

Article

Sterically Bulky NHC Adducts of GaMe₃ and InMe₃ for H₂ Activation and Lactide Polymerization

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Abstract: The sterically bulky Ga(III) and In(III) (IPr*)MMe₃ adducts (**1** and **2**) and (SI*t*Bu)MMe₃ adducts (**3** and **4**) (M = Ga, In; IPr* = 1,3-bis{2,6-bis(diphenylmethyl)-4-methylphenyl}-1,3-dihydroimidazol-2-ylidene; SI*t*Bu = 1,3-bis(1,1-dimethylethyl)-imidazolidin-2-ylidene) were prepared and structurally characterized, allowing an estimation of the steric hindrance of such Lewis pairs (yields in **1–4**: 92%, 90%, 73%, and 42%, respectively). While the IPr* adducts **1** and **2** are robust species, the more severely congested SI*t*Bu adducts **3** and **4** are more reactive and exhibit a limited stability in solution. Adduct (SI*t*Bu)GaMe₃ (**3**) reacts quickly with H₂ at room temperature to afford the corresponding amination product, 1,3-di-*tert*-butylimidazolidine (**5**), along with free GaMe₃. Such Frustrated Lewis Pair (FLP) reactivity constitutes the first instance of a H₂ activation involving a simple trialkyl GaR₃ species. Adduct **3** also mediates the ring-opening polymerization (ROP) of *rac*-lactide at room temperature to afford cyclic polylactide (PLA).

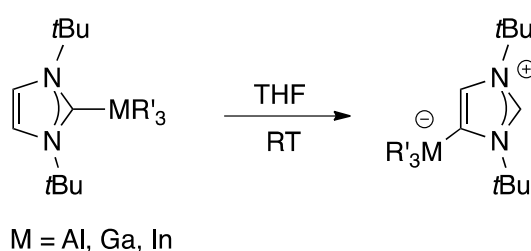
Keywords: *N*-heterocyclic carbene; gallium; indium; H₂ activation

1. Introduction

Thanks to their exceptional σ -donating properties and steric tunability, *N*-heterocyclic carbenes (NHCs) constitute a privileged class of supporting ligands for the stabilization of various metal complexes [1–5]. This has led to the widespread use of NHC-supported metal species in numerous research fields, notably in metal-based homogeneous catalysis and for the characterization of unusual organometallic motifs [6,7].

The coordination (and related reactivity studies) of NHCs to oxophilic and high-oxidation-state metal centers such as group 13 metals M(III) (M = Al, Ga, In) is currently attracting growing attention [8]. For the most part, this is due to the potential usefulness of the derived Lewis adducts for novel reactivity and/or small molecule activation, in particular through Frustrated Lewis Pair (FLP) reactivity [9]. FLP reactivity has attracted tremendous attention over the past few years thanks to the ability of sterically hindered Lewis pairs and FLPs to activate numerous polar/unsaturated substrates, including H₂ and CO₂ [9–11]. In the area of group 13 metal species, we and others have shown that sterically bulky group 13 metal Lewis adducts may display limited stability and readily isomerize to their “abnormal” counterparts for steric relief of (NHC)MMe₃ (Scheme 1, taking the example of adducts (I*t*Bu)MMe₃) [12–14].

In the case of the bulky adduct (I*t*Bu)AlMe₃, steric hindrance may also promote an unusual deprotonation of the AlMe₃ moiety by I*t*Bu in the presence of Al₂Me₆ [15]. The I*t*Bu/Al(I*t*Bu)₃ FLP system was also shown to activate H₂ at room temperature [13]. The reactivity of lower group 13 metal Ga(III)–/In(III)–NHC Lewis pairs has been less studied, though recent studies have detailed FLP activation of various polar substrates with an NHC/GaR₃ mixture (R = alkyl, carbyl) [16,17].



Scheme 1. Isomerization of *N*-heterocyclic carbene (NHC) adducts of group 13 metal complexes.

To further probe the structural features and reactivity of sterically hindered Ga(III) and In(III) of the type NHC–MR₃ (R = alkyl, carbyl), the use of bulky NHCs IPr* and SI*t*Bu (IPr* = 1, 3-bis{2,6-bis(diphenylmethyl)-4-methylphenyl}-1,3-dihydro-imidazol-2-ylidene, SI*t*Bu = 1,3-bis(1,1-dimethylethyl)-imidazolidin-2-ylidene; Figure 1) for adduct formation with GaMe₃ and InMe₃ was studied.

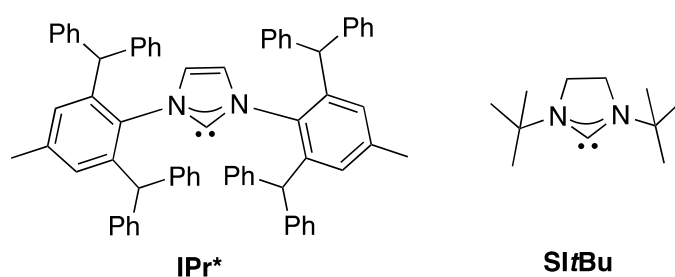


Figure 1. Structures of NHCs IPr* and SI*t*Bu.

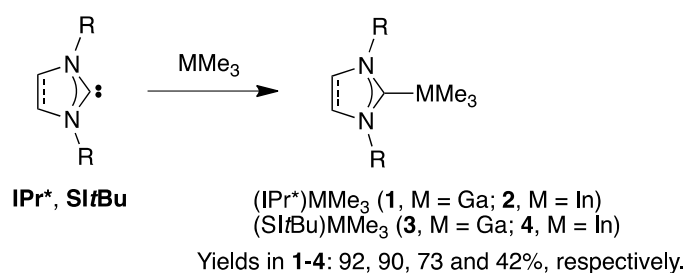
We herein report the synthesis and structural characterization of such adducts and their reactivity with H₂, leading, as described below, to the first instance of H₂ activation by a simple NHC/GaMe₃ system. Preliminary results on the use of such compounds as lactide ring-opening polymerization catalysts are also discussed.

2. Results

2.1. Adducts (IPr*)MMe₃ (**1**, M = Ga; **2**, M = In)

The superbulky NHC carbene IPr*, first reported by Marko and co-workers in 2010 [18], is frequently referred to as an “exceptionally bulky NHC with some flexible sterics” in several reports, and thus appeared to be a suitable candidate for our studies [19]. While a number of IPr*-supported complexes of late transition metals are known, the coordination of IPr* to oxophilic metal centers is thus far unreported.

The reaction of IPr*, which was prepared according to literature procedures, with a stoichiometric amount of MMe₃ (room temperature, toluene, 2 h) led to the quantitative formation of corresponding (IPr*)MMe₃ adducts (**1**, M = Ga; **2**, M = In; Scheme 2), isolated in high yield as colorless solids (90% and 92% yield, respectively) [18,19]. The NMR data for **1** and **2** are consistent with the coordination of IPr* to the M(III) centers. In particular, the ¹³C NMR C_{carbene} chemical shifts (δ 183.4 and 185.8 ppm for **1** and **2**, respectively) lie in the expected range for NHC–Ga and NHC–In species and are significantly upfield shifted versus that of free IPr* (δ 220.0 ppm). Somewhat surprisingly given the steric properties of IPr*, adducts **1** and **2** are stable species in solution at room temperature, including in a coordinative solvent such as THF. Likewise, as monitored by ¹H NMR, species **1** and **2** are thermally robust and retain their integrity upon prolonged heating (C₆D₆, 48 h, 80 °C). The latter observations sharply contrast with the instability of their (I*t*Bu)MMe₃ counterparts (Scheme 1).



Scheme 2. Synthesis of NHC adducts **1-4**.

As determined through X-ray crystallographic studies (XRD), the solid-state molecular structure of **2** confirmed the effective coordination of IPr^* to InMe_3 , resulting in a four-coordinate In(III) adopting a distorted tetrahedral geometry and coplanar to the NHC heterocyclic ring (Figure 2). The $\text{In}-\text{C}_{\text{carbene}}$ bond distance (2.330(5) Å) in **2** is a bit longer than those in $(\text{IMes})\text{InMe}_3$ and $(\text{IPr})\text{InMe}_3$ (2.292(6) and 2.309(2) Å, respectively; IMes = 1,3-bis(2,4,6-trimethylphenyl)-1,3-dihydro-imidazol-2-ylidene; IPr = 1,3-bis[2,6-bis(1-methylethyl)phenyl]-1,3-dihydro-imidazol-2-ylidene), likely reflecting greater steric hindrance between the NHC and InMe_3 in **2** [20,21]. However, the shortest contacts between IPr^* and InMe_3 ($\text{H}\cdots\text{H}$ = 2.257 Å and $\text{C}\cdots\text{H}$ = 2.747 Å) remain close to the sum of the van der Waals (vdW) radii of the corresponding atoms, in line with no severe steric congestion in **2** and in agreement with the observed stability of adduct $(\text{IPr}^*)\text{InMe}_3$ in solution [22].

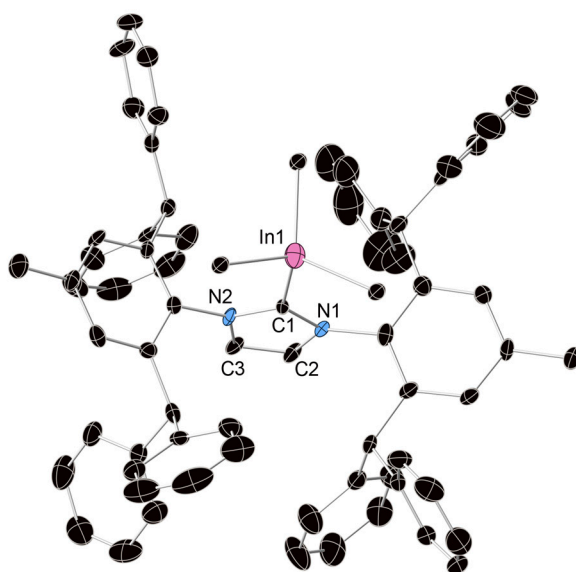


Figure 2. Molecular structure of adduct $(\text{IPr}^*)\text{InMe}_3$ (**2**, ORTEP view, the ellipsoids are at 50% probability level). Hydrogen atoms are omitted for clarity. Selected bond distances (Å): $\text{In}(1)-\text{C}(1)$ = 2.330(5), $\text{C}(1)-\text{N}(1)$ = 1.368(5), $\text{C}(1)-\text{N}(2)$ = 1.355(6), $\text{C}(2)-\text{C}(3)$ = 1.335(6).

2.2. Adducts $(\text{SttBu})\text{MMe}_3$ (**3**, $M = \text{Ga}$; **4**, $M = \text{In}$)

As earlier mentioned, the sterically hindered Lewis pairs $(\text{ItBu})\text{MMe}_3$ ($M = \text{Ga}, \text{In}$) are unstable and rearrange to the corresponding C4-bonded isomers $(a\text{ItBu})\text{MMe}_3$ (Scheme 1) [12–14]. To avoid such isomerization, the backbone-saturated carbene SttBu , prepared according to a known procedure [23], was coordinated to GaMe_3 and InMe_3 . Thus, reaction of SttBu with one equiv. of $\text{GaMe}_3/\text{InMe}_3$ (pentane, -35°C to room temperature, 30 min) led to the formation of species $(\text{SttBu})\text{MMe}_3$ (**3**, $M = \text{Ga}$; **4**, $M = \text{In}$), which were isolated in moderate to good yields as highly air-sensitive colorless solids (73% and 42% yield, respectively). Unlike adducts **1** and **2**, species **3** and **4** display a limited stability

in common solvents. While stable for days in benzene/toluene at room temperature (under inert atmosphere), they quickly decompose to unknown species in CH_2Cl_2 and THF at room temperature, in line with severely hindered Lewis pairs. The NMR data for **3** and **4** only display sharp resonances that are consistent with the proposed adduct formulation. Taking the example of the In(III) species **4**, the ^1H NMR spectrum contains a singlet resonance for the $\text{StBu}-\text{CH}_2\text{CH}_2$ moiety (δ 2.82 ppm, 4 H), upfield shielded relative to that in free StBu (δ 1.33 ppm), as well as a characteristic singlet in the In–Me region (δ 0.01 ppm, 9 H). No evidence for adduct dissociation is observable under the studied conditions for either **3** or **4** (C_6D_6 , room temperature).

The solid-state molecular structures of adducts **3** and **4**, as established by XRD studies, confirmed the effective coordination of $\text{SI}t\text{Bu}$ to the Ga(III) and In(III) metal centers, respectively (Figures 3 and 4). In species **3**, the Ga– $\text{C}_{\text{carbene}}$ bond distance (2.195(2) Å) is significantly longer (\approx 0.07 Å) than those in related adducts (SIMes)GaMe₃ and (SI*Pr*)GaMe₃ (2.124(5) and 2.137(2) Å, respectively) [21]. The latter, together with very short contacts between the NHC and the GaMe₃ moieties (shortest distances between $\text{SI}t\text{Bu}$ and GaMe₃: Ga···H = 2.581 Å, H···H = 2.009 Å, C···H = 2.550 Å) well below the sum of the vdW radii of the corresponding atoms, indicates that adduct **3** is severely crowded.

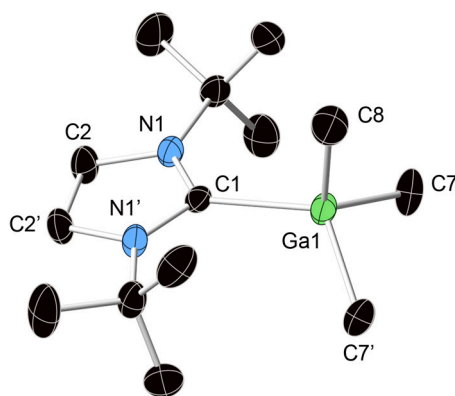


Figure 3. Molecular structure of adduct (SI*t*Bu)GaMe₃ (**3**, ORTEP view, the ellipsoids are at 50% probability level). Hydrogen atoms are omitted for clarity. Selected bond distances (Å): Ga(1)–C(1) = 2.195(2), C(1)–N(1) = 1.351(2), C(2)–C(2') = 1.496(3).

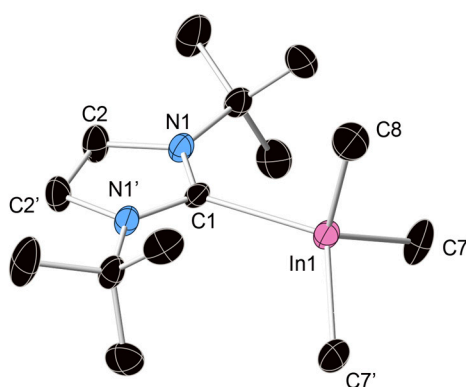


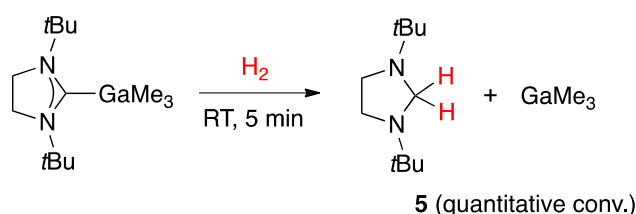
Figure 4. Molecular structure of adduct (SI*t*Bu)InMe₃ (**4**, ORTEP view, the ellipsoids are at 50% probability level). Hydrogen atoms are omitted for clarity. Selected bond distances (Å): In(1)–C(1) = 2.399(2), C(1)–N(1) = 1.350(2), C(2)–C(2') = 1.500(4).

The solid-state molecular structure of the In(III) adduct (SI*t*Bu)InMe₃ (**4**) features a longer In– $\text{C}_{\text{carbene}}$ bond distance (2.399(2) Å) versus those in (SIMes)InMe₃ and (SI*Pr*)InMe₃ (2.304(8) and 2.342(2) Å, respectively) [20,21]. Comparing adducts **3** and **4**, the longer In– $\text{C}_{\text{carbene}}$ (versus Ga– $\text{C}_{\text{carbene}}$)

bond distance decreases steric congestion in adduct **4** (versus **3**), as suggested by longer NHC/ MMe_3 atom contacts in **4** (shortest contacts: $\text{In}\cdots\text{H} = 2.642 \text{ \AA}$, $\text{H}\cdots\text{H} = 2.169 \text{ \AA}$, $\text{C}\cdots\text{H} = 2.660 \text{ \AA}$).

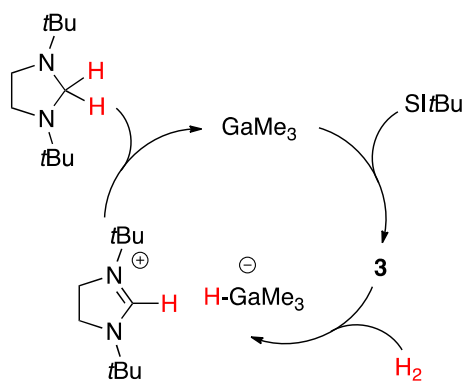
2.3. Reactivity of Adducts 1–4 with H_2

As sterically bulky Lewis adducts, the Ga- and In-based adducts are potential candidates for FLP reactivity. Ga- and In-based intermolecular FLP systems remain rare [16,17]. The reactivity of NHC adducts 1–4 with H_2 was therefore studied. In line with their stability and robustness in solution, IPr^* adducts **1** and **2** were found to not react with H_2 (1.5 bar) even under prolonged heating ($80 \text{ }^\circ\text{C}$, C_6D_6 , 48 h). In sharp contrast and satisfyingly, the most sterically hindered adduct ($\text{SI}t\text{Bu}$) GaMe_3 (**3**) exhibits FLP reactivity as it reacts quickly with H_2 (1.5 bar of H_2 , room temperature, 5 min) to quantitatively yield the corresponding amination derivative, 1,3-di-*tert*-butylimidazolidine (**5**), along with free GaMe_3 , as deduced from ^1H NMR data (Scheme 3) [24]. Note that neither $\text{SI}t\text{Bu}$ nor GaMe_3 alone react with H_2 under such conditions.



Scheme 3. Reaction of ($\text{SI}t\text{Bu}$) GaMe_3 with H_2 .

A similar H_2 activation was observed for the $\text{ItBu}/\text{Al}(i\text{Bu})_3$ FLP system with H_2 [13]. The formation of product **5** is likely to proceed via a H_2 heterolytic cleavage (mediated to **3**) to yield transient salt species ($\text{SI}t\text{Bu}-\text{H})(\text{HGaMe}_3)$ (Scheme 4). The latter may then decompose via hydride transfer from the Ga center to the C2-imidazolium atom of $\text{SI}t\text{Bu}-\text{H}^+$ to afford **5** and regenerate GaMe_3 . Consistent with the latter proposal, a $\text{SI}t\text{Bu}/\text{GaMe}_3$ mixture in a 1/0.4 ratio, i.e., with a substoichiometric amount of GaMe_3 , also rapidly reacted and led to the quantitative conversion of $\text{SI}t\text{Bu}$ to amination **5** along with 0.4 equiv. of free GaMe_3 (Figure S8). Formally, GaMe_3 thus catalyzes the formation of **5** from **3** and H_2 (Scheme 4). Unlike its Ga(III) counterpart, the In(III) adduct **4** led to a complicated mixture of products upon reaction with H_2 (1.5 bar of H_2 , room temperature, 3 h), among which only derivative **5** could be identified. The distinct reactivities towards H_2 of **3** and **4** versus **5** is certainly related to greater steric hindrance between the NHC and the MMe_3 fragments in **3** and **4**, prompting their easier dissociation and subsequent reactivity with H_2 .

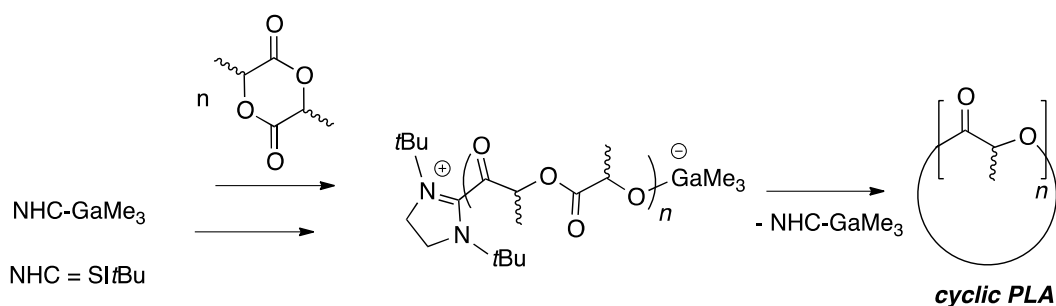


Scheme 4. GaMe_3 -catalyzed hydrogenation of $\text{SI}t\text{Bu}$ to afford imidazolidine **5** through Frustrated Lewis Pair (FLP) reactivity.

2.4. Reactivity of Adducts 1–4 with Lactide

Over the past twenty years, group 13 metal alkoxide complexes supported by various ligand platforms have been widely and successfully investigated as ring-opening polymerization (ROP) initiators of cyclic esters/carbonates for the production of well-defined biodegradable poly-esters/-carbonates [25–27]. More recently, the polymerization of polar/unsaturated monomers, including cyclic esters, initiated by simple Al-based Lewis adducts has attracted attention [28,29]. Such a Lewis pair polymerization (LPP) relies on the cooperative activation of the monomer by the Lewis acid/base fragments and may be related to FLP reactivity.

The Lewis adducts 1–4 were thus tested as lactide (LA) ROP initiators (100 equiv. of *rac*-lactide (*rac*-LA), toluene, room temperature, 18 h). Adducts 1, 2, and 4 promote the ROP of *rac*-lactide to quantitatively yield ill-defined and broadly disperse polylactide (PLA), as deduced from Size Exclusion Chromatography (SEC) data ($1000 < M_n < 5000 \text{ g}\cdot\text{mol}^{-1}$, $3 < D < 4$). On the contrary, narrow disperse PLA ($M_n = 4500 \text{ g}\cdot\text{mol}^{-1}$, $D = 1.12$) was quantitatively produced using the Ga adduct 3 as the ROP catalyst. The MALDI-TOF data of the prepared PLA display peaks that are equally spaced by 72 a.u., which is consistent with transesterified PLA (Figure S9). Also, both the mass values and the ^1H NMR data for the isolated PLA agree with the absence of any chain-end signals, and, therefore, with a cyclic PLA (Figure S10, SI). We recently reported the formation of cyclic PLA using related NHC–AlMe₃ Lewis pairs as lactide ROP catalysts [20]. It therefore seems likely that an analogous ROP mechanism is presently at play, involving a zwitterionic chain growing species that undergoes an intramolecular nucleophilic attack to form cyclic PLA and regenerate adduct 3 (Scheme 5).



Scheme 5. ROP of lactide mediated by adduct (SI*t*Bu)GaMe₃.

3. Materials and Methods

All experiments were carried out under N₂ using standard Schlenk techniques or in an MBraun Unilab glovebox (MBraun, Garching, Germany). Toluene and pentane were collected after being passed through drying columns and stored over activated molecular sieves (4 Å) for 24 h in a glovebox prior to use. Tetrahydrofuran was distilled over Na/benzophenone and stored over activated molecular sieves (4 Å) for 24 h in a glovebox prior to use. CD₂Cl₂ and C₆D₆ were distilled from CaH₂, degassed under a N₂ flow, and stored over activated molecular sieves (4 Å) in a glovebox prior to use. GaMe₃ and InMe₃ were purchased from Strem Corporation (MA, USA). IPr* and 1,3-di-*tert*-butylimidazolin-2-ylidene (SI*t*Bu) [18,23]. The NMR spectra were recorded on Bruker AC 300, 400, or 500 MHz NMR spectrometers in Teflon-valved J-Young NMR tubes. ^1H and ^{13}C chemical shifts are reported versus SiMe₄ and were determined by reference to the residual ^1H and ^{13}C solvent peaks. Mass spectra were performed at the Mass Spectrometry Department of the University of Strasbourg. Mass spectra were acquired on a time-of-flight mass spectrometer (MALDI-TOF-TOF Autoflex II TOF-TOF, Bruker Daltonics, Bremen, Germany) equipped with a nitrogen laser ($\lambda = 337 \text{ nm}$). An external multipoint calibration was carried out before each measurement with a standard peptide mixture and a standard protein mixture (depending on the mass range analysed). Scan accumulation and data processing were performed with FlexAnalysis 3.4 software (Bruker Daltonics, Bremen,

Germany). α -Cyano-4-hydroxy-cinnamic acid (CHCA), dithranol (DIT), or super-DHB (a 9/1 mixture of dihydroxybenzoid acid/2-hydroxy-5-methoxybenzoic acid) was used as the matrix for analysis of the prepared PLA samples. SEC analyses were performed on a SEC system equipped with a Shimadzu RID10A refractometer detector using HPLC-grade THF as an eluant (MilliporeSigma, MA, USA). Molecular weights and polydispersity indices (PDIs) were calculated using polystyrene standards. Molecular weight numbers (M_n) were corrected with the appropriate correcting factor (0.58) for the M_n values.

3.1. Synthesis of (IPr*)MMe₃ (1, M = Ga; 2, M = In)

In a glovebox, a toluene solution of free carbene IPr* (400 mg, 0.438 mmol) was added dropwise via a pipette of toluene solution (10 mL) of MMe₃ (M = Ga or In, 0.438 mmol) under vigorous stirring. The latter mixture was stirred for 1 h to room temperature then dried in vacuo to afford a colorless solid residue that was washed twice with pentane. It was further dried in vacuo to quantitatively afford the corresponding (IPr*)GaMe₃ (1) and (IPr*)InMe₃ (2) adducts as NMR-pure colorless solids. **Data for compound 1.** 92% yield. X-ray quality crystals were grown from a pentane/toluene solution cooled at -35 °C. ¹H NMR (400 MHz, C₆D₆): δ = -0.08 (s, 9H, Ga(CH₃)₃), 1.78 (s, 6H, *p*-CH₃), 5.02 (s, 2H, CH^{Im}), 5.69 (s, 4H, CHPh₂), 6.74–6.86 (m, 20H, CH_{Ph}), 7.04 (t, *J* = 7.5 Hz, 4H, CH_{Ph}), 7.14 (s, 4H, CH_{Ar}), 7.20 (t, *J* = 7.5 Hz, 8H, CH_{Ph}), 7.59 (d, *J* = 7.5 Hz, 8H, CH_{Ph}) ppm; ¹³C{¹H} NMR (125.8 MHz, C₆D₆): δ = -3.2 (Ga(CH₃)₃), 21.3 (*p*-CH₃), 52.2 (CHPh₂), 123.6 (CH_{Im}), 126.6, 127.2, 128.8, 129.8, 130.3, 131.1, 135.1, 140.0, 142.5, 143.2, 144.8, 183.4 (C_{carbene}) ppm. **Data for compound 2.** 90% yield. ¹H NMR (500 MHz, C₆D₆): δ = -0.11 (s, 9H, In(CH₃)₃), 1.77 (s, 6H, *p*-CH₃), 5.11 (s, 2H, CH_{Im}), 5.66 (s, 4H, CHPh₂), 6.75–6.88 (m, 20H, CH_{Ph}), 7.04 (t, *J* = 7.5 Hz, 4H, CH_{Ph}), 7.13 (s, 4H, CH_{Ar}), 7.19 (t, *J* = 7.5 Hz, 8H, CH_{Ph}), 7.52 (d, *J* = 7.5 Hz, 8H, CH_{Ph}) ppm; ¹³C{¹H} NMR (125.8 MHz, C₆D₆): δ = -7.7 (In(CH₃)₃), 21.3 (*p*-CH₃), 52.1 (CHPh₂), 124.1 (CH_{Im}), 126.7, 127.2, 128.4, 128.7, 129.8, 130.5, 131.0, 135.4, 140.1, 142.5, 143.2, 144.5, 185.8 (C_{carbene}) ppm.

3.2. (Si*t*Bu)MMe₃ (3, M = Ga; 4, M = In)

In a glovebox, a precooled pentane solution (-35 °C, 10 mL) of free carbene 1,3-di-*tert*-butylimidazol-2-ylidene (Si*t*Bu, 100.0 mg, 0.55 mmol) was added dropwise via a pipette to a precooled (-35 °C) pentane solution (5 mL) of MMe₃ (M = Ga or In, 0.55 mmol) under vigorous stirring. The resulting colorless solution was allowed to warm to room temperature, provoking, upon warming, the massive precipitation of a colorless solid. The latter suspension was stirred for 10 min at room temperature after which it was filtered through a glass frit. The collected colorless solid was dried in vacuo to afford the corresponding adduct (Si*t*Bu)MMe₃ (3, M = Ga; 4, M = In). For both 3 and 4, X-ray quality crystals were grown from a saturated pentane solution cooled at -35 °C. **Data for compound 3.** 123 mg, 73% yield. ¹H NMR (300 MHz, C₆D₆): δ = -0.06 (s, 9H, Ga(CH₃)₃), 1.32 (s, 18H, *t*Bu), 2.83 (s, 4H, (CH₂)_{Im}) ppm; ¹³C{¹H} NMR (75 MHz, C₆D₆): δ = -0.8 (Ga(CH₃)₃), 30.1 (C(CH₃)₃), 44.7 ((CH₂)_{Im}), 54.6 (C(CH₃)₃), 232.1 (C_{carbene}) ppm. **Data for compound 4.** 79 mg, 42% yield. Anal. Calcd. for C₁₄H₃₁InN: C 49.13, H 9.13; found: C 49.24, H 9.12; ¹H NMR (300 MHz, C₆D₆): δ = -0.01 (s, 9H, In(CH₃)₃), 1.31 (s, 18H, *t*Bu), 2.82 (s, 4H, (CH₂)_{Im}) ppm; ¹³C{¹H} NMR (75 MHz, C₆D₆): δ = -0.3 (In(CH₃)₃), 30.1 (C(CH₃)₃), 45.0 ((CH₂)_{Im}), 55.2 (C(CH₃)₃), 223.3 (C_{carbene}) ppm.

3.3. Reaction of Adducts 1–4 with H₂

A Teflon-valved J-Young NMR tube containing a C₆D₆ solution of the desired adduct (NHC)MMe₃ (10 mg, NHC = IPr*, *t*Bu or Si*t*Bu, M = Ga or In, 0.5 mL) was charged with H₂ (1.5 bar) at room temperature. The reaction was monitored by ¹H NMR spectroscopy until consumption of the starting (NHC)MMe₃ adduct was completed. In the case of adduct 3, immediate and quantitative conversion to 1,3-di-*tert*-butylimidazolidine and free GaMe₃ was observed.

1,3-Di-*tert*-butylimidazolidine [24]. ¹H NMR (300 MHz, C₆D₆): δ = 1.00 (s, 18H, *t*Bu), 2.70 (s, 4H, $-N-CH_2-CH_2-N-$), 3.67 (s, 2H, $N-CH_2-N$).

3.4. Typical Procedure for the ROP of Lactide Initiated by Complexes 1–4

In a N₂-filled glovebox, the desired Lewis pair initiator (0.05 mmol) was charged in a vial equipped with a Teflon[®]-tight screw-cap and *rac*-lactide solution (100 equiv., [*rac*-lactide]₀ = 1 M, toluene) was added via a syringe all at once. The reaction mixture was stirred for 18 h at room temperature and subsequently was quenched with cold MeOH, provoking the precipitation of the polymer. The latter was then washed several times with MeOH, dried in vacuo and subsequently analyzed by SEC. In most cases, a MALDI–TOF MS analysis of the isolated polymers was performed. Catalytic runs under a given set of conditions were all duplicated.

4. Conclusions

The sterically bulky NHC–GaMe₃ and NHC–InMe₃ adducts (NHC = IPr*, Si*t*Bu) were prepared and characterized, and their level of steric congestion was assessed through structural analysis. All data agree with the IPr* adducts **1** and **2** being robust and stable adducts under various conditions. In contrast, the more severely congested Si*t*Bu adducts **3** and **4** are more reactive: this is best exemplified by the fast reaction of (Si*t*Bu)GaMe₃ (**3**) with H₂ at room temperature to afford the corresponding aminal product, the mechanism of which is currently being studied. Such an FLP reactivity constitutes the first instance of a H₂ activation involving GaMe₃, and further exemplifies the usefulness of bulky NHC ligands in FLP chemistry [30]. Adduct **3** was also found to mediate the ROP of *rac*-lactide at room temperature to afford cyclic PLA.

Supplementary Materials: The following are available online www.mdpi.com/2304-6740/6/1/23/s1, CIF files for adducts **2**, **3**, and **4** (CCDC 1813207, 1813208, and 1813209, respectively). NMR spectra of all compounds. MALDI–TOF and ¹H NMR data of the produced PLA.

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