45*, 1348−1352. (c) Bourissou, D.; Guerret, O.; Gabbaï, F. P.; Bertrand, G. *Chem. Rev.* **2000**, *100*, 39−92.

(2) For reviews, see: (a) Mata, J. A.; Poyatos, M.; Peris, E. *Coord. Chem. Rev.* **2007**, *251*, 841−859. (b) Díez-González, S.; Nolan, S. P. *Annu. Rep. Prog. Chem., Sect. B* **2005**, *101*, 171−191. (c) Glorius, F., Ed. *N-Heterocyclic Carbenes in Transition Metal Catalysis, Topics in Organometallic Chemistry Vol. 28*; Springer-Verlag: Berlin/Heidelberg, Germany, 2007. (d) Nolan, S. P., Ed. *N-Heterocyclic Carbenes in Synthesis*; Wiley-VCH: Weinheim, Germany, 2006.

(3) Arduengo, A. J., III; Rasika Dias, H. V.; Calabrese, J. C.; Davidson, F. *J. Am. Chem. Soc.* **1992**, *114*, 9724−9725.

(4) For a review on group 13 hydride chemistry, see: Gardiner, M. G.; Raston, C. L. *Coord. Chem. Rev.* **1997**, *166*, 1−34.

(5) For studies on NHC group 13 trihydride adducts, see: (a) Kuhn, N.; Henkel, G.; Kratz, T.; Kreutzberg, J.; Boese, R.; Maulitz, A. H. *Chem. Ber.* **1993**, *126*, 2041−2045. (b) Francis, M. D.; Hibbs, D. E.; Hursthouse, M. B.; Jones, C.; Smithies, N. A. *J. Chem. Soc., Dalton Trans.* **1998**, 3249−3254. (c) Baker, R. J.; Cole, M. L.; Jones, C.; Mahon, M. F. *J. Chem. Soc., Dalton Trans.* **2002**, 1992−1996. For studies on NHC group 13 trimethyl adducts, see: (d) Li, X.-W.; Su, J.; Robinson, G. H. *Chem. Commun.* **1996**, 2683−2684.

(6) (a) Black, S. J.; Hibbs, D. E.; Hursthouse, M. B.; Jones, C.; Abdul Malik, K. M.; Smithies, N. A. *J. Chem. Soc., Dalton Trans.* **1997**, 4313−4319. (b) Cole, M. L.; Davies, A. J.; Jones, C. *J. Chem. Soc., Dalton Trans.* **2001**, 2451−2452.

(7) For a rare mixed hydride−halide compound, see: Abernethy, C. D.; Cole, M. L.; Jones, C. *Organometallics* **2000**, *19*, 4852−4857.

(8) For a theoretical study of group 13 trihalides, see: Beste, A.; Krämer, O.; Gerhard, A.; Frenking, G. *Eur. J. Inorg. Chem.* **1999**, 2037−2045.

(9) (a) Cowley, A. H.; Gabbaï, F. P.; Carrano, C. J.; Mokry, L. M.; Bond, M. R.; Bertrand, G. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 578−580. (b) Stasch, A.; Singh, S.; Roesky, H. W.; Noltemeyer, M.; Schmidt, H.-G. *Eur. J. Inorg. Chem.* **2004**, 4052−4055.

(10) For recent selected references, see: (a) Inoue, H.; Chatani, N.; Murai, S. *J. Org. Chem.* **2002**, *67*, 1414−1417. (b) Kobayashi, K.; Arisawa, M.; Yamaguchi, M. *J. Am. Chem. Soc.* **2002**, *124*, 8528−8529. (c) Chatani, N.; Inoue, H.; Kotsuma, T.; Murai, S. *J. Am. Chem. Soc.* **2002**, *124*, 10294−10295. (d) Viswanathan, G. S.; Wang, M.; Li, C.-J. *Angew. Chem., Int. Ed.* **2002**, *41*, 2138−2141. (e) Chatani, N.; Oshita, M.; Tobisu, M.; Ishii, Y.; Murai, S. *J. Am. Chem. Soc.* **2003**, *125*, 7812−7813. (f) Yonehara, F.; Kido, Y.; Sugimoto, H.; Morita, S.; Yamaguchi, M. *J. Org. Chem.* **2003**, *68*, 6752−6759. (g) Amemiya, R.; Fujii, A.; Yamaguchi, M. *Tetrahedron Lett.* **2004**, *45*, 4333−4335. (h) Yadav, J. S.; Reddy, B. V. S.; Padmavani, B.; Gupta, M. K. *Tetrahedron Lett.* **2004**, *45*, 7577−7579. (i) Oshita, M.; Yamashita, K.; Tobisu, M.; Chatani, N. *J. Am. Chem. Soc.* **2005**, *127*, 761−766. (j) Oshita, M.; Okazaki, T.; Ohe, K.; Chatani, N. *Org. Lett.* **2005**, *7*, 331−334. (k) Simmons, E. M.; Sarpong, R. *Org. Lett.* **2006**, *8*, 2883−2886. (l) Prajapati, D.; Gohain, M.; Gogoi, B. J. *Tetrahedron Lett.* **2006**, *47*, 3535−3539. (m) Huang, Z.-H.; Zou, J.-P.; Jiang, W.-Q. *Tetrahedron Lett.* **2006**, *47*, 7965−7968.

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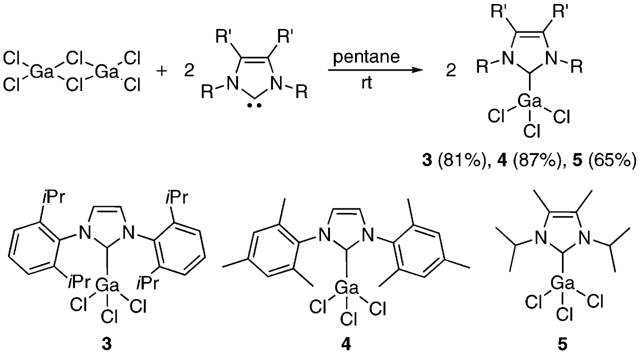
Table 1. Selected Bond Lengths (Å) and Angles (deg) of [$GaCl_3$(NHC)] 3−5

	[$GaCl_3$(IPr)], **3**	[$GaCl_3$(IMes)], **4**	[$GaCl_3$(IPrMe)], **5**
Ga−C(1)	2.016(2)	1.954(4)	2.011(4)
Ga−Cl(1)	2.173(5)	2.1674(8)	2.203(10)
Ga−Cl(2)	2.179(5)	2.1674(10)	2.197(11)
Ga−Cl(3)	2.177(6)	2.1910(8)	2.198(11)
C(2)−C(3)	1.339(3)	1.356(4)	1.373(5)
C(1)−N(1)	1.348(2)	1.376(4)	1.353(5)
C(1)−N(2)	1.351(2)	1.368(5)	1.366(5)
N(1)−C(3)	1.379(2)	1.389(5)	1.408(5)
N(2)−C(2)	1.380(3)	1.394(6)	1.401(5)
C(1)−Ga−Cl(1)	112.01(5)	113.26(8)	109.66(11)
N(1)−C(1)−N(2)	105.00(4)	102.9(3)	106.3(3)
Cl(1)−Ga−Cl(2)	107.00(2)	107.86(4)	108.40(4)
N(1)−C(3)−C(2)	106.8(2)	106.1(3)	106.6(3)

Scheme 1. Synthesis of [$GaCl_3$(NHC)] 3, 4, and 5



more, we envisaged that sterically encumbering NHC would provide increased stability to tetracoordinated Ga^{III} complexes and therefore simplify their use under aerobic conditions.

Results and Discussion

Gallium(III) trichloride was treated with 1 equiv of free N-heterocyclic carbene ligand in pentane to cleanly yield, after 1 h at room temperature, adducts of the type [$GaCl_3$(NHC)] (Scheme 1).

We first reacted IPr (*N*,*N*′-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) with $GaCl_3$, leading to complex **3**. The air- and moisture-stable white powder obtained presented the characteristic ^{1}H NMR signals for the isopropyl groups of the IPr ligand (septet at $\delta = 2.63$ ppm and 2 doublets at $\delta = 1.38$ ppm and $\delta = 1.18$ ppm). No signal for an imidazolium salt was observed. Interestingly, the resonance for the protons at the C4/C5 positions of the imidazole ring was particularly downfield ($\delta = 8.15$ ppm). The ^{13}C NMR spectrum did not bring more valuable information since we could not observe the resonance of the carbenic carbon (even with prolonged ^{13}C NMR sequence and increased d1), a feature previously reported by Roesky for compound **1**.[9b] We believe this is due to the high quadruple moment of the coordinated gallium center that broadens the signal to such an extent that it is not observable. To unambiguously confirm the structure, single crystals suitable for X-ray diffraction study were grown from a slowly evaporating acetone solution. Compound **3**, which crystallizes in the monoclinic space group $P2_1/c$, exhibited the expected atom connectivity (see Figure S1 in Supporting Information). Selected bond lengths and angles are presented in Table 1.

Using a comparable route, adducts **4** and **5** were synthesized in moderate to good yields. The [$GaCl_3$(NHC)] compounds precipitated in pentane and were washed with methanol. They were found soluble in most organic solvents but hydrocarbonated ones.

The proposed structure for compound **4** could be elucidated unambiguously by single-crystal X-ray structure analysis. [$GaCl_3$(IMes)] presented the expected atom connectivity (see Figure 2). Selected bond lengths and angles are presented in Table 1.

As a special feature, compound **4** presents in the solid state two different positions of the main molecule with an occupation ratio of 50%. These positions of the molecule are shifted with respect to each other along the *c*-axis by 0.96 Å. Probably, layers of molecules along the *c*-axes are shifted back and forward in

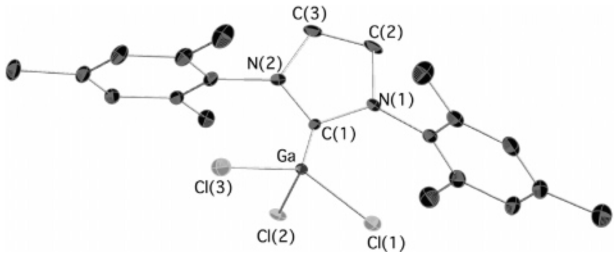


Figure 2. Crystal structure of [$GaCl_3$(IMes)] (**4**) (thermal ellipsoids at 50% probability level; hydrogen atoms are omitted for clarity).

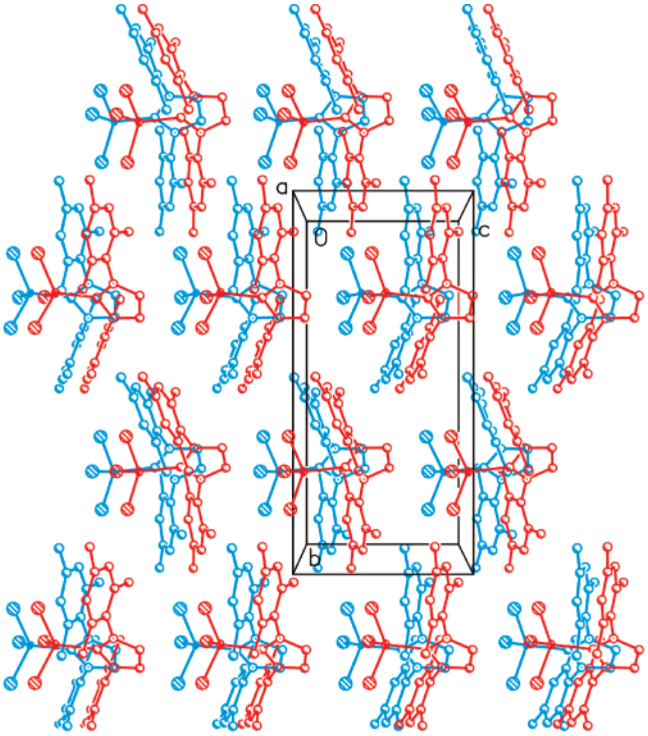


Figure 3. Crystal packing of compound **4** with view along the *a*-axis showing the shifted position of the molecules. Hydrogen atoms are omitted for clarity.

Table 2. Crystallographic Data for 3, 4, and 5

	[$GaCl_3$(IPr)], **3**	[$GaCl_3$(IMes)], **4**	[$GaCl_3$(IPrMe)], **5**
chemical formula	$C_{27}H_{36}Cl_3GaN_2$	$C_{21}H_{24}Cl_3GaN_2$	$C_{11}H_{20}Cl_3GaN_2$
M (g/mol)	564.65	480.49	356.36
T (K)	150(2)	100(2)	273(2)
cryst syst	monoclinic	orthorhombic	triclinic
space group	$P2_1/c$	$Pca2_1$	$P\bar{1}$
a (Å)	18.3566(8)	17.021(2)	9.3044(14)
b (Å)	16.1415(7)	16.803(2)	9.5428(14)
c (Å)	20.1819(8)	7.9054(11)	10.4460(16)
α (deg)	90.00	90.00	100.038(3)
β (deg)	103.0580(10)	90.00	94.926(3)
γ (deg)	90.00	90.00	117.304(2)
V (Å^3)	5825.3(4)	2261.0(5)	796.8(2)
Z	8	4	2
density(calcd) (g cm^{-3})	1.288	1.412	1.485
absorp coeff (mm^{-1})	1.237	1.580	2.212
F(000)	2352	984	364
cryst size (mm)		0.40 × 0.05 × 0.03	0.50 × 0.30 × 0.15
θ (deg)	2.12−22.50	2.70−37.58	2.475−30.851
index range hkl	−19 to +19, −17 to +17, −21 to +21	−29 to +29, −28 to +28, −7 to +13	−11 to +11, −11 to +11, −12 to +12
no. of data/restraints/params	7614/548/611	9569/25/500	2795/140/160
goodness-of-fit on F^2	0.923	1.053	1.134
R values (all data)	$R_1 = 0.0264$ $wR_2 = 0.0687$	$R_1 = 0.0647$ $wR_2 = 0.1174$	$R_1 = 0.0486$ $wR_2 = 0.1236$

the solid framework, presenting the final overlapped structure model. This particular crystal packing with the overlapped structures is presented in Figure 3. The obtained model refined in the orthorhombic polar space group $Pca2_1$ (a, 17.0210 Å; b, 16.8034 Å; c, 7.9054 Å) with excellent statistics and presented only a few correlations of atoms in close positions. Structures solved in smaller (a, 11.9750 Å; b, 11.9750 Å; c, 7.8980 Å) and larger (a, 17.0295 Å; b, 7.9029 Å; c, 33.5977 Å) orthorhombic crystal cells did not refine successfully and the R_1 value could not be lowered below 20%.

Interestingly, [$GaCl_3$(IPrMe)] (**5**) (IPrMe = 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene), which crystallizes in the triclinic space group $P\bar{1}$ (crystal structure is shown in Figure S2 in the Supporting Information, and selected bond lengths and angles are given in Table 1), presented a much shorter Ga−C(1) bond than its trihydride and trimethyl congeners, 2.011(4), 2.071(5), and 2.13(2), respectively (in Å), probably due to a stronger interaction between the NHC and the electron-poor gallium bearing three chloride ligands.

The three complexes described above adopt a slightly distorted tetragonal-pyramid geometry around the gallium center. In all cases, the gallium−carbene bond, Ga−C(1), was much shorter than the Ga−Cl bonds by 0.18 Å on average, with the IMes-containing adduct presenting the shortest of all Ga−C(1) bonds (1.954(4) Å). A consequence of this feature could be observed in the wider carbene−gallium−chloride angle when compared to the Cl−Ga−Cl angle, which is believed to be an effect of the steric pressure of the NHC substituents on the chlorides. Remarkably, this effect was significant only in **3** and **4**, both possessing bulky aryl-substituted moieties on the NHC nitrogens. The structure of **5**, showing the slight hindrance of the IPrMe ligand, presented a near-perfect tetragonal-pyramid arrangement with C−Ga−Cl and Cl−Ga−Cl angles very close to 109°.

It is noteworthy that, regardless of the steric hindrance brought about by the NHC ligand, the [$GaCl_3$(NHC)] adducts described here are indefinitely air- and moisture-stable and do not decompose in solution, even in polychlorinated solvents.[11]

In conclusion, we have reported the very straightforward synthesis of three air- and moisture-stable NHC-containing Ga^{III} complexes. These [$GaCl_3$(NHC)] adducts were fully characterized and studied by X-ray analysis for the first time. Studies aimed at employing these compounds in organometallic catalysis are ongoing in our laboratories.

Experimental Section

General Information. $GaCl_3$ was purchased as a crystalline solid from Aldrich, used as received, and stored in a glovebox. All NHCs were synthesized according to literature procedures.[12] Anhydrous pentane was used as purchased. ^1H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a Varian-400, Bruker-400, or Bruker-500 MHz spectrometer at ambient temperature in CD_2Cl_2, C_6D_6, $CDCl_3$, and acetone-d_6 containing tetramethylsilane (Cambridge Isotope Laboratories, Inc). Elemental analyses were performed at Robertson Microlit Laboratories, Inc., Madison, NJ. HRMS analyses were performed by the Mass Spectrometry Facility at the Institute of Chemical Research of Catalonia (ICIQ), Tarragona (Spain). Crystallographic data are summarized in Table 2. CCDC-628373 ([$GaCl_3$(IPr)], **3**), CCDC-631974 ([$GaCl_3$(IMes)], **4**), and CCDC-628372 ([$GaCl_3$(IPrMe)], **5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk).

Synthesis and Characterization of [$GaCl_3$(NHC)]. General Procedure. In a glovebox, in a 250 mL round-bottom flask, NHC (1 equiv) is mixed with 70 mL of pentane and stirred for 30 min. $GaCl_3$ (1 equiv), as a crystalline solid, is then added in one portion, resulting in the immediate appearance of a white precipitate. The solution is stirred for 1 h and then filtered in air. The white solid collected is then washed with MeOH and dried.

(1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene)gallium(III) Chloride (3), [$GaCl_3$(IPr)]. The general procedure, using IPr (400 mg, 1.023 mmol) and $GaCl_3$ (180 mg, 1.023 mmol), yielded 467 mg (81%) of the title compound.

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[11] As a testimony to their stability, samples of **3**, **4**, and **5** retrieved from our laboratories in New Orleans showed no signs of decomposition by ^1H and ^{13}C NMR after being subjected for three months to harsh environmental conditions (90/95 °F, high humidity, and high level of volatile chemicals) imposed by hurricane Katrina.

[12] For synthesis of NHCs, see: (a) Arduengo, A. J., III; Calabrese, J. C.; Davidson, F.; Rasika Dias, H. V.; Goerlich, J. R.; Krafczyk, R.; Marshall, W. J.; Tamm, M.; Schmutzler, R. *Helv. Chim. Acta* **1999**, *82*, 2348−2364, and references therein. (b) Trnka, T. M.; Grubbs, R. H. *Acc. Chem. Res.* **2001**, *34*, 18−29, and references therein. (c) Huang, J.; Nolan, S. P. *J. Am. Chem. Soc.* **1999**, *120*, 9889−9890.

^{1}H NMR (δ, 400 MHz, acetone-d_6): 8.15 (s, 2H, $=$CH^{Im}), 7.57 (t, $J = 7.6$ Hz, 2H, p-H$^{\mathrm{Ar}}$), 7.40 (d, $J = 7.6$ Hz, 4H, m-H$^{\mathrm{Ar}}$), 2.63 (sept, $J = 6.8$ Hz, 4H, CH(CH$_3$)$_2$), 1.38 (d, $J = 6.8$ Hz, 12H, Me), 1.18 (d, $J = 6.8$ Hz, 12H, Me). ^{13}C NMR (δ, 100 MHz, CD$_2$Cl$_2$): 145.7 (C, C$^{\mathrm{Ar}}$), 132.5 (C, C$^{\mathrm{Ar}}$), 131.4 (CH, $=$$CH^{\mathrm{Im}}$), 126.4 (CH, C$^{\mathrm{Ar}}$), 124.2 (CH, C$^{\mathrm{Ar}}$), 29.1 (CH, CH(CH$_3$)$_2$), 25.6 (CH$_3$, CH(CH$_3$)$_2$), 22.3 (CH$_3$, CH(CH$_3$)$_2$). HRMS: calcd for $C_{29}H_{39}Cl_3GaN_3Na$ (M + Na + MeCN) 626.1363, found 626.1358. Anal. Calcd for $C_{27}H_{36}Cl_3GaN_2$ (MW 564.65): C, 57.43; H, 6.43; N, 4.96. Found: C, 57.78; H, 6.15; N, 4.99.

(1,3-Dimesitylimidazol-2-ylidene)gallium(III) Chloride (4), [GaCl$_3$(IMes)]. The general procedure, using IMes (800 mg, 2.632 mmol) and GaCl$_3$ (465 mg, 2.634 mmol), yielded 1.101 g (87%) of the title compound.

^{1}H NMR (δ, 400 MHz, CDCl$_3$): 6.71 (s, 4H, H$^{\mathrm{Ar}}$), 5.78 (s, 2H, $=$CH^{Im}), 2.05 (s, 6H, p-Me), 2.00 (s, 12H, o-Me). ^{13}C NMR (δ, 100 MHz, acetone-d_6): 146.6 (C, C$^{\mathrm{Ar}}$), 136.3 (CH, $=$$CH^{\mathrm{Im}}$), 134.4 (C, C$^{\mathrm{Ar}}$), 130.2 (CH, C$^{\mathrm{Ar}}$), 127.1 (C, C$^{\mathrm{Ar}}$), 21.2 (CH$_3$, p-Me), 17.9 (CH$_3$, o-Me). HRMS: calcd for $C_{23}H_{27}Cl_2GaN_3$ (M − Cl + MeCN) 484.0838, found 484.0851. Anal. Calcd for $C_{21}H_{24}Cl_3GaN_2$ (MW 480.49): C, 52.49; H, 5.03; N, 5.83. Found: C, 52.48; H, 5.15; N, 5.99.

(1,3-Diisopropyl-4,5-dimethylimidazol-2-ylidene)gallium(III) Chloride (5), [GaCl$_3$(IPrMe)]. The general procedure, using IPrMe (364 mg, 2.00 mmol) and GaCl$_3$ (352 mg, 2.00 mmol), yielded 463 mg (65%) of the title compound.

^{1}H NMR (δ, 400 MHz, CDCl$_3$): 5.73 (sept, $J = 7.6$ Hz, 2H, CH(CH$_3$)$_2$), 1.35 (s, 6H, Me$^{\mathrm{Im}}$), 0.98 (d, $J = 7.6$ Hz, 12H, CH(CH_3)$_2$). ^{13}C NMR (δ, 100 MHz, C$_6$D$_6$): 127.4 (C, C$^{\mathrm{Im}}$), 53.4 (CH, CH(CH$_3$)$_2$), 21.6 (CH$_3$, CH(CH$_3$)$_2$), 10.4 (CH$_3$, Me$^{\mathrm{Im}}$). HRMS: calcd for $C_{13}H_{23}Cl_2GaN_3$ (M − Cl + MeCN) 360.0525, found 360.0533. Anal. Calcd for $C_{11}H_{20}Cl_3GaN_2$ (MW 356.36): C, 37.07; H, 5.66; N, 7.86. Found: C, 37.23; H, 5.85; N, 7.71.

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Supporting Information Available: Crystal structures of (**3**) and (**5**) (thermal ellipsoids at 50% probability level) and crystallographic information files (CIFs) for **3**−**5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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